

# THERMAL DEGRADATION OF POLYURETHANE FOAMS

By M. A. BOULT,† R. K. GAMADIA,† and D. H. NAPIER†

## SYNOPSIS

In view of the wide industrial usage of polyurethane foams some aspects of their behaviour have been considered under thermally extreme conditions and in a fire emergency.

Foams with and without combustion inhibitors and a foam based on the isocyanurate ring have been examined by heat penetration and weight loss measurements. Analysis of the products of decomposition has established that phosphorus compounds, cyanide, isocyanate and halogenated materials were evolved. Attention was also directed to the surface temperature at which spontaneous ignition occurred (in the range 220° to 400°C) and to the state of the charred residue. The effect upon some of these aspects of atmospheres deficient in oxygen as compared with air have been investigated.

The results obtained indicate some of the hazards liable to arise from these materials, and the degree to which they retain their serviceability under extreme conditions.

## Introduction

The rapid growth in the development of plastics has led to their use as an improvement to, or as a substitute for, traditional materials as well as to their use in applications for which traditional materials were not suitable.

The behaviour of traditional materials under both service and emergency conditions is fairly well known except when the range of operating conditions is extended or when experience or research leads to the definition of a new hazard, for example, the long-term effects of blue asbestos on operatives and the toxicology of benzene. A background of experience has not yet been built up for some of the newer materials. It is intended in this paper to draw attention to some aspects of the behaviour of polyurethane foams under both fire emergency and thermally severe service conditions. It is hoped thereby to assist in building up the background of knowledge relating to the behaviour of this material which is now being employed in a wide variety of industries. Some of the important uses include the thermal insulation of plant and pipework at both high and low temperatures, the filling of cavities in walls of buildings both in brickwork and in metal partitioning, and for the major or minor components of furniture. It is also used in clothing and footwear and in packing. It is therefore liable to be in use or on-site in considerable quantities in the chemical and process industries. Aside from these uses it may be noted that it has been used in coal mines as well as in the domestic appliances and automobile industries.

Examination of its behaviour under fire emergency and thermally severe conditions involves considerations of pyrolysis and of combustion in oxygen-deficient atmospheres. In view of the fact that polyurethane foam is somewhat thermally unstable and cannot be classed as a highly resistant organic polymer,<sup>1</sup> extensive thermal damage would be anticipated when temperatures in excess of 250°C are encountered. In order to assess the effect of conditions of

pyrolysis and of partial combustion the following have been studied:

- (1). Heat penetration rates.
- (2). Chemical stability.
- (3). Conditions for spontaneous ignition by radiating sources.
- (4). Extent of damage to the foam and the structure of the char remaining.
- (5). Toxicological properties of products evolved during decomposition of the foam.

## Types of Polyurethane Foam

Many formulations have been used to produce a wide range of foams. The first broad classification of these is into flexible and rigid foams. The former is of open-cell structure and is used extensively in furniture; a polyester-based material is used for insulating hot water and low-pressure steam pipes. The latter is of closed-cell structure and such materials are used extensively as thermal and acoustic insulants. There is a range of foams with properties intermediate to the two extremes.

Distinction may be drawn between polyurethane foams on the basis of the raw materials used in their production. They may be based on polyether or polyester with polyol initiator; again tolylene diisocyanate (TDI) or diphenylmethane diisocyanate (MDI) may have been used. Variation may also occur in the blowing agent used although carbon dioxide produced by decomposing isocyanate is usually combined with a halogenated methane. Such variations affect the properties of the foam; for example polyester foams are more flame resistant than polyether-based foams.<sup>2</sup>

†Department of Chemical Engineering and Chemical Technology, Imperial College, Prince Consort Road, London, S.W.7.

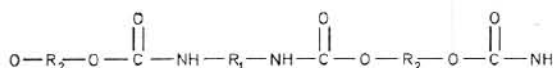
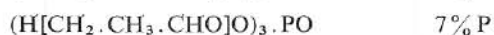
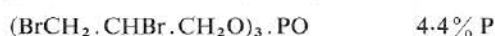


Fig. 1.—Simplest form of urethane linkage

A further important division is into those foams that have fire retardant added and those which do not. The former category may be sub-divided into:

(a) those with a fire retardant mixed in as a simple additive, e.g., *tris* (chloroethyl) phosphate (TCEP),

(b) those in which part of the polyol has been replaced by a phosphorus-containing compound, which becomes incorporated into the chemical structure of the foam, e.g., Firemaster T 23 P (Michigan Chemical Corporation)



Fyrol 6 (Stauffer Chemicals)



Reference will also be made in this paper to a foam based on MDI which is used to produce the isocyanurate ring with polyols bound in as urethanes; a rigid highly cross-linked foam results.<sup>3</sup>

The simplest form of urethane linkage is shown in Fig. 1 and the isocyanurate ring from MDI is given in Fig. 2.

