Recent Developments in Understanding the Toxicity of PTFE Thermal Decomposition Products

David A. Purser*

Department of Inhalation Toxicology, Huntingdon Research Centre, Huntingdon, Cambridgeshire, PE18 6ES, UK

Fluoropolymers, especially polytetrafluoroethylene (PTFE), have good fire-resistance properties, but their application is limited by concerns over the toxicity of their thermal decomposition products. In experiments using a tube furnace system similar to the DIN 53 436 method, the 30-minute (+ 14 days observation) LC_{50} in mass loss terms was found to be 2.9 mg l^{-1} (Standard Error 0.40) under non-flaming conditions, approximately ten times as toxic as wood and most other materials. Toxicity was due to upper respiratory tract and airway irritation, and was consistent with the known effects of carbonyl fluoride and hydrogen fluoride. When decomposed in the NBS cup furnace test under non-flaming conditions, PTFE evolved extreme-toxicity products with an LC_{50} of approximately 0.05 mg l^{-1} (mass loss), approximately 1000 times as toxic as wood and most other materials. Toxicity was due to deep lung irritation and oedema. Investigations of the range of conditions under which the extreme toxicity of PTFE products occurs in both small-scale (200-litre) and intermediate-scale (6 m^3) experiments have shown that the highest toxicity occurs when PTFE is decomposed under non-flaming conditions over a temperature range of 400–650°C, and when the primary decomposition products are subjected to continuous secondary heating. At higher or lower temperatures, when the sample is flaming, when decomposition products from wood are also present in the chamber, when secondary heating is curtailed, or when the molecule contains hydrogen as well as fluorine, the toxicity of the products is greatly reduced, tending towards the region of ten times the potency of most other materials. Extreme toxicity is associated with a particulate, but the particulate atmosphere is not always extremely toxic, the potency decreasing as the fumes age.

INTRODUCTION

Fluoropolymers, particularly polytetrafluoroethylene (PTFE), are coming into increasing use in the building and cable industries because they have many desirable properties, not least of which is their good resistance to fire. A problem with PTFE is that under certain laboratory-scale test conditions in the NBS[†] cup furnace it decomposes to form products with a toxic potency approximately 1000 times greater than those from wood or most other common materials.[1–3] However, variations in the decomposition conditions in small-scale tests can cause extreme variations in the toxic potency of the products from PTFE (Table 1)[1–7] so that under most conditions the potency is considerably less than the extreme case, but usually approximately ten times greater than that of most materials. The proposed use of PTFE/glass-fibre roofing materials for a number of large-scale developments in the United Kingdom has given rise to concern that a serious toxic hazard might exist if the extreme toxic potency conditions were to occur in a large-scale fire. The work reported here was planned to investigate the conditions under which extreme toxic potency arose, and, if possible, to identify the agent responsible, so that the toxic hazard in large-scale fires could be estimated from a chemical analysis of fire products. In parallel with these toxicological investigations, experiments were conducted at the UK Fire Research Station, Borehamwood, by P. J. Fardell and his colleagues to investigate the chemical and physical nature of the thermal decomposition products from PTFE, and also by E. Met-

calfe and A. R. Harman at Thames Polytechnic, London, UK, who investigated the possibility that relatively stable free radical species might exist in the PTFE thermal decomposition product atmospheres.[8] These groups also measured, and mathematically modelled, the air-flow patterns in the NBS chamber system.[8]

EXPERIMENTAL

Samples of PTFE were decomposed under a range of conditions in two basic types of apparatus and the toxicity was investigated by exposing rats to the products for a 30-minute period followed by a 14-day observation period. One means of decomposition was a variant of the DIN 53 436 method,[2, 9] in which a strip or pieces of material were introduced at a constant rate into a tube furnace under a stream of air and the animals were exposed to the further diluted products in a flow-through system. The other technique consisted of variations of the NBS cup furnace method,[1] in which samples of material are decomposed in a cup furnace, the products evolving into a closed 200-litre chamber. In these experiments a number of variations were made in the basic decomposition apparatus as described in the following sections, but the common feature was that the products were always generated into the closed chamber. The respiratory pattern of the rats was monitored during exposure, and the clinical condition examined during the post-exposure period, followed by post-mortem lung histopathology.

* Present address: Fire Research Station, Borehamwood, Hertfordshire, WD6 2BL, UK.
† NBS —National Bureau of Standards, now NIST.

