

# Flexible Polyurethane Foam. II. Fire Retardation by Tris(1,3-dichloro-2-propyl) Phosphate Part A. Examination of the Vapor Phase (the Flame)

M. RAVEY,<sup>1</sup> I. KEIDAR,<sup>1</sup> EDWARD D. WEIL,<sup>2</sup> ELI M. PEARCE<sup>2</sup>

<sup>1</sup> IMI Institute for Research and Development, Haifa, Israel

<sup>2</sup> Polymer Research Institute, Polytechnic University, Brooklyn, New York, USA

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**ABSTRACT:** A flexible polyurethane foam fire-retarded with 7.8% tris(1,3-dichloro-2-propyl)phosphate (TDCPP) was found to lose by volatilization 80% of this material at 200°C, a temperature at which there is as yet little decomposition of the foam. It is therefore to be expected that when this foam burns, most of its TDCPP will vaporize into the flame. The latter would therefore be expected to be the main site of activity of this retardant. However, when TDCPP was injected directly into the flame of the burning unretarded foam, no inhibiting effect was apparent. This, in contrast to the above conclusion, points to the condensed phase as the main site of the retarding activity. Although there is some additional evidence that supports the latter interpretation, it is difficult to reconcile it with the small amount of residual TDCPP available for reaction in the condensed phase. Flames of unretarded foams were also unaffected by the injection of other halogen containing materials, such as trichloropropane, HCl, and HBr. It is suggested that the temperatures of these polyurethane flames may not be sufficiently high to initiate the radical-trapping-based flame-poisoning mechanism classically attributed to the halogenated fire retardants. This could be the reason why the latter are less effective as fire retardants for polyurethanes than they are for many other substrates. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 217–229, 1998

## INTRODUCTION

The previous report dealt with the thermal decomposition of a polyether-based, water-blown, commercial type of flexible polyurethane foam.<sup>1</sup> This and the following report examine the fire retardation mechanism of tris(1,3-dichloro-2-propyl)phosphate (TDCPP) in the same foam.

Phosphorus, either alone or in combination with halogen, is the active element in most of the fire retardants used for polyurethane foams.<sup>2</sup> For flexible foams, the haloalkyl phosphates, used as additives, are the retardants of choice, with TDCPP being one of the more effective of these.<sup>2</sup>

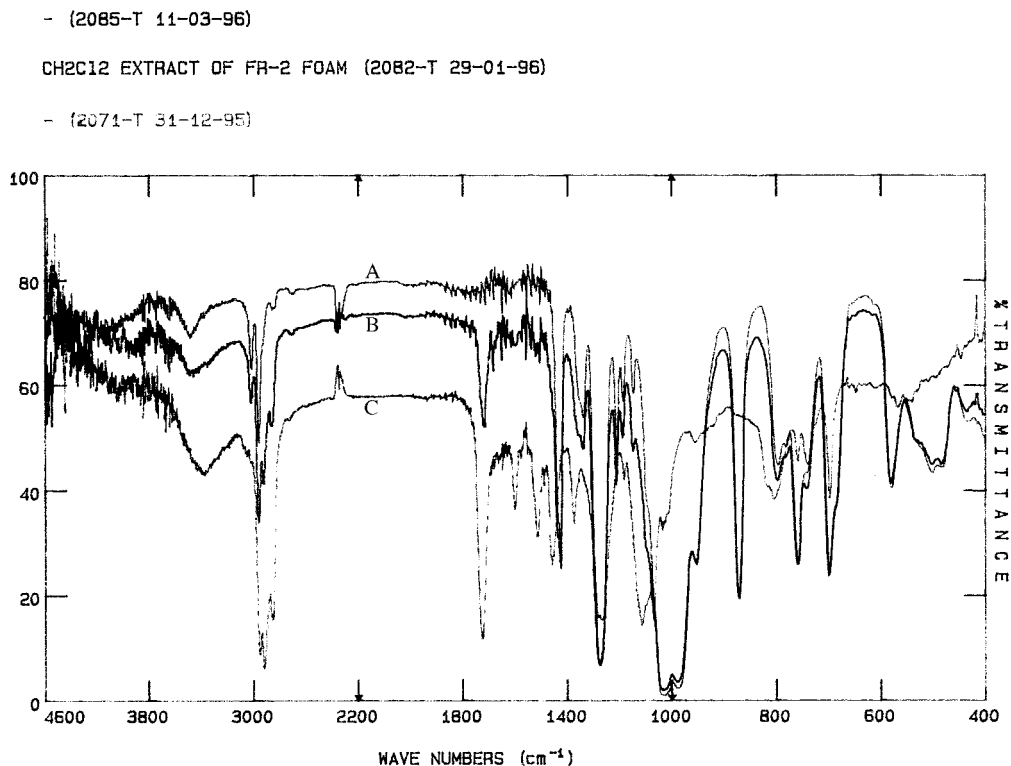
A fire retardant can act in one or both of the two following phases: the condensed phase that is in the pyrolysis zone under the flame; or in the vapor phase, the flame. This study has been divided into two parts. The first of these, reported here, presents the results of a search for inhibiting activity in the flame; none was found. This implies that TDCPP acts mainly in the condensed phase. This is the subject of the second part of this study.<sup>3</sup>

## A BRIEF REVIEW OF THE LITERATURE

In spite of the many studies performed on halo-phosphate–polyurethane systems,<sup>4–21</sup> little is certain about the mode of action of these fire retardants. Even the site of action (condensed or

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Correspondence to: M. Ravey.



**Figure 1** IR spectra of TDCPP (A) and methylene chloride extracts of retarded (B) and plain (C) foams.

vapor phase) remains to be established. Boilot et al.<sup>4</sup> claim the phosphates to be active in the vapor phase while Granzow, in a review,<sup>5</sup> concluded that, although for volatile phosphorus compounds vapor phase activity can contribute to fire retardancy, the practically important systems are generally based on inhibition by polymer-specific condensed-phase reactions. Brauman and co-worker<sup>6,7</sup> states that most phosphorus additives act in both the gaseous and condensed phases, with several mechanisms operating simultaneously. The predominant site of action and mechanism depends on the phosphorus agent, the polymer and the combustion conditions.