#### Heat Penetration Measurements

The investigations relating to heat penetration were performed by subjecting one end of a cylindrical sample of foam, 47 mm dia., to a known intensity of radiation and measuring the axial temperature histories at selected distances from the exposed face. The intensities of radiation used were 4.2 kW/m<sup>2</sup> (0.1 cal/cm<sup>2</sup> s) and 21.0 kW/m<sup>2</sup>; some comparable values from frequently encountered systems are shown in Table I.<sup>4</sup>

TABLE I.—Radiation Intensities in Some Practical Systems

	(cal/cm <sup>2</sup> s)	(kW/m <sup>2</sup> )
Summer sunshine in England	0.016	(0.672)
Radiation to cause pain in 3 s	0.25	(10.5)
Spontaneous ignition of wood after an extended period	0.7	(29.4)

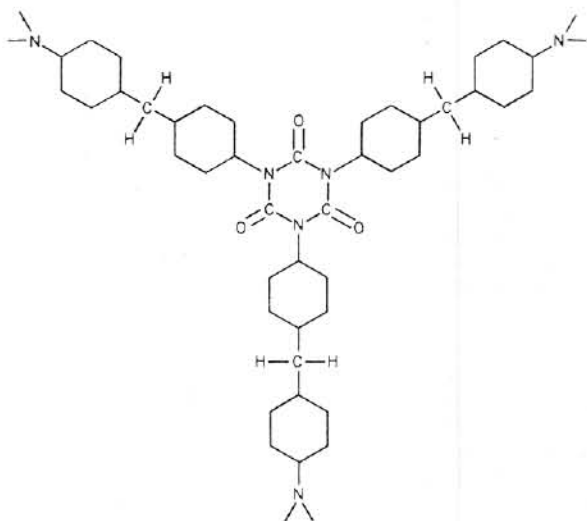


Fig. 2.—Isocyanurate ring formed from MDI

Typical temperature histories are shown in Fig. 3. The foams examined were rigid, of nominal density 32 kg/m<sup>3</sup> (2 lb/ft<sup>3</sup>). Values of thermal diffusivity were calculated by assuming the system to approximate to a semi-infinite body, subjected to constant radiation;<sup>5</sup> these values and those of some typical building materials are shown in Table II.

TABLE II.—Values of Thermal Diffusivity of Polyurethane Foams and of some Building Materials

Material	Thermal Conductivity (W/m °C)	Thermal Diffusivity (m <sup>2</sup> /s)
(a) Polyurethane foam, 20 parts TCEP in mix	23.1 × 10 <sup>-3</sup>	0.81 × 10 <sup>-6</sup>
(b) Polyurethane foam		
(c) Isocyanurate foam		
(d) Polyurethane foam with phosphorylated polyol		
Air	23.9 × 10 <sup>-3</sup>	18.7 × 10 <sup>-6</sup>
Crown glass	1150.0 × 10 <sup>-3</sup>	0.58 × 10 <sup>-6</sup>
Brick	825.0 × 10 <sup>-3</sup>	0.38 × 10 <sup>-6</sup>
Wood (spruce, across grain)	123.0 × 10 <sup>-3</sup>	0.24 × 10 <sup>-6</sup>

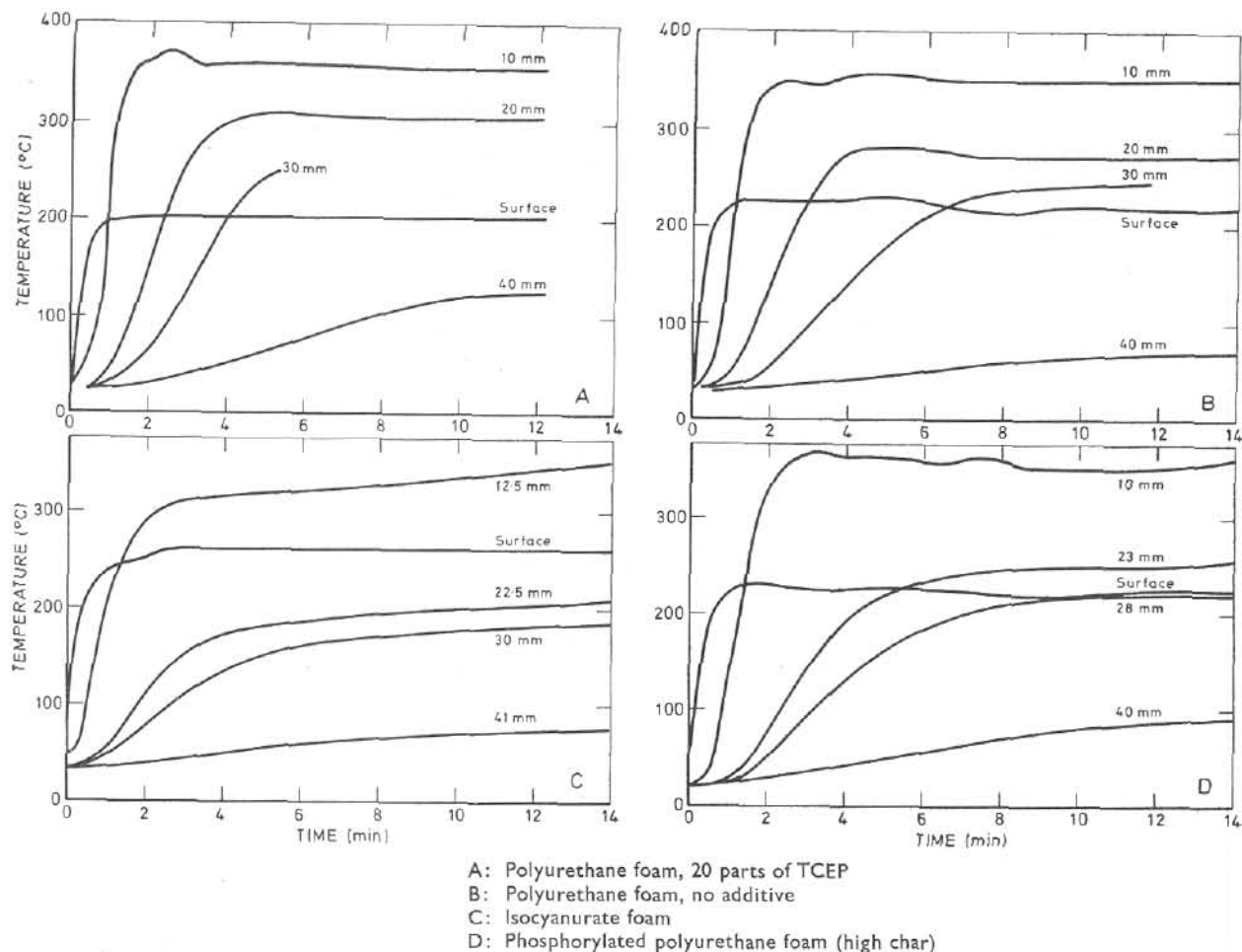
The values for polyurethane foams were calculated from the steeply rising part of the curves. Thermocouples were placed at distances behind the exposed face indicated on the curves.