Table 1. Concentrations of combustion products from PTFE and other materials causing death (LC_{50}) following a 30-minute exposure in rats

LC_{50} range (mg l^{-1})	Experiment and reference	Conditions and temp. (°C)	30-minute LC_{50} (mg l^{-1} mass loss)
5–50	Almost all materials	NF	24 (2–72)[a]
	NBS and Din:[1-3]	F	37 (3–125)[a]
		PF	20 (1–100)[a]
	PTFE methane flame[4]	F 700	> 14.2
	PTFE NBS[4]	F 850	5.4
0.5–5	PTFE DIN[5]	NF 500	2.8 (1 h)
	PTFE UPIT[6]	NF ramp	1.07
	PTFE DIN[7]	NF 450	0.95[b]
0.05–0.5	PTFE NBS[1]	? 710	0.40
	PTFE NBS[1]	NF 655	0.24
	PTFE NBS[1]	NF 663	0.16
	PTFE NBS[1]	NF 613	0.13
0.05–0.005	PTFE NBS[1]	NF 645	0.045
	PTFE NBS[1]	NF 595	0.045
	PTFE NBS[4]	NF 700	0.017

NBS: National Bureau of Standards cup furnace method.
DIN: Tube furnace methods similar to the DIN 53 436 test method.
UPIT: University of Pittsburgh test method.
NF: Non-flaming or sample unlikely to have flamed.
F: Flaming.
PF: Post-flashover.
ramp: Ramp heated.
[a] Mean and range of results from materials tested.
[b] 30-minute equivalent of 4-hour exposure assuming Haber's rule.

Tube furnace experiments

For these experiments pieces of PTFE (1–9 g) were spread evenly over 30 or 40 cm in a steel or silica boat and introduced into the tube furnace at rates of 10–97 mg min^{-1} (non-flaming) and 176 mg min^{-1} (steady flaming). The primary air flow through the furnace was 22 l min^{-1} for non-flaming conditions (temperature 600°C) and 1.5 l min^{-1} for flaming conditions (temperature 700°C). The products from the tube furnace were diluted with air at 20–176 l min^{-1} to provide the final atmosphere which was passed through a tubular polymethylmethacrylate (PMMA) chamber from which six rats were exposed snout-only. The transit time from product formation to delivery at the animals' snouts was approximately 15 seconds. The effect of humidity on the formation of toxic products was investigated by passing low-humidity laboratory air, dry air and humidified air over the sample.

NBS chamber experiments

For this series of experiments the basic apparatus was the NBS cup furnace apparatus,[1] consisting of a rectangular 200-litre PMMA chamber and a cup furnace containing a 300-ml silica beaker. The rats were exposed snout-only for 30 minutes to the chamber atmosphere. The furnace temperature was set with a thermocouple placed in a well at the bottom of the beaker, but the centre of the beaker where the samples were located was approximately 25–50°C cooler than the reference thermocouple (the temperatures shown in the tables for the NBS method are the reference thermocouple temperatures). The furnace was maintained at a constant temperature throughout the 30-minute exposure period, and the heat from the

furnace caused a rapid circulation of air round the chamber and back down into the beaker (the flow rate in the plume above the cup was approximately 34 l min^{-1} based upon measurements made by Z. Rogowski[10]. Variants on this basic method are described in the following sections.

RESULTS

Experiments using the tube furnace method

The results obtained in the study are summarized in Table 2. For the first series of experiments the DIN furnace method was used to establish the LC_{50} concentration for a 30-minute exposure to thermal decomposition products from PTFE produced under non-flaming oxidative conditions at 600°C. The products caused a severe respiratory rate decrease in the rats, typical of extreme upper respiratory tract irritation, and deaths occurred either during or within 2 hours after exposure, with some post-mortem signs of airway damage and some lung congestion. Under flaming conditions at 700°C the toxicity appeared to be similar, and altering the humidity of the furnace air under non-flaming conditions made little difference.