One proposed mechanism often cited is based on activity in the condensed phase and involves the thermal degradation of the phosphorus compound to phosphoric or polyphosphoric acids. These acids and the char, the formation of which they are said to catalyze,<sup>11,13</sup> are stated to form barriers that attenuate the transfer of heat from the flame to the substrate as well as the transport of fuel in the reverse direction.<sup>6-10</sup> Grassie and Zulfiqar<sup>12</sup> state that phosphoric acid reacts very efficiently with the carbodiimide formed by the condensation of the isocyanate released on thermolysis of the polyurethane and that this leads to

crosslinking and could present a mechanism of char formation.

Benbow and Cullis<sup>9</sup> proposed a number of mechanisms. Nonvolatile phosphorus compounds were claimed to act in the condensed phase by degrading to polyphosphoric acid (action by barrier formation). Most of the haloorgano phosphates were found to volatilize quantitatively before the polymer begins to degrade, which implies activity in the vapor phase (flame).

Inhibiting activity in the vapor phase is stated to be enhanced by the formation of hydrogen halides, which act as flame poisons. These authors<sup>9</sup> also reported that, in the presence of haloalkyl phosphates, the degradation of polyurethanes is strongly exothermic (which would hardly be expected to contribute to fire retardancy). Heating flexible polyurethane foam containing tris(2-chloroethyl)phosphate or tris(2,3-dibromopropyl)phosphate to temperatures approaching those prevailing during combustion resulted in the incorporation of halogen-phosphorus entities into the polymer structure. This produced polyurethanes of an "unusually high degree of flame retardance," clearly condensed phase activity. Yet, these authors also state that tris(2-chloroethyl)phosphate is lost quantitatively from the



ages in the foam and that this is the cause of the scorch that can occur when certain haloalkyl phosphates are present during foam production.

It can therefore be concluded that the haloalkyl phosphates decompose at temperatures within the range of those occurring in the pyrolysis zone of a burning foam. This appears to conflict with the volatilization reports.<sup>9</sup> It may, however, be a question of substrate morphology influencing the competition between phosphate loss by volatilization and its decomposition and/or reaction with the substrate. Large surfaces to volume ratios, such as those of foams, would favor phosphate volatilization, reducing the extent of decomposition or interaction. Small ratios are less conducive to volatilization as they increase the residence time of the phosphate in the pyrolysis zone, increasing the chances of decomposition and interaction.

## EXPERIMENTAL

### Polyurethane Foam Formulation

These foams were prepared at the Akzo Research Laboratory, Dobbs Ferry, New York. The plain (unretarded) foam was the same as that studied in the previous report,<sup>1</sup> in which the formulation was given. The retarded foam was of the same formulation but contained, in addition, 12 g of the flame retardant, TDCPP (FYROL FR-2, Akzo). Analysis for Cl and P (after Parr Bomb sodium peroxide fusion) gave 3.9% Cl and 0.56% P. These values are equivalent to TDCPP contents of 7.9 and 7.8%, respectively. The TDCPP content calculated from the formulation is 7.6%, which is in good agreement with the analytical results. (This value takes into account the loss by volatilization of the  $\text{CH}_2\text{Cl}_2$  used in the formulation, as well as the loss of the  $\text{CO}_2$  produced during the reaction of the tolylene diisocyanate with the water used in the formulation.)

### Thermogravimetric Analysis

Thermogravimetric analyses (TGA) were performed on a model High Res. TGA 2950 Thermal Analyzer (TA Instruments Inc., New Castle, Delaware) using both the high-resolution mode and the normal (linear programming) modes.

### Infrared Analysis

Infrared (IR) spectra were taken between salt plates on a Fourier transform spectrometer (Nicolet 5MX, Madison, Wisconsin).

### Pyrolysis-Gas Chromatography

The in-line pyrolysis-gas chromatography (Py-GC) technique has been described previously.<sup>1</sup> A model 8310B Perkin-Elmer (Norwalk CN) gas chromatograph was used.

### Gas Chromatography-Mass Spectrometry

The gas chromatography-mass spectrometry (GC-MS) instrument used was a model HP 5971 Hewlett-Packard (Avondale, Pennsylvania).

### Gas Chromatography

The (GC) instrument used was a model 3700 Varian (Palo Alto, California) gas chromatograph fitted with a 5 m  $\times$  0.53 mm HP-1 column. The temperature program used was from 50 to 280°C at 15°C/min with a helium flow of 10 mL/min.

### Flame Sampling

Flames were sampled by means of a 10-mL polypropylene syringe (Z11,691-2, Aldrich, Milwaukee, Wisconsin), to which a melting point capillary tube 100 mm long, and 1 mm i.d. (Corning 9530-2) had been fitted by means of a rubber septum (Z12,433-8 Aldrich, Milwaukee, Wisconsin). The sealed end of the melting point capillary had been cut off prior to attaching the tube to the syringe. These syringes contain a lubricant that was washed out with acetone. Sampling was performed by first depressing the plunger of the syringe, then placing the tip of the capillary in the flame and slowly withdrawing the plunger to its full extent. Acetone, 0.5 mL, was then introduced into the syringe via the capillary by means of another syringe fitted with a long needle. After swirling the acetone around the syringe walls, the washings were transferred to a small vial from which samples were drawn for GC-MS analysis.