The curves showing heat penetration are of the expected shape but there are certain notable differences between the heating rates in different foams. The heat penetration rate was greater for foam (a) containing TCEP than for the foam (b) without fire-retardant due to the "fluxing" effect of the additive whereby the cell structure was more readily broken down and heat transfer assisted. It was also observed that a decrease in heat penetration rate occurred in the order (a), (b), (d), (c) (as represented in Table II); this correlates with the decreasing cell size of the char.

Surface temperature of the samples, as measured by a shielded thermocouple, was also recorded and that for foam (b)—without additive—and foam (d)—with phosphorylated polyol—showed a marked decrease after a few minutes. This resulted from the shrinkage of the samples and consequent movement of the exposed face from the thermocouple measuring surface temperature. The fall in temperature recorded on thermocouples close to the surface of foams (a), (b) and (d) was probably due to the internal softening of the foam and to the formation of a layer of char on the thermocouples.

Isocyanurate foam behaved differently from the others as shown by the curves in Fig. 3. The foam did not shrink and charring was more gradual. Cracks were formed in the exposed surface arising from the stresses produced by heating. These resulted in fissures in the material at which decomposition continued thus widening them and aiding the processes of heat penetration.

Heat penetration curves for high modulus and rigid polyurethane foams of nominal density 64 kg/m<sup>3</sup> are shown in Fig. 4. The temperature was measured one centimetre behind the exposed face when the samples were exposed to radiation of intensity 21 kW/m<sup>2</sup> in air and in nitrogen. Curves obtained with rigid foam in both air and nitrogen were similar indicating the controlling influence of the softening and breakdown of the structure of the foam. In respect of heat penetration the behaviour of the foam of high modulus was similar to rigid foam, but the final temperature attained in nitrogen was some 80 degC lower. In comparing the final temperatures attained at 4.2 kW/m<sup>2</sup> with those in Fig. 4 it is noteworthy that the effect of a five-fold increase in intensity was minimised by the char layer formed at the exposed face; this layer will be discussed later.



The foams were all rigid, of a nominal density of  $32 \text{ kg/m}^3$ , and were subjected to an intensity of  $4.2 \text{ kW/m}^2$

Fig. 3.—Thermal penetration by irradiation. Temperature histories at various depths below heated face

Curves showing the temperature of a thermocouple inserted into the centre of a small cylinder of foam (height: 40 mm, diameter: 29 mm) which was heated at  $300^\circ\text{C}$  are given in Fig. 5; air or nitrogen was passed over the samples at the rates mentioned. The marked difference between the behaviour of the isocyanurate foam and the high modulus foam is of interest. In the case of the former, no strongly exothermic reaction occurred in air whereas for the latter, the sample temperature in air rose rapidly. This divergence in behaviour was observed to commence above about  $225^\circ\text{C}$ ; when the temperature is raised sufficiently combustion of the isocyanurate results and the sample temperature rises rapidly.