Experiments designed to investigate the effects of temperature, flaming and the presence of combustion products from flaming wood on toxicity using the NBS cup furnace

Using the NBS cup furnace method at a temperature of 575°C, the results of Levin et al.[1] were confirmed, with all

Table 2. Investigations of PTFE decomposition conditions resulting in lethality following a 30-minute exposure in rats

	Temperature (°C)	NF/F	Mass loss (mg l^{-1})	Deaths
DIN tube furnace	600	NF	2.85 SE 0.40[a]	LC_{50}
	700	F	1.00	0/6[b]

NBS cup furnace—effect of furnace temperature on lethality

	575	NF	0.054	9/9
	630	NF	0.057	3/3
	660	NF	0.064	1/9
	700	NF	0.052	0/3
	700	F	0.630	0/3

NBS cup furnace—effect of flaming wood on otherwise lethal mass of PTFE (96 mg of PTFE embedded in 2.5 g pine wood)

	575	F	13.16 wood	
			0.51 PTFE	3/6

NBS cup furnace—effect of covering cup after various times

Covered:				
2.5 min	575	NF	0.075	0/3
5 min	575	NF	0.079	0/3 toxicity 3/3[c]
10 min	575	NF	0.066	2/3 toxicity 3/3
20 min	575	NF	0.062	3/3 toxicity 3/3

Experiments designed to investigate the possibility that toxic effects result from a two-stage process, primary decomposition followed by secondary reheating of products:

Two NBS cup furnaces, one containing sample covered after 5 min

	665	NF	0.161	1/3 toxicity 3/3

One NBS cup furnaces, with a lid, primary products expelled into exposure chamber by air:

	575	NF	0.276	0/3

As above, but air from exposure chamber containing primary products recirculated through cup for secondary heating:

	668	NF	0.096	1/3

Primary decomposition in small tube at 600°C, secondary heating by cup 660°C:

Primary heating only	600	NF	0.229	0/9
Secondary heating also	600	NF	0.145	3/3

[a] LC_{50} and standard error.
[b] Number of deaths/number of rats exposed.
[c] Number of rats showing signs of toxic effects following exposure.

animals dying after exposure to 0.05 mg l^{-1} PTFE. The toxic effects were very different from those obtained using the DIN apparatus, consisting of rapid, shallow breathing during exposure, typical of pulmonary irritation, with deaths occurring principally within 2 hours after exposure or overnight. Pathological signs were of severe lung congestion. Increasing the furnace temperature appeared to decrease the toxic potency of the products, and even when a sample large enough to support flaming decomposition (121 mg) was decomposed at 700°C, no deaths occurred. When a sample of approximately ten times the lethal mass was embedded in a piece of wood and decomposed at 575°C, only half of the animals died.

Experiments designed to investigate whether extreme toxicity is a two-stage process

At this point it was suspected that the development of the toxicity might be a two-stage process, with the primary decomposition products being converted by secondary heating into extreme-toxicity products. A series of experiments was therefore conducted for which one aspect was the investigation of this possibility. For one set of

experiments the cup furnace was covered by a glass beaker after various times to restrict any secondary heating of primary evolved products. The results indicated that the toxicity increased as the exposure time of the chamber atmosphere to the furnace increased. In another experiment the cup furnace was covered after 5 minutes as above, but a second cup furnace was used as a secondary heat source, resulting in some evidence of conversion to extreme-toxicity products. In other experiments the cup was covered with a glass lid containing two ports, and the primary products were expelled into the exposure chamber with a clean air flow, so that no secondary recirculation of product through the cup was possible. In this situation no toxic effects were observed, but when the primary products were partially recycled through the cup furnace, extreme toxicity occurred.

The final experiments were performed to determine whether a decomposition model other than the cup furnace could be used to generate extreme-toxicity products. For these experiments a sample of PTFE was dropped into a small tube (5 mm ID) surrounded by a heating coil, the sample being decomposed at 600°C. The products were expelled by means of an air flow into the exposure chamber. Primary products formed in this way

were found not to be toxic, but when secondary heating was provided by an empty cup furnace at 660°C all the animals died. In all experiments there was virtually no residue following decomposition of PTFE specimens, so that mass loss concentrations and mass charge concentrations are the same.

DISCUSSION

The experiments described here were designed to investigate the conditions under which extreme-toxicity products were generated from PTFE, and also to generate these products in a concentrated form so that they could be trapped for chemical analysis. These preliminary experiments demonstrate the complexity of the problem, in that minor modifications of the generation conditions away from the basic setting of the NBS cup furnace at 575°C tend to result in the loss of extreme toxicity. The results do, however, provide some indications of the fundamental requirements for the generation of extreme-toxicity products, and when they are considered in the context of results obtained by other workers, particularly Williams et al.,[11, 12] a clearer picture emerges. The published results of toxicity studies on PTFE are summarized in Table 3. They show an extreme variation in toxic potency over 3 orders of magnitude, with 30-minute LC_{50} concentrations (including a 14-day observation period) varying from greater than $14.2 \, \mathrm{mg} \, \mathrm{l}^{-1}$ to $0.017 \, \mathrm{mg} \, \mathrm{l}^{-1}$,[4] depending upon the decomposition conditions. However, a clear pattern emerges when the decomposition conditions of the various experiments are examined.