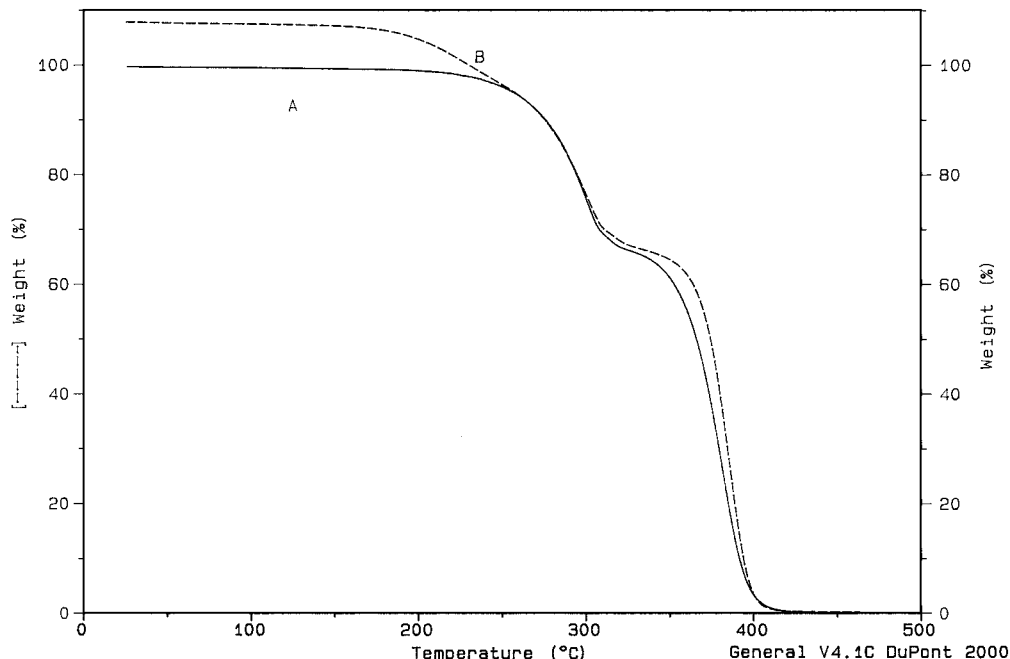
### Foam Bars

These bars were cut from blocks of the respective foams. They had a square cross section, 15 mm on each side, and were 100 mm long. For ignition, they were held vertically, being clamped at the bottom end. Ignition was from the top so that they burnt in a candle-like manner.

## RESULTS

For a fire retardant to act in the flame, by definition, it, or a flame-inhibiting decomposition prod-

Sample: A: PLAIN FOAM; B: RETARDED FOAM TGA File: A: FR-2-TGA.01  
 Size: 7.4870 mg Run Date: 6-Jul-93 00:26  
 Comment: IN NITROGEN



**Figure 2** Thermogram of plain (A) and retarded (B) foams in nitrogen (the retarded foam has been scaled to 107.8%).

uct, must enter the flame. These efforts to determine whether TDCPP is active in the flame were designed to answer the following questions. Does the TDCPP vaporize out of the pyrolysis zone and enter the flame? Or does it decompose in the pyrolysis zone to produce a volatile flame inhibitor that enters the flame? Another possibility is that the TDCPP reacts with the polyurethane substrate and that one or more of the resulting volatiles (if any) is a flame-inhibiting species.

TDCPP is used as an additive fire retardant for flexible polyurethane foams and as such is, or should be, present in (or on) the foam as the free material. Although of high molecular weight (431), TDCPP has sufficient vapor pressure to permit it to be gas-chromatographed without decomposition. This means that if it does not react with the polyurethane substrate, or does so relatively slowly, then there is a good chance that, under flaming conditions, at least part of the TDCPP will vaporize out of the pyrolyzing foam and enter the flame.

According to the formulation of this foam, it should contain 7.6% TDCPP (see the Experimental Section). Analysis for Cl and P gave TDCPP contents of 7.9 and 7.8%, respectively. Extraction of this retarded foam with methylene chloride re-

sulted in a weight loss of 7.7%. The extract had an IR spectrum very similar to that of TDCPP. The superposed spectra are given in Figure 1.

Except for two small bands at 1718  $\text{cm}^{-1}$  and 2926  $\text{cm}^{-1}$ , which are also present in the  $\text{CH}_2\text{Cl}_2$  extract of the unretarded foam, these two spectra are identical, showing that the material extracted was almost exclusively TDCPP.

These results confirm that the TDCPP is present in the foam as the free material at a concentration of 7.8%, close to the 7.6% calculated from the formulation.

### Thermogravimetric Analysis

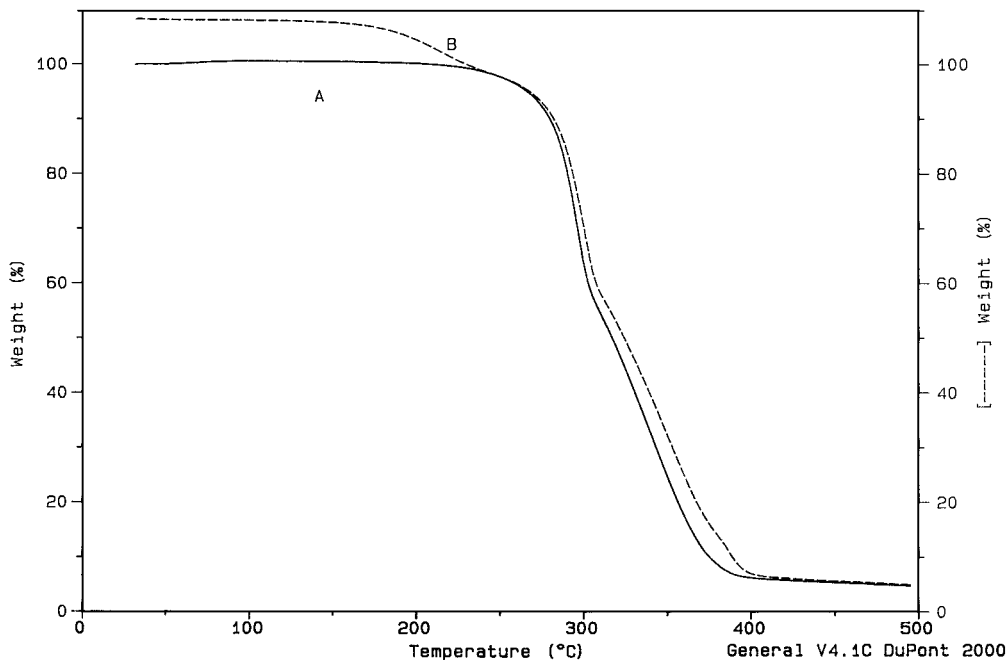
Let us assume that the TDCPP vaporizes out of the foam before the latter begins to decompose and that there is no interaction between the TDCPP and the polyurethane substrate. Then, if the thermograms of the two foams are superposed, they should overlap, except for the initial stage, during which the TDCPP is lost from the retarded foam by vaporization. However, as the retarded foam contains only 92.2% polyurethane (plus 7.8% TDCPP), whereas the plain foam contains 100%, in order to achieve curve matching, the thermogram of the retarded foam must