#### Measurements of Loss of Weight

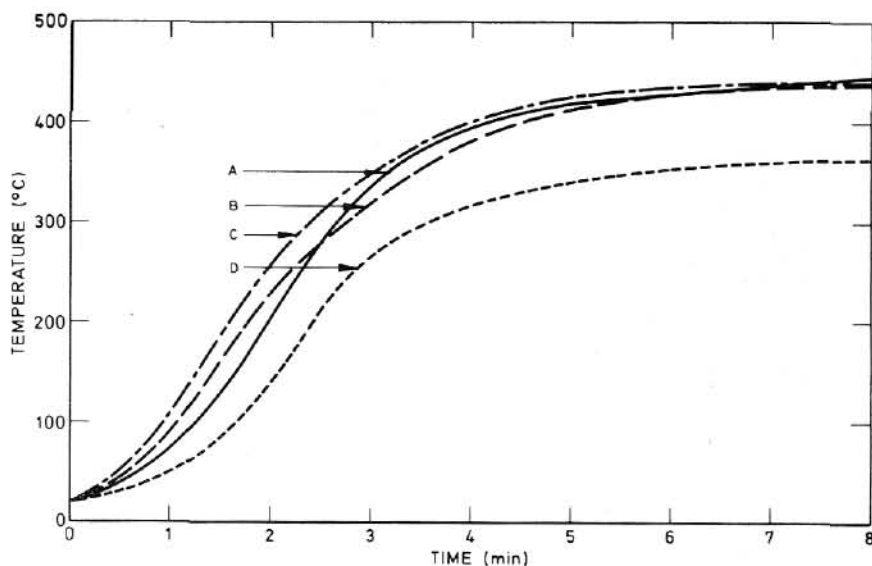
Thermal damage has been expressed in a number of ways, for example, change in appearance, surface temperature attained, and weight loss. Although it is not a complete index of the performance of a material resulting from the imposition of extreme thermal conditions, loss of weight reflects the alteration in chemical and mechanical properties of the material.

Loss of weight determinations were made by heating samples at fixed temperatures in nitrogen and in air and in atmospheres to which halogenated methanes were added.

Losses were recorded at  $230$ ,  $270$ ,  $300$ , and  $330^\circ\text{C}$ , a fresh sample (height: 40 mm, diameter: 22 or 29 mm) being used at each temperature. Some of the results obtained are shown in Table III in which they are expressed as the weight loss after 10 minutes, by which time a steady value had been reached.

When heated in air the rigid and high modulus foams behaved similarly, but when heated in nitrogen the rigid foam lost more weight because of the greater breakdown of the structure of the materials. Furthermore, products of decomposition escape readily from the high modulus foam. Thus they have little effect on subsequent stages of decomposition and on the material yet they decompose as heat penetrates into the sample. The effect on weight loss of incorporation of TCEP almost certainly involves these factors.

The effect of additions of halogenated methane to air or to nitrogen in which polyurethane foams are being heated is not clear. It seems that loss of weight of the foam may be increased probably by chemical attack. On the other hand, considerable reductions in loss of weight were also recorded; examples of both of these are given. These effects in turn varied with the type of halogenated methane used; among other factors it seems likely that the chemical stability and rate of decomposition of the methane derivatives is involved.



- A: High modulus,  
64 kg/m<sup>3</sup>, 0.3 l/min, Air  
B: Rigid,  
64 kg/m<sup>3</sup>, 0.3 l/min, Air  
C: Rigid,  
64 kg/m<sup>3</sup>, 0.3 l/min, N<sub>2</sub>  
D: High modulus,  
64 kg/m<sup>3</sup>, 0.3 l/min, N<sub>2</sub>

The foams were both without fire retardant additives and were subjected to an intensity of 21 kW/m<sup>2</sup>

Fig. 4.—Thermal penetration by irradiation. Temperature histories at one centimetre below heated face of various foams with gas flow past the sample

From curves similar to those shown in Fig. 6, activation energies have been calculated for the pyrolysis and combustion of cylinders of foam. These may be compared with higher values (165 to 200 kJ/mol) determined by TGA in the same temperature range (discussed Ref. 6). This difference in value may be anticipated in view of the dependence of the weight loss of the heated mass upon the rate of heat penetration. This physical process would be expected to exert a major effect in controlling rate.

The results obtained illustrate that severe thermal damage is to be expected under a wide variety of conditions both in air and in oxygen-deficient atmospheres.

A loss in weight in excess of half that reached in the steady condition at 330°C was usually experienced after heating at 270°C; for example, see the weight loss curves shown in Fig. 6 for high modulus foam heated in air. This was also shown by the isocyanurate foam. This degree of loss is in accord with the temperature range for decomposition of the urethane structure. However, rigid polyurethane foam without the addition of TCEP exhibits a much lower comparable weight loss (about 30%). Breakdown of the internal cellular structure and some softening of this material

causes delay and a less easy means of escape for the volatile products of decomposition.

#### Surface Ignition

Spontaneous ignition of a flammable gas mixture depends on the interrelation of energy, time, and size of energy source. In the experimental arrangement employed in the present investigation an area of foam (0.002 m<sup>2</sup>) was exposed to thermal radiation of various intensities and the required time to ignition was recorded as well as the temperature near the surface of the sample. This latter value was an estimate of the temperature of the gases evolved rather than that of the surface of the foam. The experiments took place in air but without forced circulation of the air.