The composition of the thermal decomposition products from PTFE

The primary decomposition products of PTFE[5, 7, 8, 12] consist of a mixture of vapours and particulates. The vapours are composed of carbonyl fluoride, hydrogen fluoride, tetrafluoroethylene and a range of fluorinated hydrocarbon products, including small amounts of some highly toxic species such as perfluoroisobutylene. The particulate consists of a condensate of PTFE fragments with molecular weights in the 2000–4000 range, and a range of particle sizes of which small particles in the 0.01–0.15 μm diameter size range appear to be of toxicological significance.[13, 14] When formed, the particle size is thought to be near the lower end of the range, but then increases rapidly due to aggregation.

Conditions under which PTFE evolves products with a near-normal toxic potency

The products responsible for the normal toxicity of PTFE combustion products, which can be expected in all fires involving PTFE, are likely to be mainly carbonyl fluoride and hydrogen fluoride, with a contribution from small amounts of products such as perfluoroisobutylene, and also possibly from the particulates.[5, 7, 8, 12] The toxic effect consists of irritation of the respiratory tract, which takes the form of painful sensory irritation of the eyes,

upper respiratory tract, and possibly (to a lesser extent) the lungs. In rats, signs during exposure consist of slow breathing with long pauses at the end of inspiration between successive breaths. Deaths occur during exposure or within 2 hours after, and as observed in this study (and also as reported by Lee and Williams[11]), appear to be due principally to airway damage, with some degree of lung congestion. The normal-toxicity products of PTFE are formed over a wide range of decomposition conditions including both non-flaming and flaming, although there are some important differences between the products of non-flaming and flaming decomposition.[12] The minimum temperature for significant decomposition within a short time scale (less than one hour) is approximately 450°C for PTFE.[7, 14]

The upper part of Table 3 (Experiments 1–13) shows results where extreme-toxicity products are absent (or present at very low yields), and the LC_{50} or ALC (approximate lethal concentration) of PTFE is within the normal range for the combustion products from most materials, or the ten times more toxic range. The results in Experiments 1–10 can be explained in terms of the major toxic products, carbonyl fluoride and hydrogen fluoride, without invoking any unusually toxic chemical species, and although there is some variation depending upon the exact method of decomposition, the basic effect is the same, that when PTFE is decomposed it evolves products irritant to the respiratory tract, and that these render PTFE generally somewhat more toxic than other materials on a mass loss concentration basis. The main results (Experiments 7–10) fall close to our finding with the DIN method, giving an LC_{50} of approximately $2.9 \, \mathrm{mg} \, \mathrm{l}^{-1}$ mass loss for a 30-minute exposure under both non-flaming and flaming conditions. On this basis, it could be said that the normal toxicity of PTFE combustion products is approximately ten times that of wood and most other materials. Where the toxicity is greater than this, for the results of Experiments 11–34, there is evidence that some novel, extreme toxic potency factor is present at varying yields.

Extreme-toxic potency products

The product responsible for the extreme toxicity of PTFE is associated with the particulate, and is formed only under special conditions. Its exact nature is still unknown, but on a mass loss concentration basis it is among the most potent of known toxic agents, and no known chemical product of PTFE thermal decomposition is of sufficient toxic potency to account for the observed effect (Table 4). One theory is that it may be some agent attached to the particulate, such as a peroxy-free radical.[8] Another is that no chemical reaction may take place in the lung, but that a very large number of very small particles (approximately 0.01 μm diameter) are inhaled from the extreme-toxicity atmosphere and are somehow responsible for the toxic effects upon the deep lung.[13, 14] We and others[13, 14] have found that extreme toxicity is always associated with the presence of particulate, but we have also found that the presence of particulate does not always result in extreme toxicity, suggesting that the composition of the particulate can change in some way with time, so that fresh fume, containing large numbers of small particles, is more toxic than aged fume, which has

Table 3. Concentrations of combustion products from PTFE causing death (LC_{50} or ALC) following a 30-minute exposure in rats