Sample: A: PLAIN FOAM; B: RETARDED FOAM  
 Size: 2.0400 mg  
 Comment: IN AIR

TGA

File: A: NFR-TGA.12

Run Date: 21-Jan-96 11:42



**Figure 3** Thermograms of plain (A) and retarded (B) foams in air (the retarded foam has been scaled to 107.8%).

be rescaled to match its polyurethane content to that of the plain foam. This has been done in Figure 2.

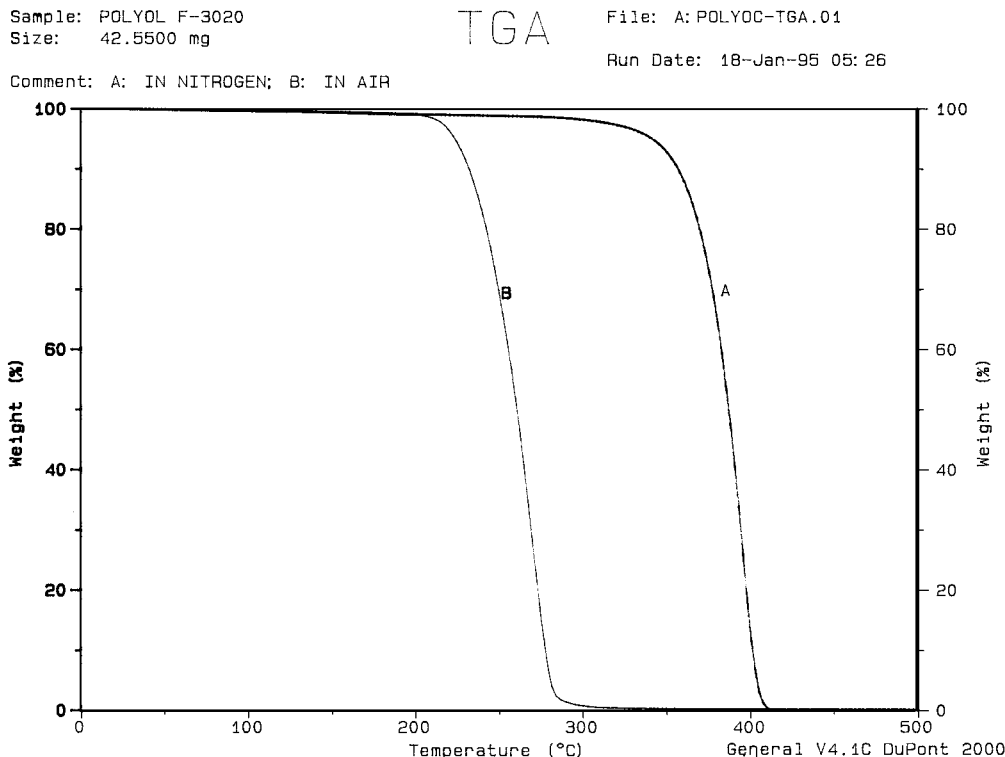
If all of the TDCPP had volatilized out of the foam before the latter began to decompose, the curves of the two foams would have converged at the 100% level. In Figure 2, the convergence point is at about 96% and 250°C, that is, past the beginning of the decomposition of the foam at about 210°C. This shows that under these TGA conditions, the foam begins to decompose before vaporization of the TDCPP has been completed. The amount of TDCPP lost by vaporization can be estimated from the difference in the weight losses of the two foams at the convergence point. This difference is 6.7%, which represents 86% of the TDCPP content of the foam.

The curves overlap for most of the first stage of the decomposition of the foam, up to about 300°C. This covers the range where the tolylene diisocyanate (TDI)-derived units are released.<sup>1</sup> Past this point, the two curves separate again during the second stage of decomposition, that of the polyether segments (300–400°C).<sup>1</sup> The overlap of the curves over the first decomposition stage indicates that there is little or no interaction between the TDCPP and the TDI-derived units. The separation between these two curves during the sec-

ond decomposition stage resulted from the shifting of the curve of the retarded foam to a higher temperature. This indicates that the TDCPP interacted with the polyether segments of the foam and that the resulting product is thermally somewhat more stable than the original polyether segments.

The thermograms of Figure 2 were run under nitrogen. As, under flaming conditions, the pyrolysis zone under the flame is exposed to air, it was considered possible that the presence of oxygen may have an effect on the reaction between the TDCPP and the polyurethane substrate. To examine this possibility, TGAs were run in air. Figure 3 gives the results. Here too the thermogram of the retarded foam has been rescaled. Comparing Figures 2 and 3, it will be seen that the presence of air effects neither the volatilization of the TDCPP nor the first stage of the decomposition of the foam (210–300°C). Air does, however, have a marked effect on the second stage of decomposition, that of the polyether chains. Under aerobic conditions, initiation of the second stage of the decomposition is lowered by about 30°C, with the resolution between the first and second stage being much poorer. In air, there is a slight increase of the residue at 400°C.

The sensitivity of polyethers to air can be seen



**Figure 4** Thermograms of polyol F-3020 in nitrogen (A) and air (B).

in Figure 4, which presents the thermograms of the polyol used in the preparation of this foam (Polyol F-3020), both in nitrogen and in air.