The results obtained are given in Table IV. In this table the relationship between rate of energy input and the time for ignition will be noted. Higher temperatures were required to cause ignition of isocyanurate foam and the flame was transitory. The temperatures recorded in this work are considerably lower than those obtained using ASTM 1929-62T, *viz.*, 420 to 450°C.<sup>7</sup> The difference arises

TABLE III.—Weight Loss of Samples of Polyurethane Foam

Material	Atmosphere	Loss after 10 minutes (%)				E kJ/mol
		230°C	270°C	300°C	330°C	
High modulus 64 kg/m <sup>3</sup>	Air	9	30	41	44	79
	Nitrogen	8	15	20	31	59
	Air+0.5% CBM†		33		50	
	Nitrogen+0.5% CBM†		14		25	
Rigid 64 kg/m <sup>3</sup>	Air		—		43	67
	Nitrogen	7	12	18	42	59
	Air+0.5% CBM†		10		42	
	Nitrogen+0.5% CBM†		15		33	
Rigid 64 kg/m <sup>3</sup> with 30% TCEP	Air	11	26	34	54	75
	Nitrogen	14			48	92
Isocyanurate 48 kg/m <sup>3</sup>	Air	9	21	25	30	
	Nitrogen	12	21	23	31	

†CBM = Chlorobromomethane



from the fact that in the present arrangement volatile matter was allowed to collect at the irradiated surface, remain hot, and not be cooled by "ignition air". The temperatures recorded in Table IV are in good agreement with that for the decomposition of the urethane structure.

While there is no basis of direct comparison between the work of Wilde and the present results, it appears that the energy intensities required for ignition are of the same order. Wilde draws attention to the rapidity of flame spread on polyurethane foams and the marked improvement recorded with isocyanurate foam when examined by B.S. 476 Part I, Section 2.<sup>6</sup>

Qualitative observations were also made of some of the combustion characteristics and these are included in Table IV. Some of these will be considered later.

#### Charred Residue

In many instances it is desirable that in the event of fire the residue of the material affected should maintain its integrity, possess reasonable mechanical strength, and so continue to act as a heat shield. If the char swells and still remains sufficiently strong to withstand the air currents that usually accompany a fire it may offer an added protection to the substrate. In the light of the variety of uses for foamed polyurethane the structure of the char becomes significant, and a description is given here of the effects observed.

When subjected to thermal radiation of intensity 4.2 kW/m<sup>2</sup> none of the materials under investigation ignited but decomposition occurred and the chars were examined.

Rigid foam without additives (32 kg/m<sup>3</sup>) yielded, after irradiation for 16 min, a char of cell size 10 mm to a depth of 15 mm from the exposed face followed by char of cell size 7 mm for a further 8 mm and finally 2 mm of discoloured foam. The heated face had receded to a distance of 7 mm from the radiant source but a layer of dense char about half a millimetre thick formed on the surface.

This layer was a characteristic of the charring of all rigid polyurethane foams; it probably arose from shrinkage and from deposition of products from cracked volatile matter as it passed through the hot zone. Rigid foam with 20 parts TCEP produced a similar char but of larger cell size. These chars were mechanically very weak, except for the thin dense char layer. Similar chars were produced from higher density (64 and 128 kg/m<sup>3</sup>) rigid foam; slight swelling occurred instead of shrinkage. Phosphorylated rigid foam shrank more, but yielded a stronger char of cell size of two millimetres.

High modulus foams shrink slightly on heating but the char, although weak, does not exhibit the softening and breakdown of the foam structure as with rigid foams.

As previously described the isocyanurate foam formed fissures on heating; a char was produced comparable in strength to the original material. Continued heating led to continuation of the decomposition, and a friable, cindery char resulted.

These results were confirmed by the chars produced from the surface ignition work; some of the observations are recorded in Table IV. For example, a block of foam without additives, 30 mm thick, burned completely in the irradiated area to a diaphanous film; spread of flame occurred for about 50 mm along the exposed face. Rigid foams to which TCEP had been added suffered more severe damage with evidence of a greater degree of softening. In contrast to this, when phosphorylated foam was exposed, extensive combustion travelled about 30 mm beyond the irradiated area and flame flashed over the entire surface, but the char did not burn and its mechanical strength was high.

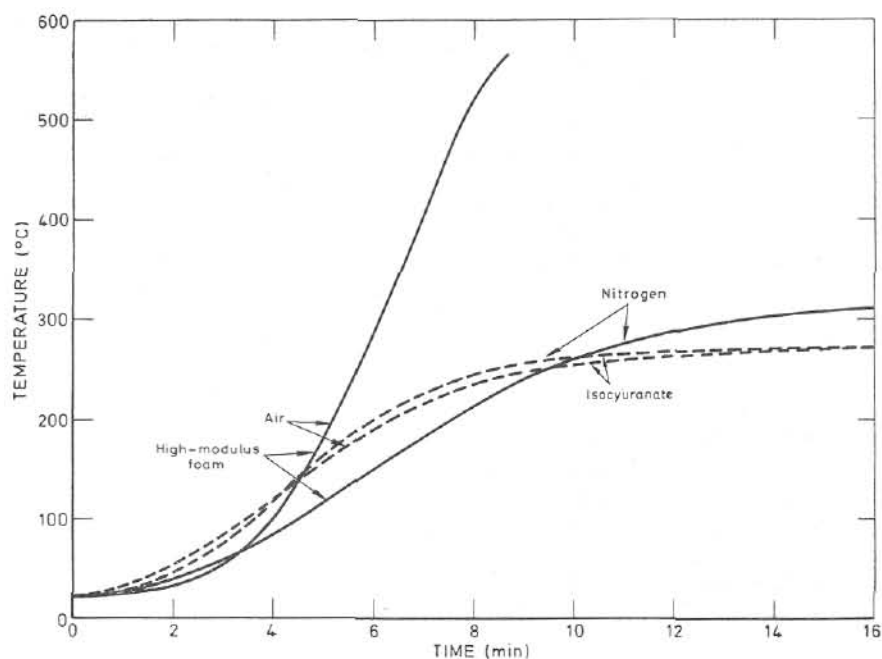
TABLE IV.—Surface Ignition Temperatures at Various Radiation Intensities

