

Flexible Polyurethane Foam. II. Fire Retardation by Tris(1,3-dichloro-2-propyl) Phosphate. Part B. Examination of the Condensed Phase (the Pyrolysis Zone)

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ABSTRACT: Tris(1,3-dichloro-2-propyl) phosphate (TDCPP) is used commercially as a fire retardant for flexible polyurethane foams. It was found to act both in the condensed (pyrolysis zone) and the vapor (flame) phases. The extent of its activity in the individual phases depends on the way in which the specimen is ignited. Under conditions of candle-like, top-down burning, retardation seems to occur mainly in the condensed phase by a mechanism apparently based largely on the barrier properties of a phosphorus-containing carbonaceous layer that builds up on top of the liquid pyrolyzing layer beneath the flame. As the formation of this barrier requires time, extinguishment in this mode is relatively slow. Extinguishment is much faster in bottom-up burning, where the flame appears to be the main site of the retardation. In this mode, because of the orientation of the specimen relative to the flame, a disproportionately large amount of TDCPP enters the flame. It is proposed that TDCPP decomposition products, HCl and other low-fuel-value materials dilute the fuel vapors sufficiently to reduce their flame propagation velocity to below that at which they stream out of the pyrolysis zone. This pushes the flame away from the pyrolysis zone, uncoupling the thermal feedback mechanism that produces the fuel. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 231–254, 1998

Key words: polyurethane foam, fire retardation, mechanism chloroalkyl phosphate, pyrolysis zone

INTRODUCTION

The haloalkyl phosphate esters are among the more effective of the fire retardants used for flexible polyurethane foams. Although a relatively large body of literature exists on this subject (for a review of the literature, see Ravey et al.¹), it holds no consensus regarding the mechanism or even the site of action of these materials, whether

in the condensed phase (the pyrolysis zone immediately below the flame) or the vapor phase (the flame).

The previous study¹ involved attempts to detect retarding activity in the flame of a flexible polyurethane foam fire retarded with tris(1,3-dichloro-2-propyl) phosphate (TDCPP); but, in spite of a number of different experimental approaches, no such in-flame retarding activity could be detected, which, by default, pointed to the condensed phase as the site of the retarding activity. If this is indeed so, then, as most of the TDCPP was found to vaporize at temperatures at

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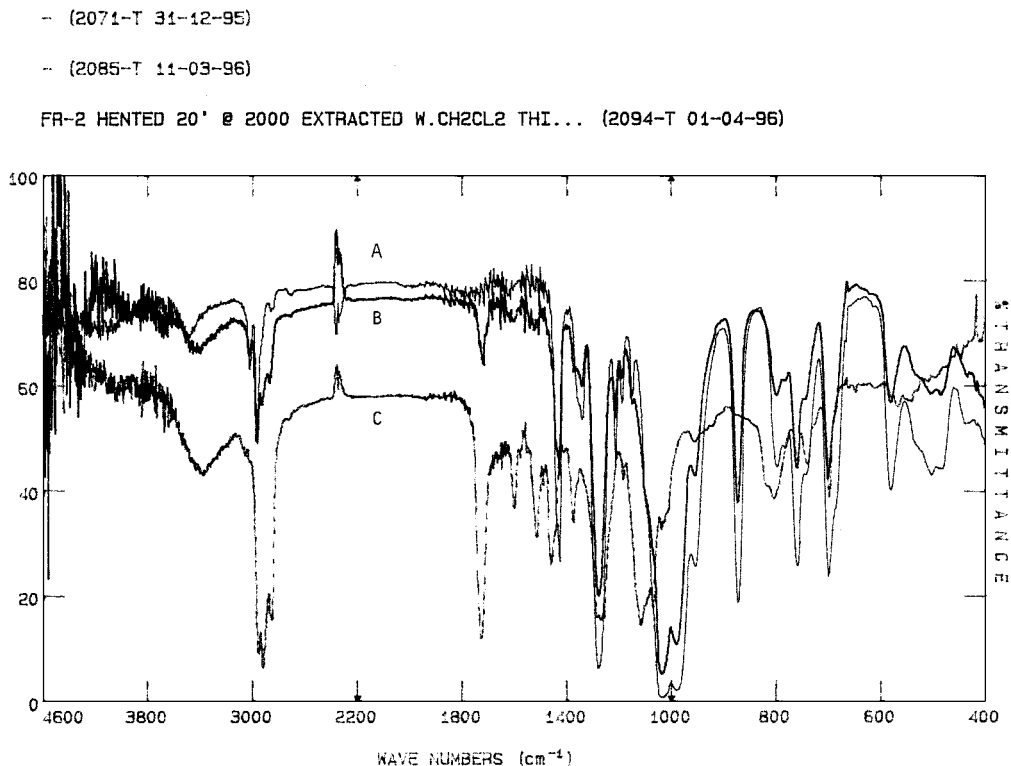


Figure 1 IR spectra of TDCPP (A) and methylene chloride extracts of plain (C) and in-test-tube heat-treated, retarded (B) foams.

which the foam just begins to decompose,¹ this implies that only a part of the TDCPP added to the foam is actually involved in the retarding action.

This, the second part of this study, reports the results of an examination of the condensed phase as the site of the retarding activity.

EXPERIMENTAL

Foam Formulation

The foam formulation has been given previously.¹

Sources of Chemicals

Tris(1,3-dichloro-2-propyl)phosphate (TDCPP) was supplied as Fyrol FR-2 by Akzo Chemicals Inc., Dobbs Ferry, NY. Polyol F-3020 was supplied by Arco Chemical Co. Newton Square, PA. 2,4-Diaminotoluene (DAT) was supplied by Aldrich Chemical Co. Inc., Milwaukee, WI, p/n 10,191-5.

Thermogravimetric Analysis

These were run under a nitrogen flow of 100 mL/min on a model High Res TGA 2950 Thermal Analyzer (TA Instruments Inc., New Castle, Delaware). The purge gas flow of this instrument is divided into two streams: one purges the balance section (40 mL/min); the other purges the furnace (60 mL/min). When runs were made in air, the nitrogen flow through the furnace was replaced by air (60 mL/min) while maintaining the 40 mL/min nitrogen purge through the balance.

Infrared Spectra

Infrared (IR) spectra were taken on a Fourier transform infrared (FTIR) spectrometer (Nicolet 5MX, Madison, WI), liquids between NaCl plates and solids in KBr pellets.

Scanning Electron Micrographs

Scanning electron micrographs these were obtained on a Jeol JSM electron microscope. Samples were gold-coated.

Table I Yields and Analytical Results for the Liquid Fractions of the Pyrolysis Residues of the Two Foams

Foam	Yield (%)	C (%)	H (%)	N (%)	H/C Ratio ^a	P (%)	Cl (%)	Cl/P Ratio ^a
Plain	65.2	61.1	9.6	0.42	1.9			
±	0.8 (8)	0.6 (6)	0.3 (6)	0.09 (6)				
Retarded	61.0	60.5	10.2	0.76	2.0	0.44	0.14	0.3
±	1.9 (6)	0.5 (4)	0.3 (4)	0.09 (4)		0.02 (2)	0.005 (2)	

Note: These are average values; the number of runs or determinations are given in parenthesis.

^a Atomic ratio.

Pyrolysis–Gas Chromatography

The in-line technique used has here been detailed previously.²

Foam Bars

These were cut from blocks of the respective foams. They were 100 mm long and of square cross section, with 15 mm sides. They were held vertically, being clamped at the bottom for top–down (candle like) burning and at the top for bottom–up burning.

Composite Bars

The composite bar test has been described and discussed previously.¹

Analysis

Elemental analysis (C, H, and N) was run on an NA 1500 Analyzer (Carlo Erba, Milan, Italy).

Amine determinations were performed by non-aqueous titration with perchloric acid in acetic acid. Phosphorus and chlorine were determined after sodium peroxide fusion in a Parr bomb, with phosphorus determined colorimetrically and chlorine determined argentometrically. Phosphoric acid was determined by nonaqueous titration with *N*-ethylpiperidine in acetone.

RESULTS AND DISCUSSION

A number of techniques were applied to examine the activity of TDCPP in the condensed phase.

Heat Treatment of Foams

The previous experiments, which established the large extent of volatilization of the retardant (80%), were performed by pyrolysis–gas chromatography (Py–GC) under a flow of helium on mil-

Table II Yields and Analytical Results for the Solid Fractions of the Pyrolysis Residues of the Two Foams

Foam	Yield (%)	C (%)	H (%)	N (%)	H/C Ratio ^b	N/C Ratio ^b	P (%)
Plain	2.2	61.5	5.8	13.7	1.1	0.19	
±	0.6 (8)	1.5 (6)	0.6 (6)	1.1 (6)			
Retarded	10.0	63.5	6.2	15.2	1.2	0.20	1.0
±	1.4 (6)	0.7 (4)	0.1 (4)	0.3 (4)			0.05 (2)
Yellow smoke of plain foam ^a		59.7	6.6	12.3	1.3	0.18	

Note: These are average values; the number of determinations are given in parenthesis.

^a Data from Ravey and Pearce.²

^b Atomic ratio.

NFR FOAM PYROLYSIS @ 340° 4', CLEAR BROWN LIQUID (1950-T 18-01-95)

FR-2 FOAM PYROLYZED @ 340° 2' CLEAR BROWN LIQUID (1951-T 18-01-95)

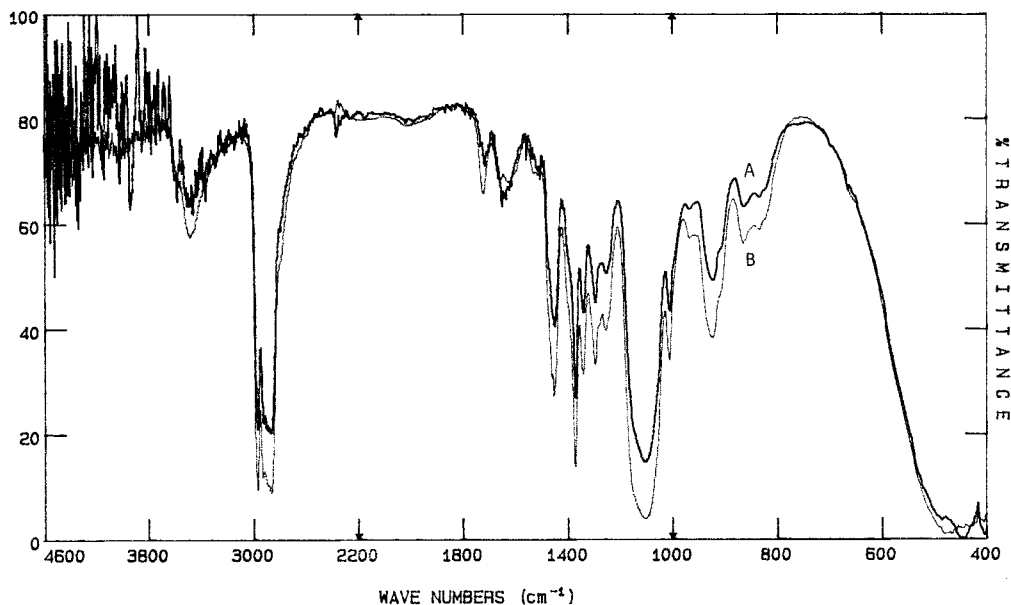


Figure 2 IR spectra of pyrolysis liquid-phase residues of retarded (A) and plain (B) foams.

ligram-sized samples at 200°C.¹ The previous work has now been extended to pyrolysis in air. These new experiments were performed on a larger scale. Bars of foam (0.6–0.7 g), both plain (unretarded) and retarded, were heated for 15 min at 200°C in an oven with forced air circulation. Although both foams darkened slightly, no changes in flexibility, resilience, shape, or dimensions were noted. Weight losses were 2.7 and 9.4% for the plain and retarded foams, respectively. The latter figure is similar to the thermogravimetric analysis (TGA) results under nitrogen.¹ This shows that heating the foam in air gives results that, at least on a weight loss basis, are similar to those obtained by heating under nitrogen.¹ That is, in air too, most of the retardant appears to be lost by vaporization before much of the foam decomposes.