#### Pyrolysis-Gas Chromatography

TGA indicated that most of the TDCPP vaporizes out of the foam during pyrolysis. Both to confirm the identity of the volatiles as TDCPP and to determine the extent of the volatilization, low-temperature Py-GC was applied, using the in-line gas chromatographic setup described previously.<sup>1</sup> The pyrogram shown in Figure 5 was obtained at 200°C, a temperature sufficiently low to minimize the formation of volatile decomposition products of the foam (as shown by TGA; see Fig. 2). The major peak at 19 min was identified as TDCPP by retention time comparison with an authentic sample. The two small peaks immediately following the major peak also appear on chromatograms of the authentic material and probably represent its isomers. The absence of low boilers indicates that, at this temperature, the TDCPP does not decompose (its major low boiling decomposition product is 1,2,3-trichloropropane; bp 156°C<sup>23</sup>). Using external standard calibration, duplicate runs showed that 77 and 81% of the TDCPP content of the foam vaporized off (and was recovered

as TDCPP) at 200°C. The weight losses of the two foam samples were 9.1 and 9.6%, respectively. In both cases, the residual foams were barely discolored, retained their cellular morphology, and remained flexible.

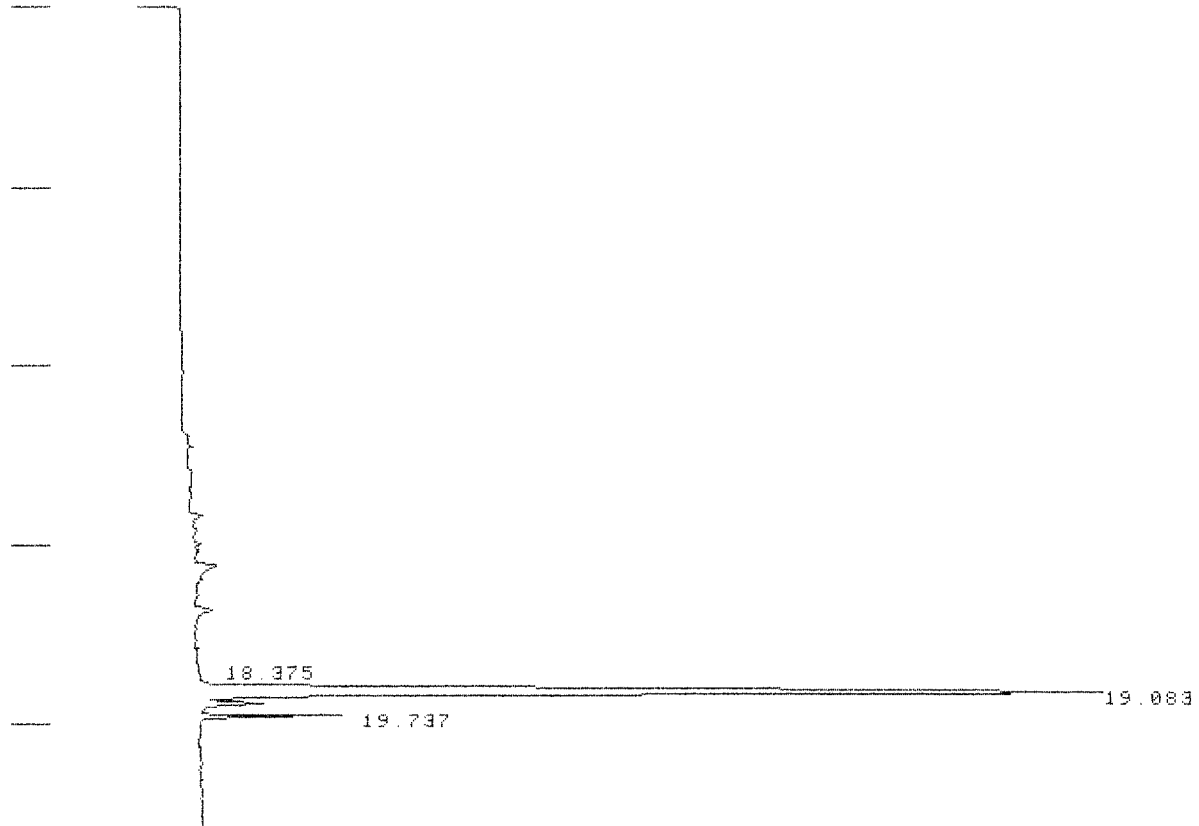
These results are in good agreement with the above TGA estimate of 86%. However, weight losses of over 9% indicate that more than just the TDCPP volatilized off the foam.

#### Flame Sampling

Py-GC has confirmed that most of the TDCPP in the foam vaporizes out on pyrolysis. The object of flame sampling was to verify the presence of TDCPP, or its decomposition products, in the flame. It was performed by drawing vapors and gases from inside the flame of the burning foams (both retarded and plain) into a syringe, as described in the experimental section. With both foams, the syringe filled with dark yellowish hazes that settled out rather slowly. Although acetone soluble materials were found to be present, these aerosols appear to consist mostly of yellow-brown acetone insoluble particles, which probably represent the yellow smoke discussed in Part I of this study.<sup>1</sup>