LC_{50} or ALC[a] range of (mg l⁻¹) material and reference	Experiment	Primary heating Temp (°C)	Time (min)	Secondary heating Temp. (°C)	Time (min)	LC_{50} or ALC (mg l⁻¹ mass loss)
5–50						
1[b] Tefzel[17]	NBS	F 580	30	Cup 580	30	30.2
2 PTFE[4]	Methane flame	F 700	1	None		> 14.2
3 PTFE[12]	NBS	F 700	2	None		8.6
4 PTFE[12]	NBS	F 850	1	Cup 850–15 min⁻¹	30	5.4
5 PTFE[12]	Methane flame	F 700	1	Cup 400–14 min⁻¹	30	> 4.7
0.5–5						
6 Tefzel[17]	NBS	NF 530	30	Cup 530	30	3.3
7 PTFE[17]	NBS	F 700	1	Cup 700–15 min⁻¹	3	2.9
8 PTFE[21]	DIN	NF 600	30	None		2.9
		F 700	30	None		> 1.0
9 PTFE[5]	DIN	NF 500	60	None	15	2.8
10 PTFE[18]	NBS radiant	F 5 W cm⁻²	15	rad 5 W cm⁻²		2.74
11 PTFE[6]	UPIT	NF ramp	30	Some possible	30	1.07
12 PTFE[22]	NBS	F 700	30	Cup 700		> 0.63
13 PTFE[22]	NBS				30	
	+ flaming wood	F 575	30	Cup 575		0.51
0.05–0.5						
14 PTFE[12]	Methane flame	F 700	1	Cup 450–15 min⁻¹	30	0.45
15 PTFE[1]	NBS	F 710	30	Cup 710	30	0.40
16 PTFE[1]	NBS	NF 655	30	Cup 655	30	0.24
17 PTFE[12]	Methane flame	F 700	1	Cup 600–15 min⁻¹	30	0.20
18 PTFE[1]	NBS	NF 663	30	Cup 663	30	0.16
19 PTFE[12]	Methane flame	F 700	1	Methane flame	30	0.16
20 PTFE[1]	Glass tube	NF 600	7	Cup 660	30	0.15
21 PTFE[1]	NBS	NF 613	30	Cup 613	30	0.13
22 PTFE[12]	NBS	NF 700	1	Cup 700–15 min⁻¹	4	0.12
23 PTFE[22]	NBS	NF 665	30	Cup 665	30	0.10
24 PTFE[17]	NBS	NF 590	30	Cup 590	30	0.08
25 PTFE[12]	NBS	NF 700	1	Cup 700–15 min⁻¹	14	0.07
0.05–0.005						
26 PTFE[18]	NBS radiant	NF 5 W cm⁻²	30	rad 5 W cm⁻²	30	0.052
27 PTFE[12]	Methane flame	F 700	1	Cup 850–15 min⁻¹	30	0.05
28 PTFE[22]	NBS	NF 700	30	Cup 700	30	> 0.05
29 PTFE[22]	NBS	NF 575	30	Cup 575	30	0.05
30 PTFE[1]	NBS	NF 540	30	Cup 540	30	0.05
31 PTFE[1]	NBS	NF 645	30	Cup 645	30	0.045
32 PTFE[12]	NBS	NF 595	30	Cup 595	30	0.045
33 PTFE[12]	Methane flame	F 700	1	Cup 700–15 min⁻¹	30	0.036
34 PTFE[4]	NBS	NF 700	1	Cup 700–15 min⁻¹	29	0.017

[a] ALC: Approximate lethal concentration.
[b] Experiment number.
NBS: National Bureau of Standards cup furnace method.
DIN: Tube furnace methods similar to the DIN 53436 test method.
UPIT: University of Pittsburgh test method.
NBS radiant: Radiant heater version of NBS.
Methane flame: Sample heated over a methane flame for primary decomposition.
(in one case methane flame used for secondary decomposition also)
Cup: Cup furnace used for secondary heating.
NF: Non-flaming or sample unlikely to have flamed.
F: Flaming.
ramp: Ramp heated.