Radiation intensity (kW/m <sup>2</sup> )	Foam	Ignition		Observations
		Time (s)	Temp. (°C)	
6.3	1	No ignition		Chars have large cavities
	2			
	3			
	4			
	5			
8.4	1	5	250	Black sooty smoke. Flame extinguished without irradiation.
	2	4	230	Grey sooty smoke. Some spread of combustion.
	3	4.5	225	Grey sooty smoke.
	4	5	225	Some spread of flame, some shrinkage. Good char.
	5	No ignition		
12.6	1	2.5	250	Combustion penetrated and spread.
	2	3	240	Complete combustion of irradiated area. Extensive spreading.
	3	2	230	Extensive combustion; material softened.
	4	2	240	Flame spread over whole face. Good char.
	5	7.5	400	Small flame, self-extinguished after 20 s.
16.8	1	2.5	250	Complete combustion of irradiated area. Some spread of flame.
	2	1.5	240	Almost complete combustion.
	3	1.5	240	Extensive combustion. Material softened.
	4	<0.5	250	Considerable spread of combustion. Good char.
	5	3.5	380	Small transient flame. Some white smoke.
Rigid Foam 32 kg/m <sup>3</sup>		1: no additive.		
		2: 20 parts TCEP in mix.		
		3: 30 parts TCEP in mix.		
		4: phosphorylated polyol.		
		5: isocyanurate, no additive incorporated.		

#### Heating Effects with Oil Contamination

Cubes (side 25 mm) of high modulus polyurethane foam without additives were allowed to take up chosen amounts of mineral oil (without anti-oxidant). Their temperature was raised in an oven to values at which there was evidence of self-heating. These values are given in Table V where the steady oven temperature is designated as the equilibrium value and the rise recorded was that of a thermocouple embedded in the sample.

For purposes of comparison some experiments were carried out with similar-sized cubes of asbestos lagging. When the temperature at which heating commenced was the same for both materials a much larger effect was observed with the asbestos than with the polyurethane foam. Thus in practice oil-contaminated polyurethane foam will offer less hazard than oil-contaminated asbestos in situations where self-heating may occur, unless the service temperature is initially too high to justify the use of polyurethanes. This is due to the relatively rapid consumption of the oxygen enclosed in the foam and the restricted permeability of the material which prevents further supply of oxygen. In addition as the rigidity, *i.e.*, closed-cell character, of the foam is increased,



A: Isocyanurate foam, 48 kg/m<sup>3</sup>, 0.4 l/min, gas  
 B: High modulus foam, 64 kg/m<sup>3</sup>, 0.5 l/min, gas  
 The furnace temperature was 300°C. The sample was a cylinder of height 40 mm and diameter 29 mm

Fig. 5.—Thermal penetration. Temperature histories at the centre of a sample heated in a furnace with gases passed over the sample

the hazard is likely to be reduced even further. Addition of a combustion inhibitor to the polyurethane foam might improve this situation still further, particularly if the starting temperature was somewhat higher.

#### Toxicological Aspects of Thermal Degradation

Examination of the chemical structure of polyurethanes suggests that a variety of materials will be produced when it decomposes. The following have been found among the products of decomposition:<sup>9</sup> hydrocarbons, aldehydes, alcohols, organic acids, oxides of carbon and hydrogen. When combustion inhibitors are added thermal degradation is likely to yield further compounds of less predictable composition.

A few aspects of the toxicological hazards likely to arise during thermal degradation will be discussed here. Firstly, it has frequently been stated that carbon monoxide presents the greatest toxicological hazard during a fire emergency involving cellulosic or plastic materials. Its concentration depends on both the fire load and oxygen

for example, physiological and psychological effects as well as impeding firefighting and rescue operations. Organic materials are certain to produce some carbon monoxide during thermal degradation; in addition attention must be paid to their smoke-forming propensity.

The fate of the phosphorus additives during thermal degradation is a matter of some concern in view of the highly toxic nature of some phosphorus compounds. Some investigations<sup>10</sup> have been made by heating polyurethane foams to which phosphorus additions had been made in various atmospheres and at several temperatures as shown in Table VI. It will be noted that under only one set of the conditions used was phosphorus not emitted. These phosphorus compounds were of low volatility and could be collected in a trap cooled in ice. Infra-red examination of these materials indicated the presence of POC, POC<sub>2</sub>H<sub>5</sub>, and P=O groupings.

These experiments showed that other toxic materials evolved included: hydrogen cyanide, amines, isocyanate, and halogenated compounds. Both temperature of the foam and the atmosphere in which it was heated determined the concentration and nature of the materials produced.

The results are in agreement with those of Bott, Firth, and Jones<sup>11</sup> who also detected oxides of nitrogen when polyurethane was heated in air to 600° in one case and 750°C in the other.