The chromatograms of the acetone solubles of

CHART SPEED 0.5 CM/MIN  
 ATTEN: 16 ZERO: 5% 5 MIN/TICK



RECALCULATE ON FILE: M2001

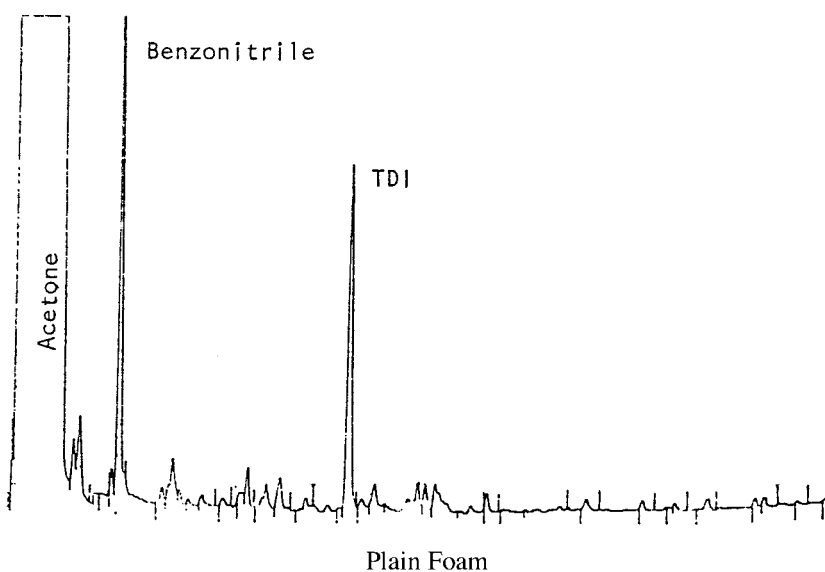
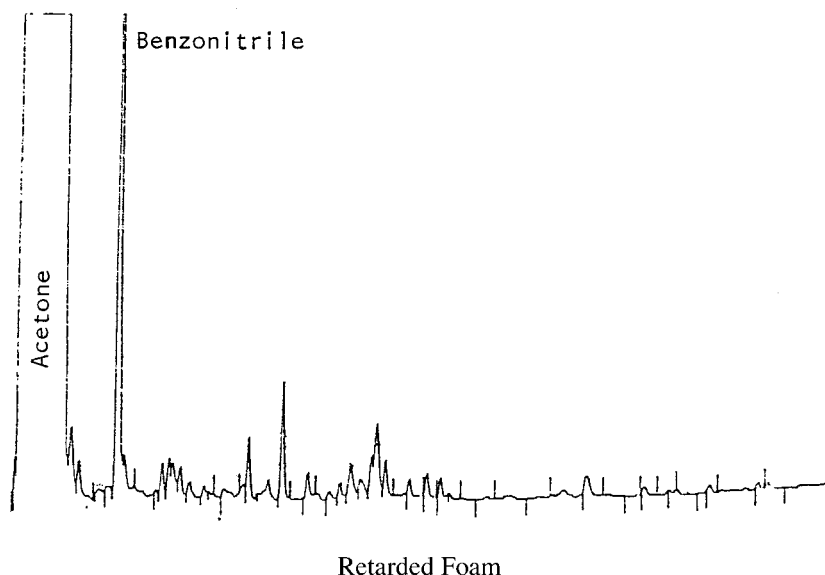
CHANNEL: 3A - 1 TITLE: 11:18 29 FEB 96

SAMPLE: 0.359MG FR-2 METHOD: MANI-P CALCULATION: A% - ANALYS - OP

PEAK NO	PEAK NAME	RESULT AREA%	TIME (MIN)	TIME OFFSET	AREA COUNTS	SEP CODE	W1/2 (SEC)
1		100.00	19.083		1563799	VV	9.00
TOTALS:		100.00			1563799		
DETECTED PKS:		4	REJECTED PKS:		3		
DIVISOR:		1.00000	AMT STD:		1.00000	MULTIPLIER: 1.00000	
NOISE:		11.4	OFFSET:		-76		

Figure 5 Pyrogram at 200°C of retarded foam.





**Figure 6** Gas chromatograms of acetone solubles of flame extracts of plain and retarded foam.

the extracts of the flames of the plain and the retarded foams are given in Figure 6. Both contained benzonitrile as a major component. However, whereas this was the only major component in the flame extract of the retarded foam, that of the plain foam also contained TDI as a major component. TDCPP (which is soluble in acetone) was not detected in the flame extract of the retarded foam.

Benzonitrile was not detected in the pyroly-

zates of the plain foam examined in the previous study.<sup>1</sup> As that pyrolysis was performed in nitrogen, this suggests that the benzonitrile detected in the flame is an oxidation product of the TDI or diamino toluene (DAT, which is also formed during the pyrolysis<sup>1</sup>). Benzonitrile could also be a product of thermal cracking, with the temperature inside the flame undoubtedly being much higher than the maximum pyrolysis temperature employed previously (360°C).<sup>1</sup> Another possibil-

ity is ammoxidation of the methyl group of TDI (or DAT). This suggestion has two simplifying advantages: it would explain the absence of dinitriles, and it does not require breaking the C—N bond of TDI (or DAT) to be reformed as the C—C bond linking the nitrile group to the benzene ring.

Similar examination of the flames of foams containing various other additives showed TDI to be present whenever such additives contained halogens. Additives yielding TDI in the flame included TDCPP, tris(2-chloroethyl) phosphate, pentabromodiphenyl oxide, 1,3,5-trichlorobenzene, and poly(vinyl chloride) (PVC). Phosphorus does not seem to be involved in the appearance of TDI in the flames, as the latter was not detected in flames of foams containing nonhalogen phosphate additives, such as tributyl- and triphenyl-phosphates, as well as resorcinol bis(diphenylphosphate). These results suggest that the presence of halogen in the flame inhibits the oxidation of the TDI, which is one of the products released upon pyrolysis of this polyurethane foam.<sup>1</sup>

In no case could any of the aliphatic phosphates be detected in flames of foams containing such additives. The aromatic phosphates, on the other hand, were all detectable in the respective flames. This indicates that the aliphatic phosphates decompose more rapidly in these flames than do the aromatic ones, which is not unexpected. As TDCPP is an aliphatic phosphate, the lack of its detection in the flame is therefore probably due to its rapid decomposition rather than its nonentry into the flame.

Support for the entry of the TDCPP into the flame was obtained by holding a water-wetted wad of glass wool in the flame of a burning bar of retarded foam. Subjecting the glass wool to the colorimetric phosphate test gave a positive result. The presence of phosphate, as well as ionic chloride in the flame, showed that TDCPP or its decomposition products had entered the flame.

On the basis of the results so far, which show that most of the TDCPP does enter the flame, it could logically be concluded that the flame is the major site of the retardation. For final confirmation, TDCPP was injected directly into the flame of a burning bar of plain (nonretarded) foam. The results were quite unexpected.