The heat-treated retarded bars of foam when ignited did not self extinguish as do retarded bars that have not been heat-treated. They did, however, appear to burn more slowly than the plain bars, indicating some retardation. Heat treatment had no visibly apparent effect on the burning behavior of a plain foam bar.

Confirmation that retardation was indeed con-

ferred on the foam by the heat treatment was obtained with the aid of the composite bar burn test,¹ which not only showed that in spite of the loss of a major portion of the retardant, the TDCPP derived material remaining in the foam did confer some retarding effect, but also indicated this to be largely condensed phase effect. Further support for a condensed phase effect is derived from the fact that this heat-treated foam contained no free, vaporizable TDCPP.

That the part of the TDCPP that did not vaporize out of the foam was incorporated into the polymer was confirmed by analysis of the foam after solvent extraction (see below). As only a small part of the retardant was incorporated, and as previous work¹ had indicated TDCPP to have little or no effect on the flame when injected directly into it, the following question arose: Can the retarding effect be increased by incorporating more of the retardant into the polyurethane substrate? To answer this question, it is first necessary to answer a second one: Can increased incorporation be achieved by extending the contact time between the TDCPP and the foam at 200°C, for example, by preventing or reducing the rate of volatilization of the retardant? (There is little point

FR-2 PYROL. 340/2' ETOH INSOL RESIDUE (1984-T 07-03-95)

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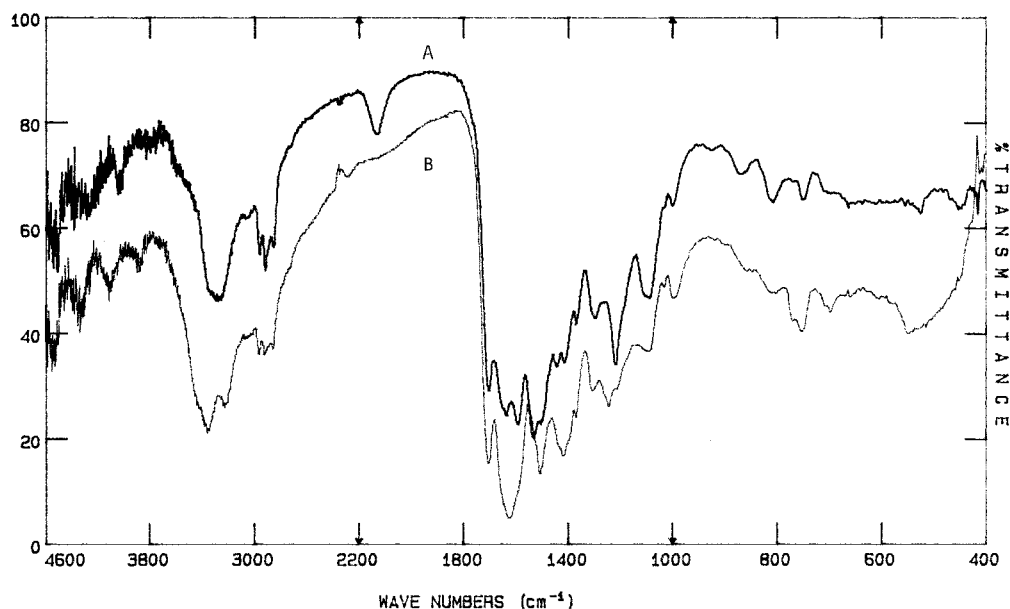


Figure 3 IR spectra of pyrolysis solid-phase residues of plain (A) and retarded (B) foams.

in trying to increase the incorporation by raising the temperature much above 200°C as the structure of the foam will begin to collapse.)

To answer this second question, the heat treatment was repeated, but with the bar of retarded foam placed inside a test tube loosely capped with aluminum foil. The same temperature of 200°C was used, but the heating period was extended by 5 min to a total of 20 min, to allow time for the heat to penetrate into the test tube. Judging by its high molecular weight (431), the vapor pressure of TDCPP at 200°C can be expected to be well below atmospheric pressure, so that even loose capping of the test tube, by preventing ventilation of its contents, should suffice to prevent loss of TDCPP vapors from the system. This assumption proved correct. Weight losses of less than 0.4% were recorded for such runs, showing the TDCPP to have remained in the test tube and, therefore, in contact with the foam, throughout the heat treatment. Such bars remained self-extinguishing, similarly to the bars that were not heat-treated. Extraction of such a bar with methylene chloride (in which the TDCPP is soluble) led to a weight loss of 7.6%, very close to the initial 7.8% TDCPP content of this foam¹ and the 7.7% weight

loss on solvent extracting a nonheat treated retarded bar of foam.¹

Figure 1 gives the IR spectrum of TDCPP as well as those of the extracts (after removal of the solvent) of the plain (not heat-treated) and in-test-tube heat-treated retarded foams. It will be seen that the latter extract is mostly TDCPP. The small additional bands that are present can all be assigned to the extract of the plain foam. These probably represent components of the foam formulation that were not incorporated into the polymeric structure during its preparation. These materials would also be expected to be present in the retarded foam.

The results show the following.

1. Preventing the vaporization of TDCPP during heating at 200°C, thus keeping it in contact with the foam, did not increase the extent of the reaction between them.
2. The TDCPP, which does not react with the foam at 200°C, will remain on it, apparently largely unchanged, if ventilation is prevented. If ventilation is not prevented, the TDCPP will vaporize off.
3. At 200°C, only a small part of the polymer (or

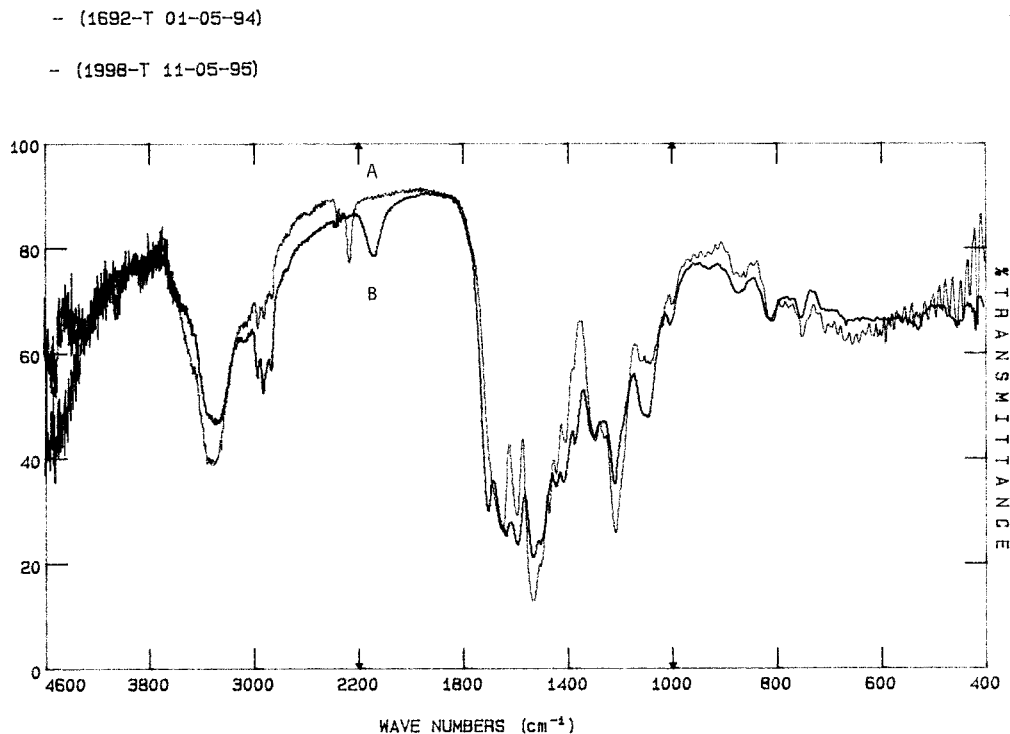


Figure 4 IR spectra of the smoke (A) and the solid pyrolysis residue (B), both of the plain foam.

a small amount of its decomposition products) is involved (or available) for reaction with the retardant.

As the answer to the second question is negative, this left us without an experimental technique to help answer the first question.

Another question then arose. With which section of the polymeric structure of the foam does the TDCPP react: urethane, urea, biuret, or the polyether chains? Or does it react with a decomposition product and, if so, which one? Although the polyether chains seem the least likely candidate for reaction with the TDCPP, previous TGA work¹ did suggest, though somewhat indirectly, that the polyether sections were involved somehow; but as these represent 65% of the foam, this would not explain why only 20% of the retardant (present at only at 7.8%) reacted.

The tolylene diisocyanate (TDI) derived moieties would appear to be more likely candidates for reaction with the TDCPP. Crook and Haggis³ proposed a reaction between the urea crosslinks and the cyclic phosphate ester often formed on heating linear haloalkyl phosphates. Urea crosslinks are stated to represent about half of the

crosslinks in flexible foams.^{4,5} This will be discussed further, below.

Analysis of the Heat-Treated Foams

The heat-treated foams were analyzed for P and Cl. The retarded foam heated in the open mode (not in test tube) at 200°C contained 0.08% P and < 0.2% Cl. This P content represents 15% of the TDCPP originally in the foam. This is in fair agreement with the Py-GC result of 20% (80% vaporization loss) at this temperature.¹ This also showed that, in air, as under the anaerobic conditions of Py-GC, the material that vaporizes out of the foam is mostly TDCPP. The foam heated in the test tube, which lost almost no weight, was found to contain 0.63% P and 3.6% Cl. (The increase in P content relative to the untreated foam is probably artifactual, possibly due to a nonuniform redistribution of the TDCPP in the test tube as the vapor condenses on cooling. P and Cl analysis were performed on separate pieces of the foam bar.) The untreated retarded foam contained 0.56% P and 3.4% Cl. After methylene chloride extraction, the in-test-tube heat-treated foam bar was found to contain 0.08% P and < 0.2% Cl,

Table III Yields and Analytical Results for the Drip Tars

Foam	Yield (%)	C (%)	H (%)	N (%)	H/C Ratio ^a	P (%)	Cl (%)	—NH ₂ (%)
Plain	63.2	60.7	9.7	1.06	1.9			0.28
±	2.2	0.4	0.2	0.08				0.02
	(3)	(3)	(3)	(4)				(2)
Retarded	62.7	59.2	9.7	1.35	2.0	0.37	0.45	0.14
±	2.1	1.2	0.1	0.04		0.006	0.09	0.01
	(7)	(3)	(2)	(3)		(3)	(2)	(2)

Note: These are average values; the number of runs or determinations are given in parenthesis.

^a Atomic ratio.

exactly the same as the foam bar heated openly in the oven. This is further evidence that although confined heating at 200°C retained the TDCPP on the foam, it did not increase the extent of reaction between them.

Pyrolysis of Foams

Loss of TDCPP by Volatilization

At 200°C, the foam still retained its structure, with decomposition being minimal. At higher temperatures (above 250°C), the foam begins to decompose at a faster rate, with the major decomposition products being TDI, diaminotoluene (DAT), the regenerated polyol, and a (putative) double-bond terminate polyether.² As TDCPP is soluble in the polyol used in the formulation of this foam² (and probably also in the polyether decomposition product), heating the foam to temperatures at which the polyol is regenerated would be expected to result, paradoxically, in the retention of more of the TDCPP than when it is subjected to a lower temperature. Temperatures above about 250°C would therefore be expected to result in an increase in the extent of reaction between the TDCPP and the decomposition products of the foam. This is due to the following three causes: (1) increased reaction rates at higher temperatures, (2) increased retention of the TDCPP due to reduction of its vapor pressure resulting from its dissolution in the regenerated polyol, and (3) increase in the formation of foam decomposition products that can react with the TDCPP. For example, TDCPP has been reported to react rapidly with diaminotoluene,⁵ a major decomposition product of this foam.² The cyclic phosphate esters formed on heating linear haloalkyl phosphates⁵

have also been reported to react readily with aromatic amines.⁶

These expectations were confirmed by Py-GC. At 250°C, where the foam still retained its structure, the loss of TDCPP increased to 85%, probably because the higher temperature increased the rate of vaporization. However, at 300 and 330°C, where the foam decomposed, collapsing to a liquid, TDCPP losses were reduced to 49 and 44%, respectively, indicating that the TDCPP does react with the decomposition products of the foam.