TABLE V.—Temperature Rise in Polyurethane Foam with Absorbed Oil

Material	Oil (ml/cube)	Temperature			Rate (°C/min)
		Equilibrium (°C)	Rise (°C)	Time (min.)	
Asbestos	4	165	114	4	28.5
	5	165	109	5	21.8
	6	163	109	5	21.8
High modulus polyurethane foam 64 kg/m <sup>3</sup>	2	157	30	17	1.8
	3	167	31	13	2.4
	4	163	10	65	0.2

availability; alteration of these quantities alters both the quantity and concentration of carbon monoxide produced. These parameters often alter the nature as well as the quantity and concentration of products, thereby rendering a complete assessment of toxic hazards both difficult and protracted. Secondly, generation of smoke presents several hazards,

TABLE VI.—Evolution of Phosphorus Compounds during Thermal Degradation

Temperature (°C)	Material	Atmosphere		
		N <sub>2</sub>	6%O <sub>2</sub> -94%N <sub>2</sub>	Air
220	1	—	+	+
	2	+	+	+
320	1	+	+	+
	2	+	+	+
400	1	+	+	+
	2	+	+	+

Rigid Foam (64 kg/m<sup>3</sup>)  
 1: containing Fyrol 6  
 2: 30 parts TCEP in mix  
 +P present  
 -P absent

TABLE VII.—Odour Rating of Degradation Products of Polyurethane Foams

Foam	Temperature (°C):			320	400
	220			N <sub>2</sub>	N <sub>2</sub>
Atmosphere:	N <sub>2</sub>	6%O <sub>2</sub> — 94%N <sub>2</sub>	Air	N <sub>2</sub>	N <sub>2</sub>
1	2	2	2	4	4
2	2	2	2	3	4
3	1	1	1	2	3
4	0	1	1	2	3

Odour increasing from 0 (no odour) →1 (just detectable)  
 →2 (definite odour)→3 (strong odour)→4 (overpowering odour)  
 Foam 1 Rigid polyurethane 64 kg/m<sup>3</sup>, containing Fyrol 6  
 Foam 2 Rigid polyurethane, 64 kg/m<sup>3</sup>, containing 30 parts TCEP  
 Foam 3 Flexible polyurethane 32 kg/m<sup>3</sup>, without additives  
 Foam 4 Rigid isocyanurate 32 kg/m<sup>3</sup>

An attempt<sup>10</sup> was made to allocate to the products from thermal degradation an index of odour as judged by a panel of six persons. The observations are summarised in Table VII. While extremely unpleasant odours present a problem, they are a warning of the presence of the materials mentioned above. This is of undoubted value in alerting to emergency conditions.

#### Discussion

Detailed analysis of the mechanism of degradation of polyurethane foams has not been attempted here, but it is noteworthy that the heat penetration curves given in Fig. 3 do not exhibit a downward trend in temperature. This results from a combination of the breakdown of the structure of the foam both at the surface and between cells and of

exothermic effects. These latter have been mentioned in reporting the results shown in Fig. 5. With some materials the physical factors in heat penetration outweigh the exothermic effects as evidenced by the curves for isocyanurate foam shown in Fig. 3C.

As with all organic materials, polyurethane foam under thermal stress or in fire emergency conditions presents a hazard, that is, there is a fuel supply and a source of carbon monoxide. The degree of hazard varies with the amount of ventilation of the fire and the fire load; elemental composition of the material also plays an important role.

Several highly toxic compounds have been detected among the decomposition products of polyurethane foams and the phosphorus compounds have still to be categorised. However it is likely that the short-term hazard will depend largely on the dilution rate. This is not dissimilar to experience with many traditional materials which also generated highly toxic materials.<sup>12</sup> Often the full toxicological hazard of the decomposition products of a material will only be realised under conditions that seldom occur in practice.

It is however necessary to match the material used to the purpose and mode of use as well as to considerations of location of installation. The toxicological hazard depends not only on oxygen availability but on foam type and on additives incorporated in the foam; these factors are also of importance in several aspects of thermal degradation examined in this paper.

The work of Wilde<sup>8</sup> with tubes and ventilated ducts made from rigid polyurethane foam illustrates the effect of the combustion system on the behaviour of the material. Thus with the former the material exhibited greater flammability than in sheet form due to trapping of the heat in the system and to induced air supply. With the latter the hazards of combustion were found to be increased by the high intensity and rapid spread of combustion.