### Flame Injection of TDCPP

As is to be expected, almost by definition, the plain and retarded foams burn in different manners. A bar of plain foam burns with a flame that continuously increases in size, and, as it grows, the flame

tends to move down, enveloping the parts of the bar below the burning top. A black tar-like material forms in the pyrolysis zone beneath the flame, and as the latter grows, this tar builds up and spills down the sides of the bar, collapsing the foam structure in its path. A bar of retarded foam, on the other hand, is difficult to ignite and, once ignited, burns with a small, continuously diminishing flame that finally snuffs out. The tar-like material below the flame of the retarded foam is much more viscous than that of the plain foam.

Several modes were used to inject or place the TDCPP in the flame of a burning bar of plain foam. The initial attempt involved holding a small wad of glass wool wetted with TDCPP in the flame. Although the flame became very smoky, it gave no sign of dying or even diminishing. In a second attempt, the open end of a capillary melting point tube ( $100 \times 1$  mm i.d.) filled with TDCPP was pushed into the flame. The TDCPP boiled and sputtered out of the capillary; the flame became smoky, but, again, there was no indication of its diminishing. In a third attempt, several strands of glass wool fibers were twisted into a small loop of a size that would just fit around the flame. The loop was wetted with TDCPP and then held around the flame of a burning bar of plain foam so that the flame touched the TDCPP wetted loop. The intention here was to have the vapors of the TDCPP enter the flame from its oxygen-rich side. The previous two trials involved placing the TDCPP in the center (more or less) of the flame, which is the oxygen-poor part. This again just gave rise to a smoky flame without having any noticeable effect on its size. In a final attempt, a melting point capillary was embedded in the center of a bar of plain foam, which had been slit along its length. The capillary, which had previously been filled with TDCPP, was placed inside the bar so that it was in its center and parallel to its long axis. When the bar was positioned vertically, the open end of the capillary was uppermost and about 15 mm below the top of the bar. On igniting the bar at its top, it burned down with the usual increasing flame size. The flame became smoky when it reached the top of the capillary. It continued to burn with an ever increasing size and was therefore finally extinguished manually. A length of about 15 mm of the upper part of the capillary had been exposed. The fact that 7 mm of the upper part of the capillary was empty showed that TDCPP had volatilized out of the capillary, so that injecting the TDCPP into the flame from below also had no noticeable inhibiting effect on the flame. Assuming that the 7 mm of TDCPP

had vaporized out of the capillary while a similar length of foam was consumed by the flame, this is equivalent to a concentration of about 12% of TDCPP in the foam, which is much higher than the 7.8% loading that renders the foam self-extinguishing when ignited at the top.

If the TDCPP is active in the flame, injecting it directly into the flame would have been expected to lead, if not directly to extinguishment, then at the very least to a noticeable diminishing of its size, particularly as the injection of neat TDCPP undoubtedly results in a concentration in the flame that is far higher than that to be expected from the 7.8% present in the retarded foam. The total lack of any noticeable effect on the size of the flame therefore makes it very difficult to support the contention that the flame is the site of the major retarding activity, as some of the literature sources claim or propose.<sup>4,6,7</sup> On the other hand, the fact that most of the TDCPP vaporizes out of the foam before the latter begins to decompose makes it very difficult to consider the main area of its action to be in the condensed phase.

#### Composite Bar Test

To further help in differentiating between vapor and condensed phase activity, another test was devised. Two bars of foam, one plain, the other retarded, were split in half lengthwise. Two of these halves, one of each type of foam, were joined along their cut faces and held together by a few turns of lightly wound cotton thread. This produced a composite bar, with only half of its cross section containing TDCPP. This composite bar was positioned vertically and ignited at the top, in the usual manner. It was allowed to burn down to a stub of about 3 cm, at which stage, the flame was extinguished manually. These experiments were repeated several times with reproducible results. The flame advanced downward faster on the unretarded half so that the top of the manually extinguished stubs had a slope of about 45°. As these composite bars contained only one-half of the TDCPP that the retarded bar contained, they would not be expected to self-extinguish.

As a consequence of the turbulence inside flames, a retardant entering a flame would be expected to be distributed rapidly uniformly throughout the flame, even if it entered from a localized source, as is the case of the composite bar. A retardant active in the flame, by whatever mechanism, would therefore be expected to reduce the thermal feedback to the substrate below the

flame more or less uniformly across the area exposed to the flame, particularly for the small flames involved in this study. In other words, in the case of the retarding action being solely in the flame, the two halves of the composite foam bar should burn down at more or less the same rate (assuming both halves of the bar have the same density) so that the top of the stub will remain horizontal, in spite of the fact that only one-half of its cross section contained the retardant.

On the other hand, an inhibitor active in the condensed phase, by whatever mode of action (barrier formation, endothermicity, carbonization), can be expected to have a much more localized effect, with there being no mechanism to extend the inhibiting effect beyond those areas in which the inhibitor is present and active. As a result, the substrate containing the inhibitor would be expected to be consumed at a slower rate than an adjacent nonretarded one, even when both are burning under and supplying fuel to the same flame, so that in the case of the major inhibiting activity being in the condensed phase, the stub of the burning bar would be expected to present a surface that slopes up on the retarded side of the bar. However, although such a sloping upper surface would indicate condensed phase activity, it does not necessarily exclude concomitant activity in the flame. While a sloping upper surface may indicate either condensed phase or condensed plus vapor phase activity, a horizontal upper surface indicates only vapor phase activity, exclusive of any marked condensed phase activity.

The fact that the stub of the composite bar had a surface that sloped up on the TDCPP containing half bar therefore indicates the inhibition to be mostly in the condensed phase; but, as stated above, it does not exclude the possibility of concomitant activity in the flame.