Examination of Decomposition Products

On pyrolysis at 340°C under helium flow,² both foams yielded three phases: volatiles, a liquid residue, and a black solid one. The results for the liquid residue are given in Table I; those for the solid residue are given in Table II. (The volatiles of the plain foam have been examined previously.²)

The only significant compositional difference between these two liquid residues (aside from the P and Cl) lies in their nitrogen contents, with that of the retarded foam liquid residue being almost double that of the plain foam. The low Cl/P ratio, 0.3, of the retarded foam liquid residue indicates that TDCPP is not present as the free material, which has a Cl/P ratio of 6. It also indicates that a reaction occurred between the TDCPP and the polyurethane and that this resulted in the incorporation of the phosphorus into the polymer, with the concomitant loss of most of the chlorine.

The H/C ratios of these two liquid residues (1.9 and 2.0) points to the presence of the aliphatic CH₂ units (rather than the aromatic CH units). This is supported by the strong CH₂ absorptions in the 2900 cm⁻¹ region of the IR spectra of these materials in Figure 2. As these two spectra are almost identical to each other and as the spectrum

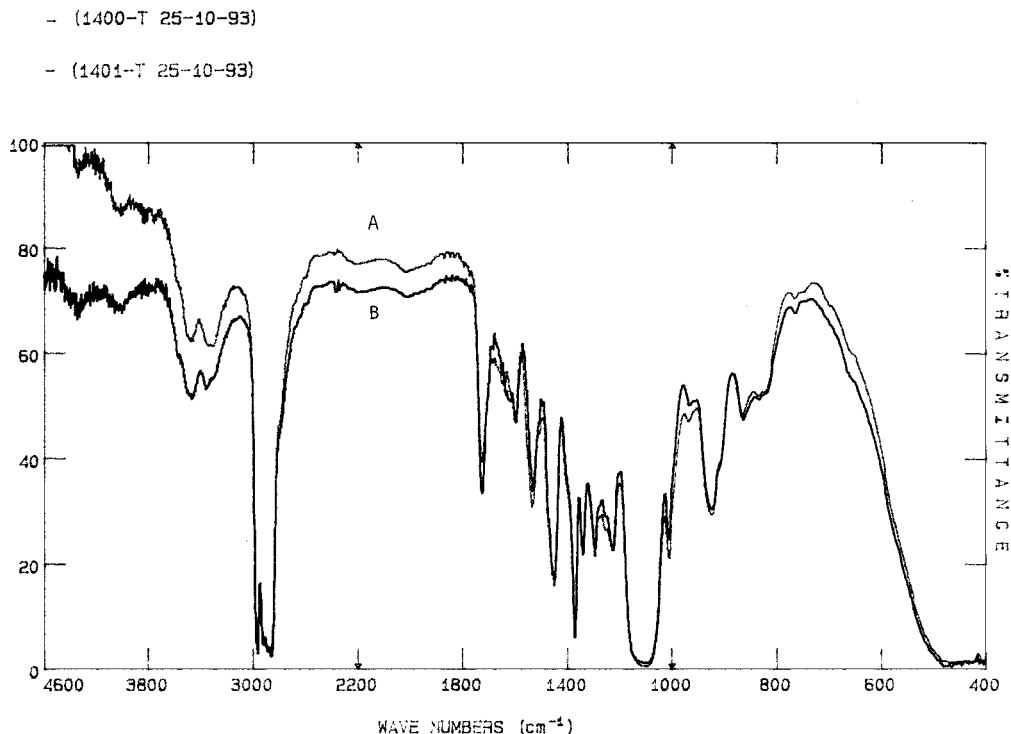


Figure 5 IR spectra of drip tars of plain (A) and retarded (B) foam.

of the liquid phase of the plain foam was found to be very similar to that of the polyol,² it can be concluded that the liquid residue of the retarded foam also consists mostly of the aliphatic polyol used in the preparation of this foam.

These liquid residues therefore appear to consist essentially of the polyether chains of the polyol used in the preparation of the foam and some with nitrogen-containing end groups derived from the TDI-based moieties present in the polyurethane structure before its decomposition. The phosphorus, which is probably attached to some of these nitrogen end groups, may have been attached before or at the beginning of the breakdown of the polyurethane structure. This may involve the urea crosslinks, as suggested by Crook and Haggis,³ or an aminotolylene chain terminal produced by the dissociation of only one of the two carbamate groups on the benzene ring, a dissociation involving mechanism II, as discussed in² (also see below).

It can be seen from Table II that the presence of TDCPP in the foam resulted in an almost five-fold increase in the yield of the solid residue. The 1% phosphorus present in this residue represents 18% of that originally present in the foam as TDCPP.

Figure 3 gives the spectra of the solid phases of the two residues. These two materials appear to be aromatic ureas, probably polymeric. The strong band near 3300 cm^{-1} is indicative of 1,3-disubstituted ureas, as are the strong bands centered around 1630 cm^{-1} .⁹ The weak C—H absorptions in the 2900 cm^{-1} region are indicative of aromatics and therefore exclude the participation of polyether fractions in the formation of these solids. The value of the H/C ratio (1.1 and 1.2; Table II) for these solid phases also shows them to be aromatic. Although the spectra of the two solid residues in Figure 3 are very similar, they do exhibit some differences. A significant one is the absence of the carbodiimide absorbance at 2140 cm^{-1} in the spectrum of the solid derived from the retarded foam. This suggests that the TDCPP was involved in a reaction with the carbodiimide that is present in the solid pyrolysis residue of the plain foam. Grassie and Zulfiqar⁷ state that phosphoric acid reacts very efficiently with the carbodiimide formed by the self-condensation of the isocyanate released on thermolysis of the polyurethane and that this leads to crosslinking and could present a mechanism of char formation. TDCPP may react in a similar manner.

If these solids contain little or no polyether

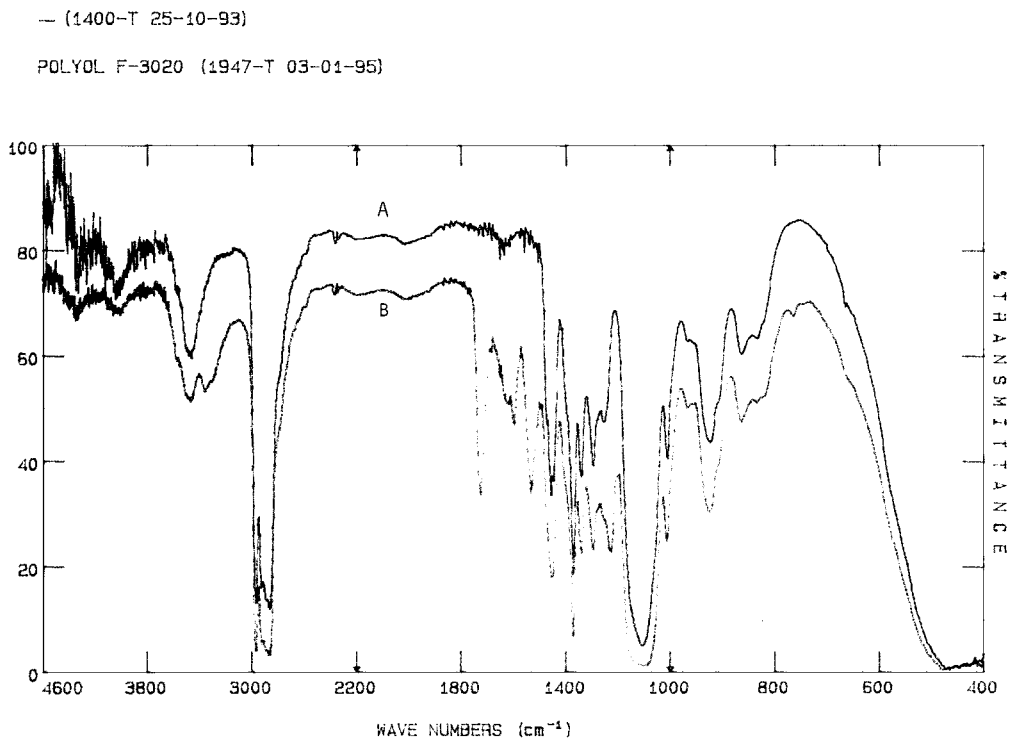


Figure 6 IR spectra of polyol (A) and drip tar (B) of plain foam.

fragments, then they must be based primarily on TDI-derived moieties. TDI has an H/C ratio of 0.67 and DAT, 1.4; the linear polyurea formed when TDI and DAT react in a 1 : 1 molar ratio, 1.0; the polycarbodiimide derived from this polyurea by loss of water, 0.75. The ratios found, 1.1 and 1.2 (Table II), are closest to the polyurea and, as discussed above, the IR spectrum also suggests a polyurea. However, the N/C ratios of these solids, 0.19 and 0.20 (Table II), are lower than 0.25, the value calculated for a TDI-DAT polyurea, which suggests a more condensed system (see also below).

An additional point of interest, one that was not noted previously,² is the similarity of the spectra of the solid pyrolysis residue and the "yellow smoke" of the plain foam (Fig. 4). The latter seems to be the major component of the pyrolysis volatiles of this foam.² Both materials appear to be polyureas. The elemental compositions of the yellow smoke of the plain foam is also given in Table II. The main significant differences between these two spectra are that the solid residue has a carbodiimide band at 2140 cm⁻¹ and a urethane and/or isocyanurate band as a shoulder at 1720 cm⁻¹, while the smoke has an isocyanate absorbance at 2270 cm⁻¹. Both materials exhibit the

strong 3300 cm⁻¹ band, characteristic of 1,3-disubstituted ureas. Although both materials appear to be polyureas, they exhibit at least two major differences: one in appearance, or color; the other in solubility. The smoke is dark yellow to pale brown; the solid residue is dark brown to black. The color difference could be due to the differences in their states of division. The difference in solubility, however, reflects a structural difference. The smoke is readily soluble at room temperature in both dimethylformamide and dimethylsulfoxide to give clear yellow solutions, and the solid residue is insoluble, even in the heated solvents. As the solid residue does not even swell in these solvents, it is probably highly crosslinked.

Examination of Pyrolysis Zone Materials, the Drip Tars

The materials in the pyrolysis zones immediately below the flames of both foams (plain and retarded) are black, viscous, tar-like fluids. These tars can be collected by holding the foam bars in a horizontal position, igniting them at one end and letting the tars drip off in front of the advancing flame.