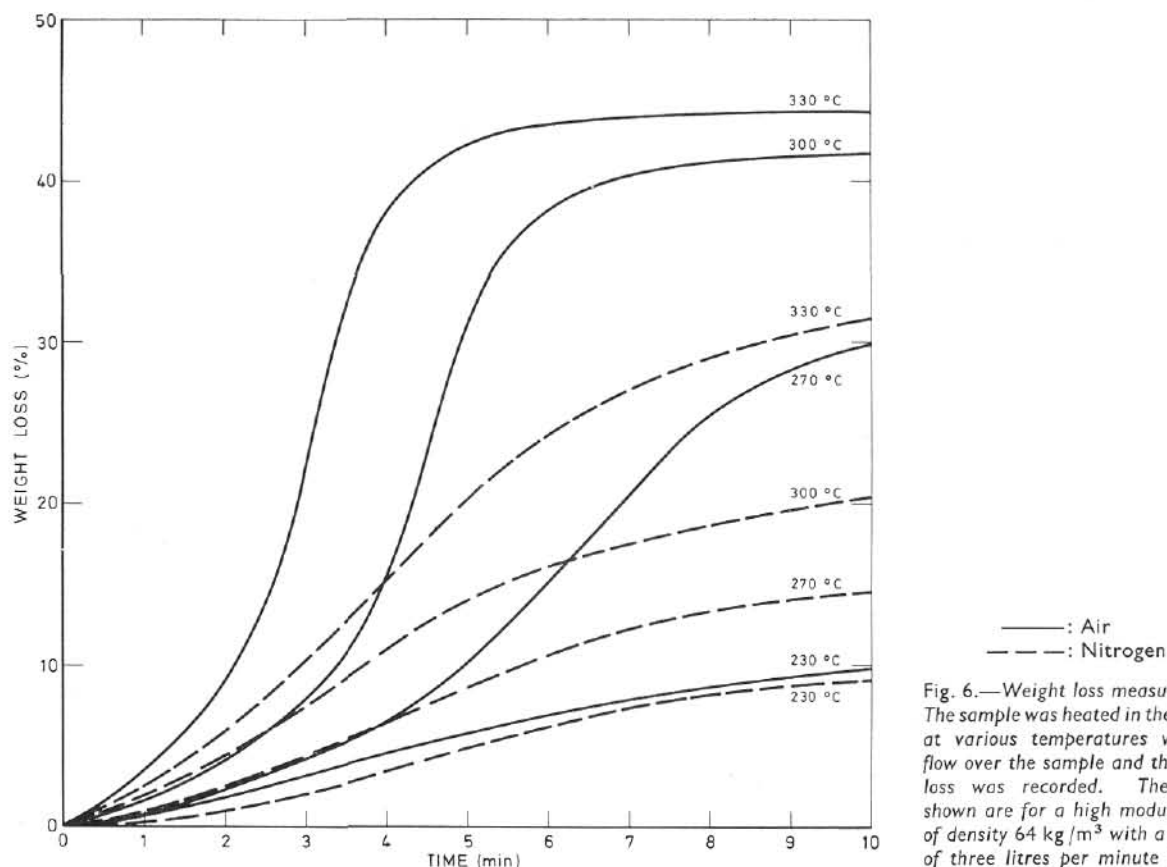


Fig. 6.—Weight loss measurements. The sample was heated in the furnace at various temperatures with gas flow over the sample and the weight loss was recorded. The results shown are for a high modulus foam of density 64 kg/m<sup>3</sup> with a gas flow of three litres per minute

The work reported above is continuing and other techniques will be brought to bear on the assessment of the behaviour of polyurethane foam in service and in disaster. A longer term aim is to set up a mathematical model based on the experimental work, so that some aspects of the behaviour of polyurethane foams under extreme conditions may be predicted.

#### Acknowledgments

The authors gratefully acknowledge support of this work initially by the British Aircraft Corporation (for R.K.G.) and subsequently and presently by the British Rigid Urethane Foam Manufacturers Association (for M.A.B.).

#### References

- <sup>1</sup> Jones, J. Idris. *Chemistry in Britain*, 1970, **6**, 251.
- <sup>2</sup> Singh, A., Weissbein, L., and Mollica, J. C. *Rubber Age*, 1966, **99**, Dec. p. 77.
- <sup>3</sup> Ball, G. W., Haggis, G. A., Hurd, R., and Wood, J. F. *Journal of Cellular Plastics*, 1968, **4**, 248.

- <sup>4</sup> Lawson, D. I. *Fire Research Bulletin* No. 1 1954 (London: H.M.S.O.).
- <sup>5</sup> Carlsaw, H. S., and Jaeger, J. C. "Conduction of Heat in Solids", 1959, p. 75. (London: Oxford University Press).
- <sup>6</sup> Tilley, J. N., Nadeau, H. G., Reymore, H. E., Wasceziak, P. H., and Sayigh, A. A. R. *Journal of cellular Plastics*, 1968, **4**, 2.
- <sup>7</sup> Buist, J. M., Hurd, R., and Stafford, R. L. in Buist, J. M., (Ed.). "Advances in Polyurethane Technology", 1968. (London: MacLaren and Sons Ltd.).
- <sup>8</sup> D. G. Wilde, *Heat. vent. Engr*, 1968, **42**, 283, *Idem*, *Colliery Guard.*, 1968, **216**, 587.
- <sup>9</sup> Hilado, C. J. in Bruins, P. F. (Ed.). "Polyurethane Technology", 1969. (New York: Inter-science Publishers Inc.).
- <sup>10</sup> Napier, D. H., and Wong, T. W. *British Polymer Journal*, (in press).
- <sup>11</sup> Bott, R., Firth, J. G., and Jones, T. A. *British Polymer Journal*, 1969, **1**, 203.
- <sup>12</sup> Rasbash, D. J. in *Conference Supplement* No. 2, Jan. 1967, p. 55. (London: The Plastics Institute).

*The manuscript of this paper was received on 30 November, 1970.*