#### Examination of the Halogen Theory

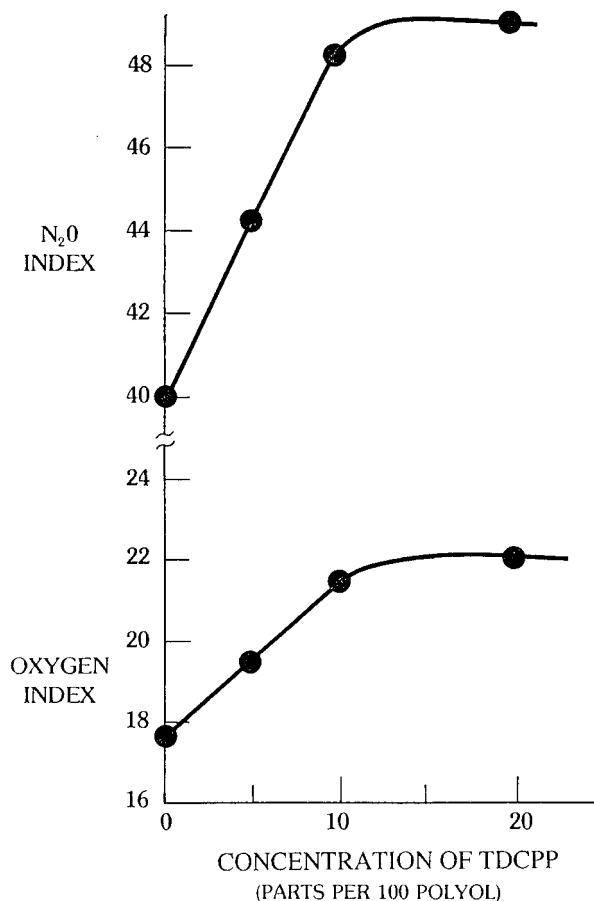
Organohalogen compounds are effective fire retardants for many substrates,<sup>26</sup> and it is widely accepted that they act mainly in the vapor phase by serving as potential sources of hydrogen halides, stated to be the actual inhibiting species.<sup>27</sup> TDCPP contains 49% chlorine, and, although this is a low concentration for a halogen-based fire retardant, some activity in the flame would have been expected when injecting it directly into the flame. As a control another chlorocarbon was chosen for flame injection, one with a higher chlorine content, 1,2,3-trichloropropane. This is a major thermal decomposition product of TDCPP,<sup>23</sup> con-

tains 72% chlorine, and would be expected to readily undergo thermal dehydrochlorination to produce HCl, the commonly presumed flame poison.<sup>27</sup> Trichloropropane was injected into the flame of a burning bar of plain foam by means of a 0.25 mm i.d. fused silica capillary attached to a syringe filled with this material. Although the flame became smoky, this too had no noticeable effect on its size.

As it is fairly safe to assume that this trichloropropane will release HCl in the flame. This implied that HCl also has no inhibiting effect on this type of polyurethane flame. The obvious next step then was to inject HCl directly into the flame. This was done, again with a 0.25-mm fused silica capillary. Dry gaseous HCl, as well as HBr, were injected (independently) into the flames of burning bars of plain foam. The capillaries were kept in the flames as the bars burned down, but the flames kept increasing in size, showing no signs of any inhibition by these gases. This was quite unexpected.

Interruption by hydrogen halides of the oxidative free radical chain reactions that occur in flames has been the generally accepted mechanism of halogen-based flame retardants since the seminal work of Rosser et al. in 1959.<sup>27</sup> They worked with premixed hydrocarbon flames at temperatures averaging above 1500°K. These authors stressed the importance of high temperatures to initiate the inhibition of flame propagation by bromine and HBr.<sup>27</sup> The flames we studied were diffusion flames, which can be expected to develop temperatures well below those prevailing in premixed hydrocarbon flames. The temperatures of these polyurethane flames may be too low for the halogen-based mechanism to become operative. The work of Fenimore and Martin<sup>28</sup> supports this suggestion. They added HCl and chlorine (independently) to the atmosphere in which a bar of polyethylene was burning, a diffusion flame undoubtedly well below 1500°K. Neither of these gases had an inhibiting effect on the flame.

The nitrous oxide index (NOI) test<sup>29</sup> is used to differentiate between alternative mechanisms of oxidation in flames. This test is run in parallel with the oxygen index test, replacing the oxygen with nitrous oxide for the NOI. If the plots of the two tests are parallel, then this is taken to indicate that the oxidative processes supporting such flames are not based on free radical chain reactions, whereas such a mechanism can be taken to be operative for flames burning in air if these two tests produce plots that are not parallel.<sup>29</sup> When



**Figure 7** Nitrous oxide and oxygen indices as functions of TDCPP concentration.

these two tests were applied to the plain foam, they gave parallel plots, indicating that the polyurethane flame is not based on a free radical oxidative chain reaction (see Fig. 7). As halogen inhibition is stated to operate by interrupting the oxidative free radical chain reaction,<sup>27</sup> the absence of such a mechanism would render the halogens ineffective as inhibitors of such flames.

Another possibility is that the halogen (in this case, chlorine), radicals are absorbed on the particles of the yellow smoke (the putative polyurea aerosol<sup>1</sup>) or act as nucleation sites for these particles. This could prevent these radicals from participating in the processes that interrupt the oxidative chain reaction.

Other workers<sup>30</sup> have questioned, on a general basis, the halogen radical theory, proposing dilution and other physical endothermic effects as alternative mechanisms for the inhibition.

The activity of the TDCPP in the condensed phase (the pyrolysis zone) will be the subject of a future article.<sup>3</sup>

## CONCLUSIONS

Regarding the site of activity of the TDCPP, the results are somewhat ambiguous. The relative ease with which TDCPP vaporizes out of the retarded foam would be expected to favor activity in the flame. However, the flame injection work found no support for this view. The results of the composite bar test indicate that retardation occurs in the condensed phase. This is supported by evidence of interaction between the TDCPP and the foam. However, the relatively small amount of TDCPP involved in the latter makes it difficult to accept this as the main basis of the retardation. The basis of retardation by halogens has classically been ascribed to interruption of the oxidative radical chain mechanism occurring in the flame. This mechanism is stated to require high temperatures. The lack of a retardation effect on injecting halogenated materials into the flame of the unretarded foam could be due to the relatively low temperature of this flame.

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