The retarded foam is self-extinguishing and ne-

NFR FOAM PYROLYSIS @ 340° 4', CLEAR BROWN LIQUID (1950-T 18-01-95)

- (1400-T 25-10-93)

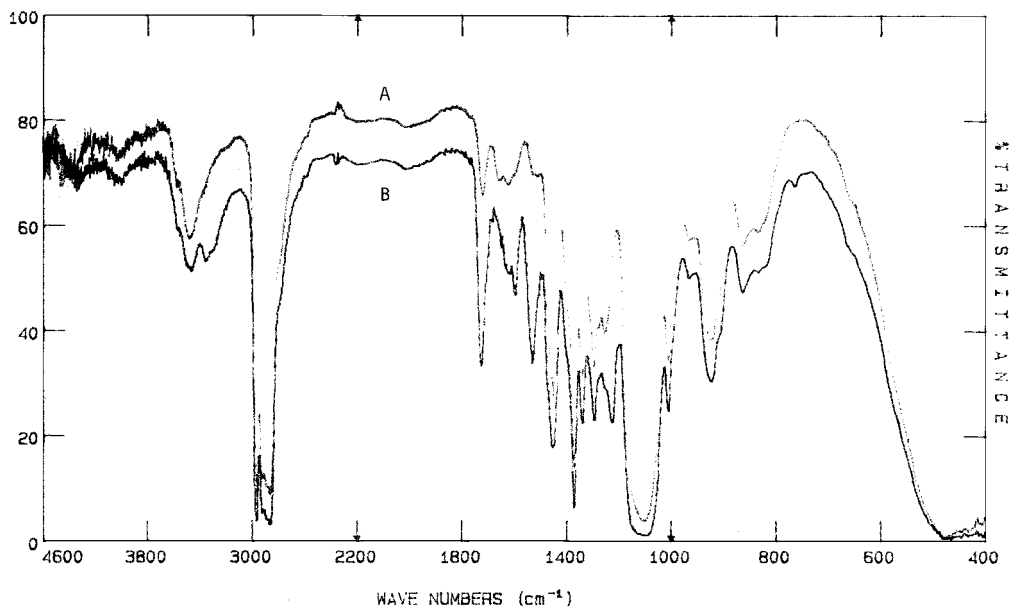


Figure 7 IR spectra of pyrolysis liquid residue (A) and drip tar (B), both of the plain foam.

cessitates continuous reignition in order to collect the tar. The yields and analysis of these drip tars are given in Table III. The yields are slightly lower than the combined phases (liquid + solid) of the pyrolysis residues given in Tables I and II. The tar derived from the retarded foam is much more viscous than that of the plain foam and contains more acetone insoluble solids.

The H/C ratios of these two tars (Table III) indicate them to be mainly aliphatic. Suggesting that, as for the liquid phases of the pyrolysis residues, these tars also consist mostly of the regenerated polyol. Their nitrogen contents, which are somewhat higher than those of the equivalent pyrolysis liquid phase residues, indicates a higher concentration of nitrogenous end groups. As in the case of the pyrolysis residues, the nitrogen content of the tar derived from the retarded foam is higher than that of the plain foam. These tars are probably constituted of a mixture of the solid and liquid fractions of the respective pyrolysis residues.

A phosphorus content of 0.37% in the tar represents 41% of the phosphorus of the TDCPP originally in the foam, indicating a TDCPP loss of 59%, undoubtedly by vaporization. Considering the dif-

ference of conditions between the Py-GC work and the tar collection, the respective losses of 49 and 59% are in fair agreement. This also demonstrates that the pyrolysis study¹ did not produce qualitatively artifactual results and that, under actual burning conditions, over half of the TDCPP does vaporize out of these foam bars.

The low chlorine content of the tar of the retarded foam (relative to its P content) indicates that, as already mentioned above, the reaction between the TDCPP and the foam involves the formation of relatively low-boiling chlorine-containing materials, which vaporize out of the tar. These could be 1,2,3-trichloropropane, formed by thermal decomposition of the TDCPP.⁸

In spite of differences of viscosity and phosphorus contents, no significant difference is apparent in the spectra of the two tars (Fig. 5).

Figure 6 gives the spectra of the tar of the plain foam superposed on that of the polyol used in the preparation of the foam. The difference between the two spectra is not very large, from which it is clear that the polyol is the main basis of the tars. This conclusion is supported by their H/C ratios (1.9 and 2.0; Table III). All of the absorptions of the tar that are not present in the polyol can be

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FR-2 FOAM PYROLYZED @ 340° 2' CLEAR BROWN LIQUID (1951-T 16-01-95)

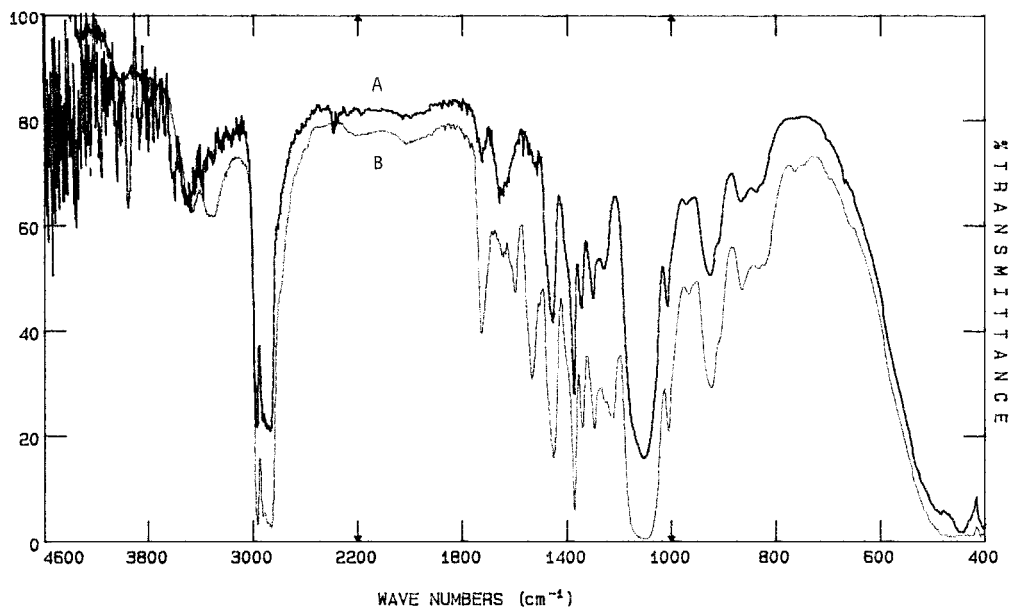


Figure 8 IR spectra of pyrolysis liquid residue (A) and drip tar (B), both of the retarded foam.

assigned⁹ to derivatives of TDI. The band at 1730 cm^{-1} can be assigned to urethane and/or isocyanurate, the doublet at $1630/1590\text{ cm}^{-1}$ to urea derivatives, the band at 1530 cm^{-1} to triazine, and that at 1230 cm^{-1} to urethane. The doublet at $3460/3320\text{ cm}^{-1}$ is characteristic of primary aromatic amines. (The first band of the amine's doublet overlaps and therefore masks the band of the polyol's hydroxy group.) As free DAT was not detected (GC) in these tars (nor was TDI), this doublet probably represents aminotoluene end groups on polyether chains. The lower amine content of the retarded foam derived tar (Table III) tends to confirm that the TDCPP reacted with an amine group (see also below).

Figures 7 and 8 compare the spectra of the liquid phases of the pyrolysis residues with those of the drip tars of the plain and retarded foams, respectively. Both tars contain more amine and isocyanurate than do the liquid pyrolysis residues, in agreement with their higher nitrogen contents (Tables I and III).

"Piggy-Back" Burns

The above results show that the TDCPP reacts with the foam in the condensed phase. The follow-

ing question then arises: Are these condensed phase reactions involved in the retarding activity of the TDCPP? To further examine this question, piggy-back burns were performed. These provided additional evidence of a condensed phase retarding activity by indicating that a retarding factor is formed in the pyrolysis zone under the flame.

The piggy-back burn involves vertically positioning one foam bar on top of another (long axes vertical). The upper bar is then ignited at its top and allowed to burn down to ignite the lower bar. In the first system examined, the upper bar was of plain foam while the lower one was of retarded foam. However, before the upper (plain) bar was positioned on top of the the lower (retarded) bar, the latter had been ignited and allowed to self extinguish. The plain bar was then placed on the tar layer of the resulting stub. After ignition, the upper, plain bar burnt down, being totally consumed (as usual). The flame, however, failed to ignite the lower bar, extinguishing when it reached the tar layer on the stub of the latter.

When this same experiment was repeated with a retarded bar that had not previously been ignited and allowed to self-extinguish (again with

Table IV Analysis of the Crust Formed on the Retarded Foam

C (%)	H (%)	N (%)	H/C Ratio ^a	N/C Ratio ^a	P (%)	O ^b (%)
58.4	4.0	9.3	0.8	0.14	5.1	23.2

Note: The crust was obtained by multiple reignitions.

^a Atomic ratio.

^b By difference.

the plain bar on top), the flame did ignite the retarded bar, and both bars were completely consumed. This difference in behavior can be explained as follows. In the first case, preignition, followed by self-extinguishment of the retarded bar, results in the formation of a fire-retarding factor in the tar layer on the stub of the retarded bar (hence, the self extinguishment). When the upper, plain bar had been consumed and the flame had reached the stub of the lower, retarded bar, it extinguished on the tar layer containing the retarding factor. In the second case, no such preformed tar layer existed. Therefore, there was no retarding factor, so that there was nothing to extinguish or even inhibit the flame when it reached the lower, retarded bar, which it consequently ignited. However, after ignition by the upper bar, the lower, retarded bar behaved uncharacteristically. It did not self-extinguish, as a retarded bar would when ignited by a gas flame, but was totally consumed by the flame. This can be explained as follows. When the flame reached the lower bar, it was accompanied by tar from the upper bar of plain foam. Consequently, the tar being formed under the flame of the retarded foam became diluted with this residual tar from the bar of plain foam. This reduced the concentration of the retarding factor in the tar of the retarded bar. As it seems fairly safe to assume that for self-extinguishment of the flame, a certain minimum concentration of the retarding factor is required, this would explain the effect (or rather lack of it). This behavior is further support for the view that the TDCPP acts in the condensed phase.

Crust Formation

In order to examine the retarding factor, which appears to be formed in the tar, it was necessary to concentrate and isolate it.

When the top of a bar of retarded foam posi-

tioned vertically is ignited, it burns with a small flame, which self-extinguishes. The length of burn depends to some extent on the size and duration of application of the igniting flame (see below for an explanation of this behavior). The stub of such a self-extinguished bar of retarded foam can be reignited. Such reignitions can be repeated a number of times, but this becomes progressively more difficult, with the lengths of burn to self-extinguishment becoming progressively shorter. After several such cycles of self-extinguishment and reignition, the tar on the stub becomes covered with a thin black solid crust. Such a crust layer is not apparent on the stub of a self-extinguished bar after the first ignition but becomes visible during subsequent reignitions. If this tar layer is cut off to reexpose the underlying foam, the resulting stub can be ignited as readily as a previously unignited bar of retarded foam.

This suggests that the retarding factor that develops in or on the tar consists of an incipient solid layer which, on repeated reignitions, builds up sufficiently to form a visible crust. The formation of even a very thin layer of this type in the tar, if sufficiently stable thermally and mechanically, would make quite an effective flame-retarding component. It would present a barrier that attenuates the feedback of thermal energy from the flame to the pyrolysis zone, thus reducing the rate of fuel production. It would also impede transport of the fuel from the pyrolysis zone to the flame.

Although similar, though less viscous, tar layers are also found on stubs of manually extinguished (flame blown out) bars of plain foam. These present no impediment to reignition of the stub.

The tar (plus the crust) of such a multiply reignited bar of retarded foam was analyzed and found to contain 2.4% N, 0.76% P, and 0.94% Cl. As show above in Table III, the drip tar of a retarded foam bar contained 1.33% N, 0.38% P, and 0.38% Cl. Clearly, these three elements had built up in the pyrolysis zone during the repeated reignitions. The fact that the P/N ratio remained fairly constant is evidence that the reaction between the TDCPP and the substrate results in the retention of nitrogen in the pyrolysis zone. As already mentioned above, this reaction appears to involve amino groups as the concentration of these is halved, from 0.28% in the drip tar of the plain foam to 0.14% in that of the retarded foam (Table III). An obvious candidate for such a reac-

CARBONACEOUS LAYER (2116-T 17-06-96)

FR-2 PYROL. 340/2' ETOH INSOL RESIDUE (1984-T 07-03-95)

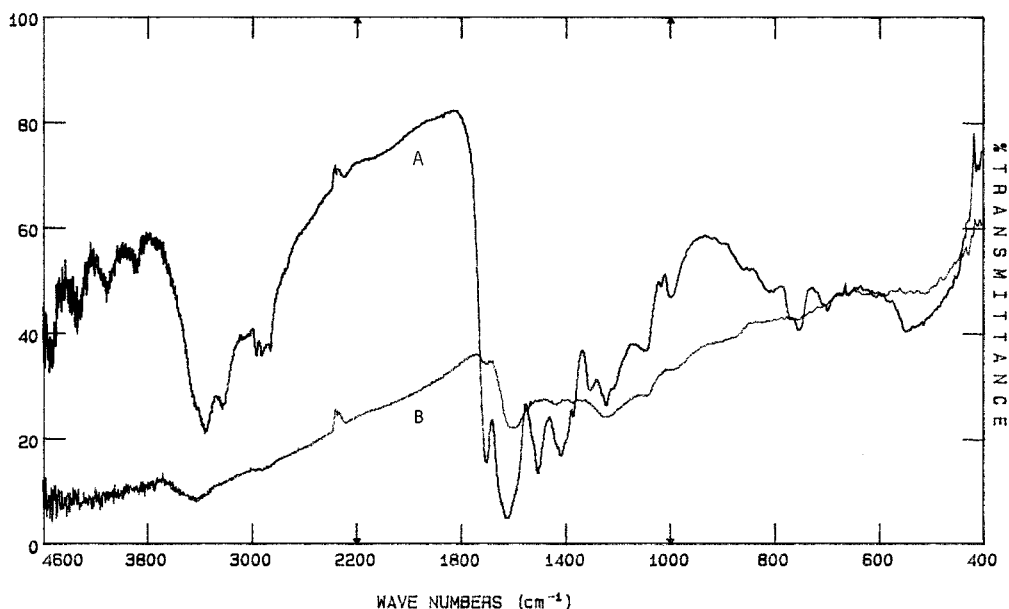


Figure 9 IR spectra of the solid residue (A) and the crust (B), both of the retarded foam.

tion is DAT or, perhaps even more likely, a polyether chain terminated by an aminotolylene unit.

The crusts on the tar layers of several such multiply reignited bars of retarded foam were lifted off the stubs with a pair of tweezers and washed free of tar with acetone and methylene chloride. The analysis of the black solid carbonaceous material is given in Table IV.

Of particular interest is the high phosphorus content of the crust, at 5.1%. The high oxygen content suggests that the phosphorus may be present as phosphate. (Insufficient material was available for chlorine analysis. However, judging by the low chlorine contents of the tars and solid pyrolysis residues, the chlorine content of the crust would also be expected to be low. The difference between the sum of C, H, N, and P and 100 was therefore taken to represent the oxygen content.)

The IR spectrum of the crust is given on Figure 9, together with that of the solid phase of the pyrolysis residue of the retarded foam. The spectrum of the crust is almost closed. This, together with its low hydrogen content, suggests a highly condensed structure. The small absorptions that can be seen are at the wavelengths of the major bands

of the solid pyrolysis residue, suggesting the latter to be the source material for the crust, with the TDCPP enhancing its formation possibly by reacting with the carbodiimide groups.

Figure 10 gives the scanning electron micrograph of the crust.

Reactions Between TDCPP and Foam Decomposition Products

From the above results, it can be concluded that the TDCPP reacts with the polyurethane substrate and/or one or more of its decomposition products. Crust formation probably involves one (or more) of these reactions. The major products of the decomposition of this foam are TDI, DAT, the regenerated polyol, and the putative double-bond terminated polyether.² With the object of establishing with which of the first three of these materials (the fourth was not available) the TDCPP reacts, mixtures of TDCPP with the individual materials (1 : 1 molar) were examined by thermogravimetric analysis (TGA) under nitrogen.

Figure 11 gives the thermogram of a mixture containing 29% TDI and 71% TDCPP, as well as the thermograms of the individual materials. The

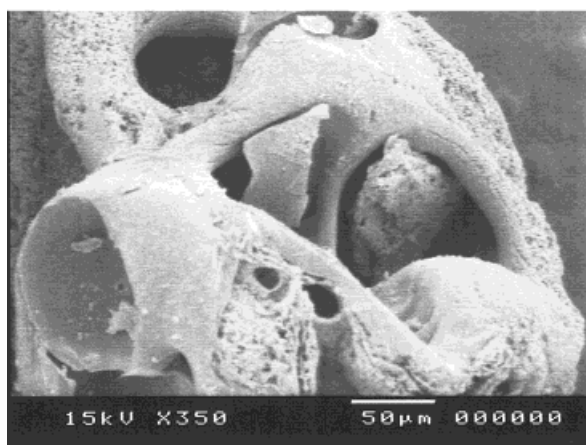
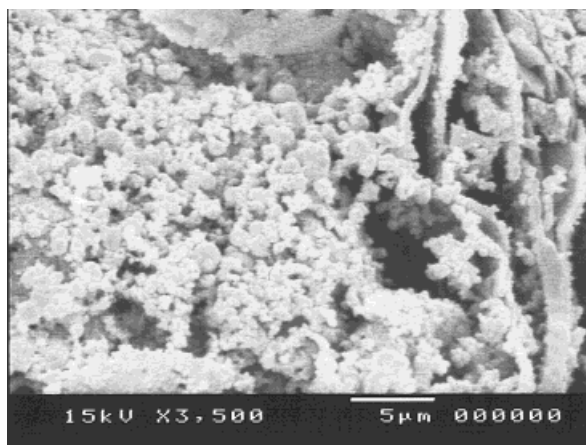


Figure 10 Scanning electron micrograph of solid carbonaceous material in the pyrolysis zone under the flame of the retarded foam.

step in the curve of the mixture at a weight loss of 26% shows that most of the lower boiling TDI vaporized out of the system before much reaction could occur between the two materials. A reaction between these two materials is therefore probably not involved in the retardation mechanism.

Figure 12 gives the thermogram of a mixture of 86% Polyol 3020 and 14% TDCPP, as well as those of the individual materials. This mixture gives a smooth curve without a step, which suggests that a reaction occurred between these two materials. Nonvolatile residue is not apparent on the thermogram; therefore, this reaction is not the basis of the crust formation. Confirmation of a reaction between these two materials was obtained by heating this same mixture in a small

open vial on a hot plate set at 350°. The mixture bubbled and darkened to give a dark viscous liquid on cooling. The phosphorus content of the mixture rose from 1.0% before heating to 1.8% after heating, with the chlorine content dropping from 7.1% to 2.3%. The Cl and P contents of the heated mixture represent an atomic ratio of 0.9. As TDCPP has a Cl/P atomic ratio of 6, this shows that the reaction between these two materials involved the loss of much of the chlorine of the TDCPP. An ester interchange involving the release of 1,3-dichloropropane-2-ol (bp 174°C) may be involved. This reaction would explain the presence of phosphorus in the liquid phase of the pyrolysis residue. Oligomerization of the TDCPP¹⁸ is of course also a possibility. This would, however, yield a Cl/P ratio of 3.

TDCPP has been reported to react rapidly with diaminotoluene.⁵ This is borne out by Figure 13, which gives the thermogram of a mixture of 22% DAT and 78% TDCPP, as well as those of the two individual materials. These thermograms show clearly that reaction occurs between these two materials, leaving a nonvolatile residue, which, at 300°C, accounts for 25% of the weight of the original mixture, with 10% still remaining, even at 500°C.

A mixture of TDCPP and DAT placed on a spatula held in a Bunsen burner flame was found to exhibit intumescent behavior, frothing up to form a solid carbonaceous, friable foam. This reaction could very well play a major role in the formation of the crust.

The Phosphoric Acids Mechanism

Frequent reference has been made in the literature to a retardation mechanism of the halo-alkyl phosphates that is based on their thermal decomposition to phosphoric or polyphosphoric acids, which are claimed to act as barriers.^{7,10-15} However, none of these references actually reported these acids to be present in the pyrolysis zone under the flame. Two studies on the thermal decomposition of linear halo-alkyl phosphates^{8,16} not only do not mention the formation of these acids as the free acids, judging from the reported decomposition products, as well as the proposed mechanisms, this also seems highly unlikely.

Wet indicator paper applied to the tar of the retarded foam gave a pH near 7.5. Nonaqueous titration of this tar indicated that if these acids are present, this can be so only in trace quantities. It would therefore appear that although the for-

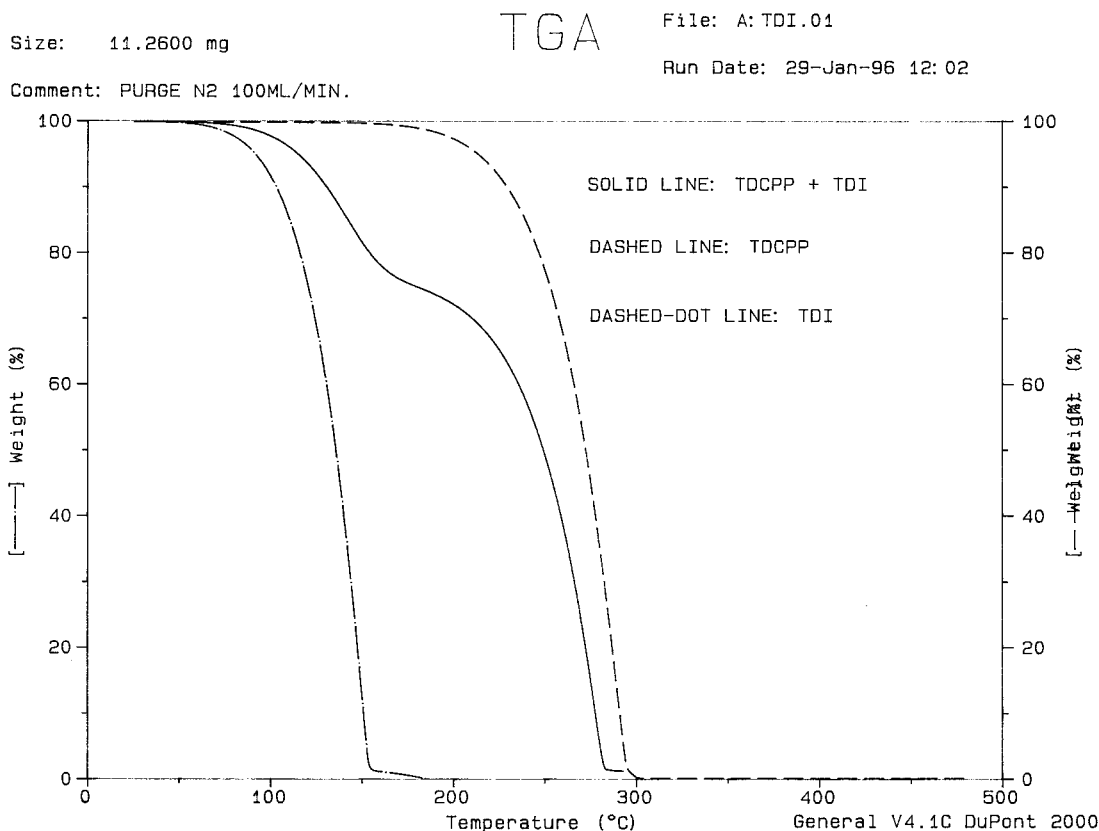


Figure 11 Thermograms of TDCPP, TDI, and their mixture.

mation of free phosphoric acids may be involved when inorganic phosphates are used as fire retardants,¹⁷ this is much less likely to be the basis of the mechanism in the case of the halo-alkyl phosphates.

Site of Activity of TDCPP

A previous study¹ has shown that TDCPP has no visibly apparent retarding effect when injected directly into flames of burning bars of plain foam. This implies that TDCPP is not active in the flame, from which it could be inferred that the main retarding activity occurs in the condensed phase. However, the present study shows that the amount of TDCPP involved in condensed phase reactions is small (about 20% of the TDCPP in the foam), which makes it difficult to see how this could be the main basis of the retarding effect, even if it is based on barrier formation.

Further attempts to establish the site of retarding activity revealed, quite unexpectedly, that this depends on the way the bar is ignited. Ignit-

ing a vertically positioned bar of retarded foam at its top, so as to initiate candle-like top-down burning, results in a small flame, which slowly dwindles and finally self-extinguishes. If, however, the bar is ignited at its bottom (bottom-up burning), it becomes rapidly enveloped in a large flame, which extinguishes almost as soon as the igniting flame is removed. Such rapid self-extinguishment, following removal of the igniting flame, indicates that the fuel vapors produced are insufficiently flammable to sustain a self-supporting flame. It is unlikely that the condensed phase is the site of the retardation in this mode, as after self-extinguishment, only about 10% of the surface of the stub is covered by tar (see below).

The difference in burning behavior following the two modes of ignition should result in markedly different thermal outputs. The very much larger flame produced by bottom-up ignition envelopes the bar and would not only be expected to have a very much larger thermal output due to its much larger size, but it would also be expected to result in a very much larger thermal feedback

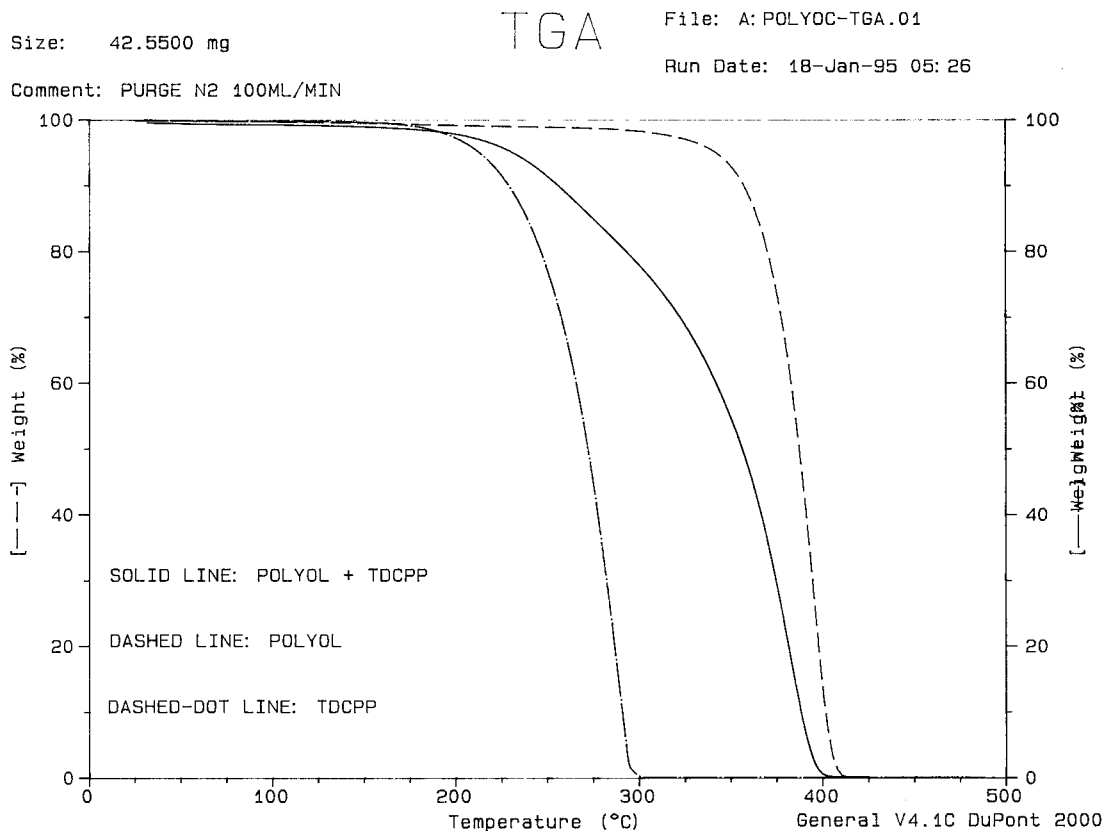


Figure 12 Thermograms of TDCPP, Polyol 3020, and their mixture.

due to the large area of the bar contacted by the flame. This should result in a much larger overall rate of fuel production in bottom-up burning relative to that produced by the small flame of top-down burning. On these grounds, it would have been expected that a flame retardant, any flame retardant active in any phase, would be much more effective in the top-down mode, in which it has to contend with a much smaller rate of thermal output. Yet, as described above, the behavior, at least in the present case with TDCPP, is the very opposite of this expectation.

The pyrolysis work described above, as well as the previously reported TGA work,¹ have both shown that TDCPP vaporizes out of the foam at temperatures below the decomposition temperature of the foam. In the bottom-up mode of burning, the large enveloping flame can therefore be expected to "cook out" TDCPP from those regions of the foam bar, which, although heated by the flame, have not yet reached temperatures at which there is significant decomposition of the foam. This cooked-out TDCPP will therefore not be accompanied by much fuel vapor so that its

entry into the flame will raise its concentration there above that present in the flame of the top-down mode.

Experimental evidence supporting this "cooking out" hypothesis was obtained in the following manner. A bar of retarded foam was ignited in the bottom-up mode. After self-extinguishment, the stub was extracted with ether. The ether was removed from both the stub and the extract by a stream of nitrogen. The extract (which also contained regenerated polyol) was analyzed for P and Cl. The TDCPP content of the stub was then calculated from the weight of the extracted stub, the weight of the extract, and the P and Cl contents of the extract. Three such runs gave the following TDCPP contents for the stubs: -4.6%, 4.9%, and 5.1%, based on Cl analysis, and 4.8%, 5.2%, 5.6%, based on P, respectively. (The slightly higher phosphorus contents of the stubs is consistent with the finding, discussed above, that on heating the retarded foam, some of the TDCPP is incorporated into the foam, and that this incorporation involves the loss of part of the chlorine.) These values, although somewhat spread, are well

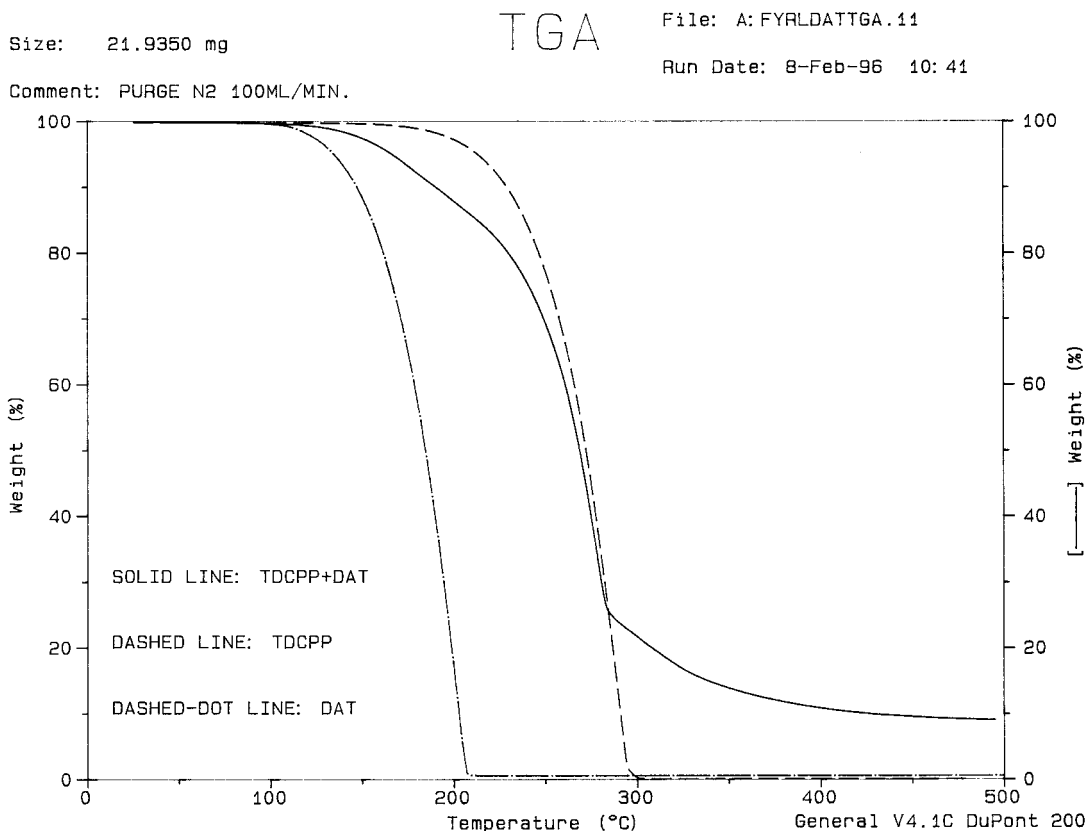


Figure 13 Thermograms of TDCPP, DAT, and their mixture.

below the 7.8% TDCPP content of the retarded foam (7.7% was recovered by a similar extraction and analysis of an unignited bar of retarded foam), lending strong support to the "cooking-out" hypothesis.

In the top-down mode, it was found that the time of burn to self-extinguishment depends to a certain extent on the duration of application of the igniting flame: the longer the duration, the longer the burn time to self-extinguishment. This effect can also be put down to the volatility of the TDCPP. Application of the igniting flame to the top of the bar will cook out TDCPP from a region of the foam bar below the pyrolysis zone, a region that is heated sufficiently to vaporize the TDCPP, but not enough to decompose the foam. This will create a TDCPP-depleted zone just below the pyrolysis zone. The longer the igniting flame is applied, the deeper the depletion zone and, consequently, the longer the burn period to self-extinguishment after removal of the igniting flame. This effect will tend to increase even further the

difference in concentration of TDCPP in the flames of the two burning modes.

There are other difference between the two burning modes that are also relevant to this discussion. One of these involves the extent to which the flame-exposed areas of the foam are covered by tar. In top-down burning, the top of the bar of foam below the flame rapidly becomes completely covered by a layer of tar. Bottom-up ignition, on the other hand, results in a flash burn, in which the flame contacts much of the surface of the foam bar. After self-extinguishment (which, in this mode, occurs almost immediately upon removal of the igniting flame), the surface of the bar that had been exposed to the flame is covered with small drops of tar that, however, cover only about 10% of the flame-scorched surface. This low surface coverage by the tar is actually not surprising as the melting of the foam to form the tar involves an almost 60-fold reduction in volume. (The density of the foam is 0.028 g/mL, and that of the polyol is 1.02 g/mL. Taking into account that the

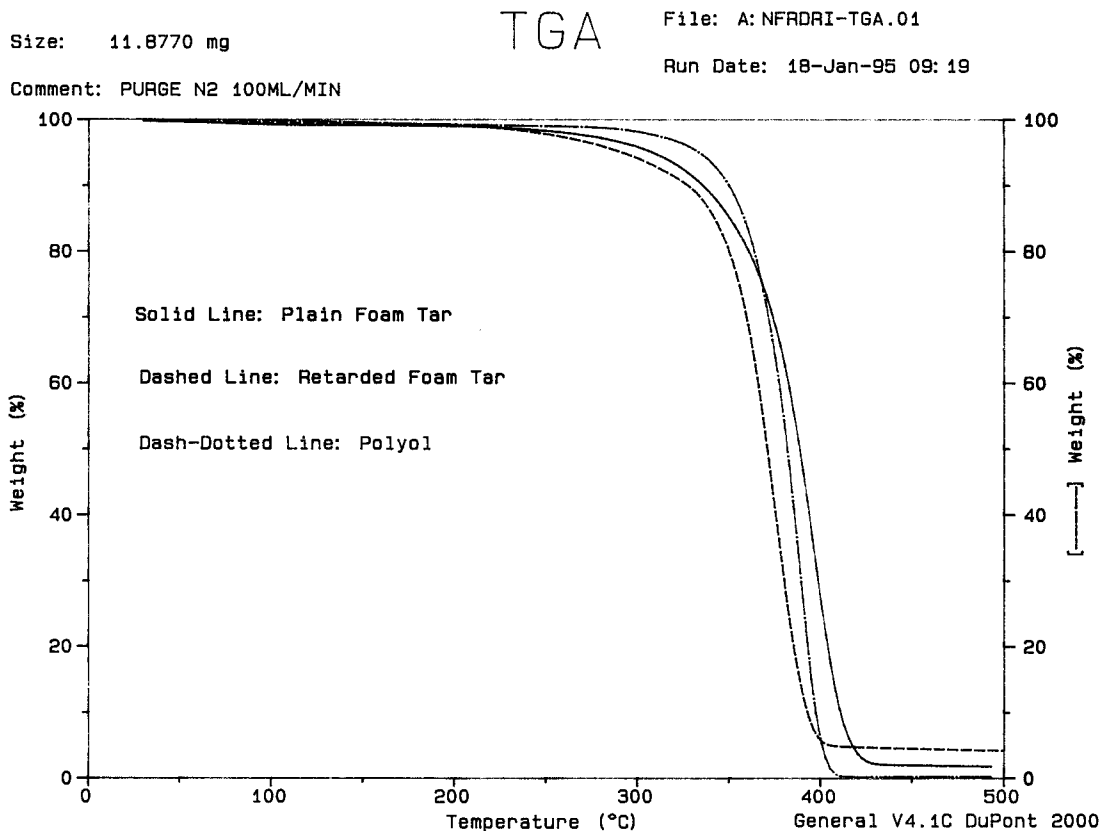


Figure 14 Thermograms in nitrogen of the tars of the plain and the retarded foams and of the polyol.

tar represents 63% of the foam (Table III), this gives a volume reduction by a factor of 58 in going from the foam to the tar.) It is clear that retardation in the condensed phase, while it can play a major role in top-down burning in which the burning surface is totally covered by tar, cannot play such a role under bottom-up burning conditions where the tar covers only a small fraction of the surface. This is especially so if retardation in the condensed phase is based on barrier formation; the rapidity of extinguishment on bottom-up ignition would not appear to extend sufficient time to allow the buildup of an effective barrier. These conclusions are further strengthened by the results of the edge-painting experiments described below.

Edge-Painted TDCPP

In another attempt to differentiate between retarding activity in the flame and the condensed phase, the four edges of a plain bar of foam were

painted with TDCPP. (To facilitate this, the TDCPP used for this purpose was colored blue with a very small amount of ballpoint pen ink.) In view of the minimal fraction of the foam bar wetted by the TDCPP, this mode should result in a minimal involvement of condensed phase inhibition, but should have little or no effect on the extent of inhibition in the flame. A bar of plain foam thus edge painted with TDCPP to a loading of 7.2% (of the weight of the foam) and ignited top-down burnt down markedly more rapidly in its center, leaving the four TDCPP painted edges sticking up (rather like a four-poster bed). The bar did not self extinguish. This behavior is indicative of inhibition in the condensed phase in those regions where the TDCPP had been painted. But because of the minimal cross-sectional coverage, it did not suffice to achieve self extinguishment. This also showed that in this mode the flame is not the main site of the inhibition.

Another plain bar, similarly edge-painted, was ignited, this time bottom-up. The flame extin-

Sample: NFR Drip Tar
 Size: 4.8170 mg
 Method: TGA 500°C.10°C/MIN.
 Comment: PURGE AIR.

TGA

File: C:DRITAR-TGA.01

Run Date: 4-Jan-97 16:38

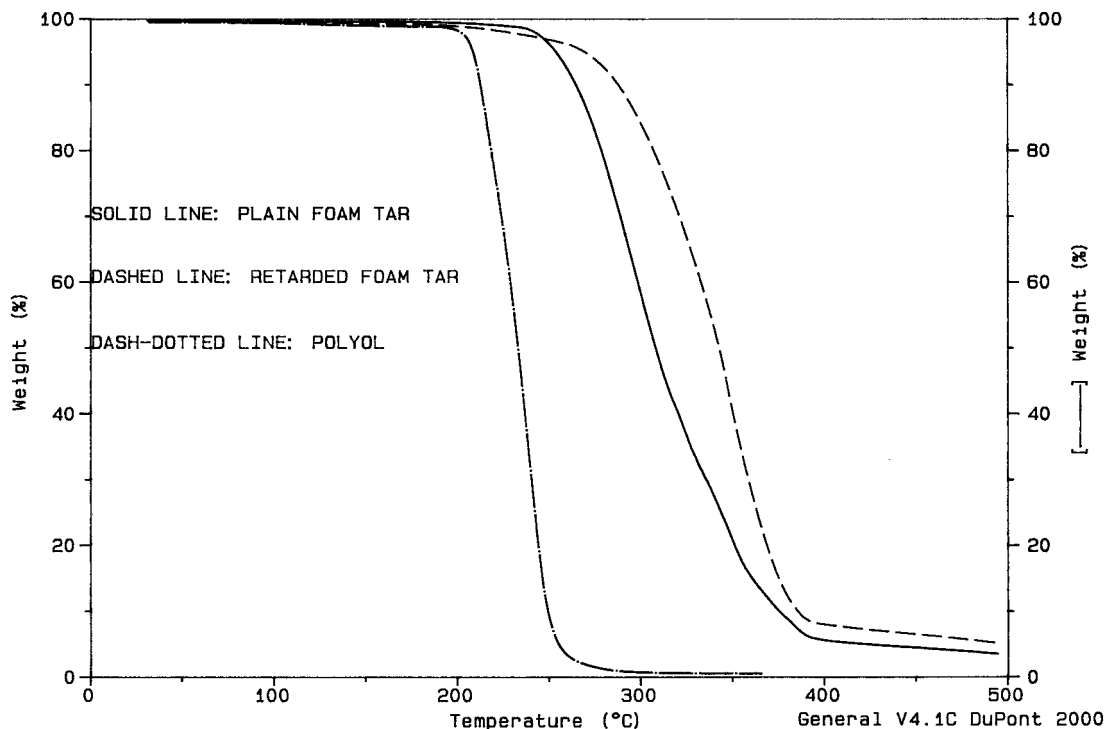


Figure 15 Thermograms in air of the tars of the plain and the retarded foams and of the polyol.

guished immediately upon removal of the igniting flame. Such rapid extinguishment based on so little of the cross section of the bar containing the retardant is highly unlikely to have involved any significant contribution from retardation in the condensed phase. Rather, it indicates that in this mode of ignition, the major part of the retardation occurs in the flame.

As has been shown previously by TGA,² the unretarded foam decomposes in two stages. The first involves the splitting out of TDI-based moieties (TDI and DAT, but apparently mostly a TDI-DAT polyurea, the yellow smoke), leaving a residue consisting largely of the regenerated polyol which then decomposes in a second stage at a higher temperature. The polyol is of high molecular weight (3000), and, as a result, its ambient temperature vapor pressure is too low to support a flame and it, therefore, cannot be ignited without a wick. TGA shows (Fig. 14) that only above about 350°C does the polyol begin to decompose (or volatilize) at a significant rate, which means

that in order for the polyol to undergo self-supportive burning, it must be above this temperature. The tars, as discussed above, are essentially regenerated polyols and, similarly to the latter, are also difficult to ignite. They yield TGA curves that are very similar to that of the polyol (the TGAs of both the tars and the polyol in nitrogen are recorded in Fig. 14). This suggests that the molecular weights of these tars lie in the same range as that of the polyol. This is further confirmation that the first stage of decomposition of the polyurethane involves the dissociative loss by vaporization of the aromatic (TDI-based) units, with little or no degradation of the polyether chains occurring during this stage of the decomposition.²

It has been shown previously² that the thermal stability of the polyol is very sensitive to the presence of oxygen. The two tars, in spite of their compositional similarity to the polyol, appear to be much less sensitive to oxygen than the latter, with the tar of the retarded foam being the more stable of the two. This suggests that the tars and, in

Size: 11.8770 mg
Method: TGA 500°

TGA

File: A: NFRDRI-TGA.01

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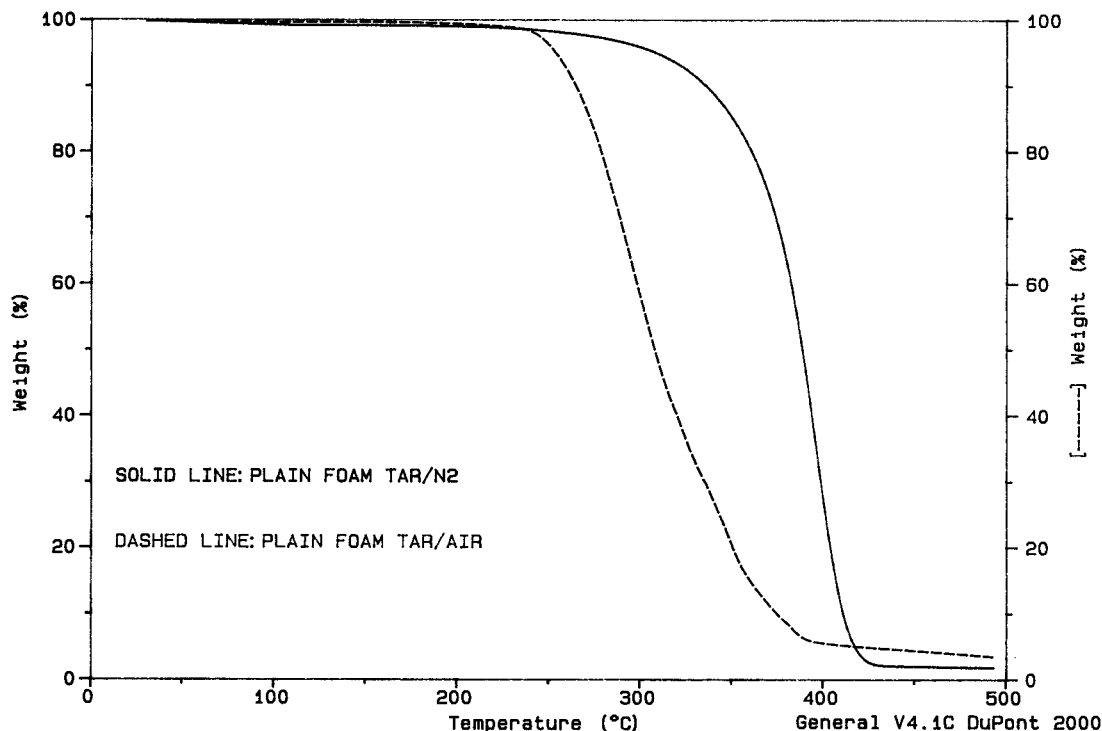


Figure 16 Thermograms of the plain foam tar in nitrogen and air.

particular, that of the retarded foam, are even more difficult to ignite than the polyol. Figure 15 shows the TGAs of these three materials in air. Figures 16 and 17 give the TGA curves of the tars of the plain and retarded foams, respectively, both in nitrogen and in air. (The tars, being regenerated polyol, also have long polyether chains. Their reduced sensitivity to oxygen is therefore somewhat unexpected. As the major difference between the tars and the polyol appears to lie in the end groups on the polyether chains, these may be involved in this effect. Alternatively, a component of the tar may act as an antioxidant.)

There is another significant difference between the two burning modes. During top-down burning, the regenerated polyol collects as a tar under the flame and is consumed by it, with the structure of the undecomposed part of the foam acting as a wick. Therefore, in this mode, there is total consumption of all the components of the foam. On the other hand, in bottom-up burning, the fuel that feeds the flame during the flash burn appears to be based mostly on the initial decomposition

product of the polyurethane, its TDI-based aromatic component.² Under such conditions, the time of burn is probably too short to cause any significant decomposition of the difficult to ignite tar residue left as small drops on the surface of the foam. This suggests, therefore, that the fuels of the two ignition modes differ markedly. Assuming that during the flash burn off of bottom-up ignition only the aromatic fraction of the polyurethane is split out and vaporized to provide the initial fuel for the flame and that all of the chlorine of the TDCPP entering the flame is converted to HCl, then, at a loading of 7.8% TDCPP, the HCl would represent close to 40% of the volume of the vapors emitted (this is the molar concentration, with the concentration by weight being 13%).

The flame extraction work¹ has shown that the aliphatic phosphates decompose rapidly and completely in flames of this foam. No chloro-C₃s were detected in such flames, whereas inorganic chloride and phosphate were detected.¹ Paciorek et al.¹⁶ recovered 30% of the chlorine of TDCPP as HCl at 370°C under oxidative conditions. The temperature

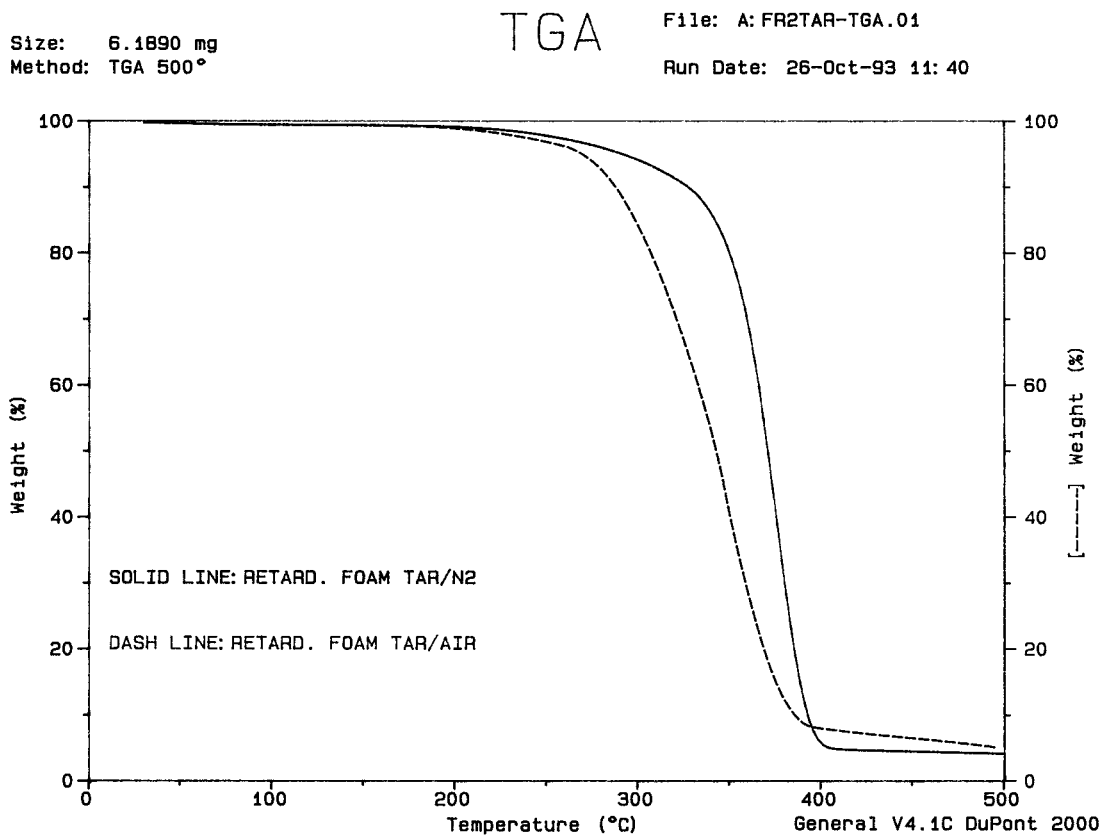


Figure 17 Thermograms of the retarded foam tar in nitrogen and in air.

in the flame is undoubtedly higher and could therefore be expected to lead to an increase of the formation of HCl. Extensive decomposition of the TDCPP to HCl is therefore quite a reasonable assumption; but even if not all of the chlorine is released as HCl, the latter most probably still represents a significant fraction of the vapors produced under bottom-up burning conditions. The above discussed cooking-out effect can be expected to still increase further the HCl concentration in the fuel vapor. The TDI-DAT polyurea probably appears in the fuel vapor as an aerosol,² which would tend to increase even further the effective volume concentration of the HCl in the fuel. In other words, the effectiveness of TDCPP in bottom-up ignition could be accounted for by a simple nonfuel gas dilution effect, with HCl being the diluent.¹⁸ Previous work¹ supports this interpretation, having shown by the nitrous oxide test¹⁹ as well as by work based on flame injection, that in the present system, the chlorine is not involved chemically as a flame poison. There are previous claims that the flame-retarding action of the halogens is based on physical effects, such

as fuel dilution, endothermic vaporization, and cracking,²⁰⁻²³ rather than on chemical processes based on the trapping of radicals.^{24,25}

The reduced flammability of the HCl-diluted fuel vapors produced under bottom-up ignition cannot, however, be the whole story, as on this basis, the injection of TDCPP directly into the flame of a burning bar of plain foam would have been expected to produce the same effect, particularly as this results in a very high TDCPP concentration in the flame. However, as previously reported,¹ this does not happen, and the flame keeps on burning. An additional effect must therefore come into play.

The poorly flammable, TDCPP-diluted, fuel vapors will have a low flame propagation velocity (hence, the poor flammability). This will tend to push the flame away from the pyrolysis zone and its source of fuel, thus reducing thermal feedback and, consequently, the rate of fuel production. This effect is site specific, occurring in the dark, preoxidation region of the flame. Injecting TDCPP into the heat and light-emitting bulk part of the

TDI-DAT POLYUREA (2134-T 29-07-96)

- (1692-T 01-05-94)

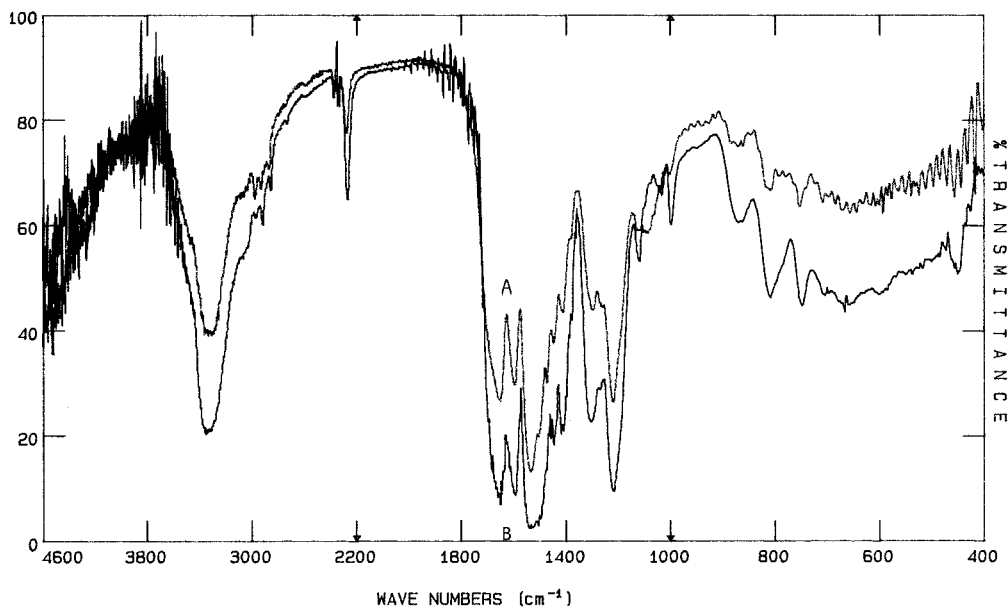


Figure 18 IR spectra of the plain foam smoke (A) and the solvent-precipitated TDI-DAT polyurea (B).

flame (of the plain foam), as was done previously,¹ apparently does not dilute the fuel vapors close enough to the pyrolysis zone to bring the dilution effect into play. (Flame injection of a fire retardant would be expected to show a retarding effect if its retardation mechanism is based on flame poisoning. Flame injection could therefore serve as a simple and quick screening test for this mechanism.)

In the top-down mode of burning, the extent of dilution of the fuel vapors by HCl is very much less than it is in the bottom-up mode. This is so for three reasons, as follows: (1) the formation of a TDCPP depletion zone by the igniting flame will reduce the concentration of TDCPP in the flame, (2) there is no cooking out effect to raise the concentration of the TDCPP in the flame as there is in bottom-up burning, and (3) the fact that in this mode the tar does burn. The latter increases fuel production by a factor of about three, with the polyol representing two-thirds of the weight of the foam. As the dilution effect requires relatively high concentrations of inert diluent, this would explain the absence of a significant retarding effect in the vapor phase during top-down burning.

CONCLUSION

The results of this work indicate that for this combination of flexible polyurethane foam and fire retardant, the orientation of the specimen, while burning, has a critical influence on the mechanism of retardation.

Bottom-up ignition results in a flash burn, which lasts only as long as the igniting flame is applied. After self-extinguishment, the surface of the residual stub of foam is studded with droplets of tar. These droplets, which cover only about 10% of the surface of the stub, were shown by IR spectroscopy to consist essentially of the polyol component of the polyurethane. The fuel for this flash burn therefore appears to consist mostly of the initial volatile decomposition product of the polyurethane,² the tolylene diisocyanate-based aromatic fraction, which represents one-third of the substance of the polyurethane. Analysis of the stub left after self-extinguishment showed it to contain a markedly lower concentration of the fire-retardant TDCPP than originally present in the foam. The missing TDCPP was most probably cooked out of the foam by the up-drafting flame

and then entered the flame. Taken together, these two findings indicate that during bottom-up burning, there is a much higher concentration of TDCPP in the flame than there is during top-down burning. In the latter case, all of the components of the polyurethane contribute to fuel formation, and, as up-drafting of the flame around the foam does not occur, extensive cooking-out of the TDCPP cannot take place. It is proposed that, in the bottom-up mode, the relatively high concentration of low-fuel-value decomposition products of the TDCPP (mostly HCl) in the fuel vapors lowers their flame propagation velocity to below that at which these vapors stream out of the pyrolysis zone. Such a velocity inversion will tend to push the flame away from the pyrolysis zone, disrupting, or at least attenuating, the thermal feedback loop that feeds the flame.

In the top-down mode, the pyrolysis zone under the flame consists of tar, which is essentially polyol and which rapidly covers all of the burning surface. The liquid tar is held by the structure of the undecomposed foam below it, and which therefore acts as a wick. As the foam burns down and the tar is consumed by the flame, a carbonaceous layer builds up on it. This carbonaceous layer, which was shown by analysis to contain phosphorus, can be expected to act as a barrier, attenuating the transfer of heat and fuel; this action is probably the basis of the retarding mechanism in this burning orientation. The amount of TDCPP that can enter the flame in this mode is limited and too small to have much of a dilution-based retarding effect. The fact that the buildup of the carbonaceous layer requires time would explain why extinguishment is slow in this mode.

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ADDENDUM

In a previous study,² the yellow smoke produced on pyrolysis of the unretarded foam was shown

to have an IR spectrum very similar to a smoke prepared by mixing the vapors of TDI and DAT. The method used was rather crude and did not permit controlling the ratio of the two reactants. A TDI-DAT polyurea has now been prepared under better-controlled, but possibly less-representative, conditions by mixing stoichiometric amounts (molar ratio 1 : 1) of these two materials dissolved in methylene chloride. The polyurea precipitated out as a fine white powder and, similarly, to the in-vapor prepared material, is soluble in dimethylformamide, but not in acetone. Its spectrum is almost identical to that of the pyrolytic smoke of the foam (both in KBr; Fig. 18). This strengthens the concept that the yellow smoke actually is a TDI-DAT linear polyurea.

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