smaller numbers of much larger particles. Similarly, if the particles are mixed with other particles such as those from wood smoke, then a greater rate of agglomeration is predicted, and the wood smoke/PTFE particle agglomerates, as well as being larger, may behave in a different way when they deposit in the lung. This may explain our finding that the presence of wood smoke appeared to decrease the toxic potency of an otherwise lethal amount of PTFE. A detailed examination of the relationship between particle size and number and toxic potency is given in the paper by Clarke et al.,[14] which was also presented at the Interflam '90 Conference. The work shows extreme toxicity associated with the presence of very small particles (approximately 0.01 μm diameter) and much reduced toxicity associated with the presence of larger particles (approximately 0.1 μm diameter). The increased toxic potency of the small particles compared to the large ones may result partly from an increased deposition efficiency (by approximately a factor of three) of the smaller particles due to more rapid diffusion within

Table 4. 30-Minute LC_{50} concentrations of toxic vapours and gases compared with those of combustion products from PTFE and other materials in rats

Material	LC_{50} range and LC_{50} (mg l^{-1})	LC_{50} (ppm)
	0.01–0.1	
PTFE COMBUSTION PRODUCTS (Williams[4])	0.017	3.2
2-fluoroethylfluoroacetate	0.02	5.7
PTFE COMBUSTION PRODUCTS (Levin[1])	0.045	
Perfluoroisobutylene	0.047	
	0.1–1.0	
Phosphine	0.12	88
Hydrogen cyanide	0.23	200
Nitrogen dioxide	0.30	155
Chlorine	0.30	100
Phosgene (carbonyl chloride)	0.31	75
Acrolein	0.32	135
Fluorine	0.58	370
Toluene diisocyanate	0.73	100
Formaldehyde	0.92	825
	1.0–10	
Sulphur dioxide	1.07	400
Hydrogen fluoride	1.88	2250
Carbonyl fluoride	1.96	720
o-chlorobenzyidene malonitrile	2.16	275
α-chloroacetophenone	2.25	350
Carbon monoxide	3.79	3250
Hydrogen chloride	5.77	3800
Acrylonitrile	9.50	4300
	10–100	
Combustion product from most materials	Average and	
—NBS and DIN methods:	(range)[3]	
Non-flaming oxidative decomposition	24 (2–72)	
(wood NBS)	27	
(wood DIN)	29	
Well-ventilated flaming decomposition	37 (3–125)	
(wood NBS)	48	
Vitiated post-flashover decomposition	20 (1–100)	
(wood DIN)	32	

All LC_{50} concentrations normalized to a 30-minute exposure time assuming Haber's rule (gas data from NIOSH,[21] combustion product data from Purser[3]).

the lung, but does not explain the actual mechanism of toxicity.

One possible mode of action may be that the unique physical surface properties of the fluorocarbon particles may interfere in some way with the integrity of lung cell membranes. However, another possibility is that the presence of a very large number of very small particles is the key point, and that almost any atmosphere composed of such small particles would be damaging. Evidence that this could be the case is derived from work on a chemically inert 'nuisance' dust, titanium dioxide. Recent research has shown that when the dust is in the form of very small particles of a size range similar to that of the PTFE particles, and when the particles are present in very large numbers, they overwhelm the particle-scavenging role of the alveolar macrophage and pass rapidly into the lung interstitium, where small particles in particular set up an inflammatory response.[15, 16]

When small pieces of PTFE are decomposed in such a way as to produce extreme toxicity, the normal toxicity products are present at concentrations too low to have a toxic effect. Rats exposed under these conditions do not

show signs of sensory irritation, but at some time during a 30-minute exposure they develop a pattern of rapid shallow breathing, indicative of irritation of the deep lung. The rats die usually within a few hours after exposure or overnight, and the pathological signs are of severe pulmonary oedema and congestion.

The conditions required for the formation of extreme-toxicity products

The extreme-toxicity products were originally produced in one type of laboratory small-scale apparatus,[1] under very specific decomposition conditions. It has since been demonstrated here and in other studies,[1, 4–7, 12, 17, 18] that extreme-toxicity products can be formed in a number of different ways with both non-flaming and flaming heat sources (Table 3), but suitable decomposition conditions require the following essential features:

(1) There must be a primary decomposition phase in which the material is broken down into the normal moderately toxic vapour and particulate products. It

is possible that extreme-toxicity products are not formed at this point or that, if they are, they retain their extreme toxic potency for only a short time (possibly only 10–60 seconds, or a few minutes). The critical temperature range for this primary phase is between approximately 450°C (below which the decomposition is very slow) and approximately 800°C (above which the primary products are not suitable for conversion to extreme toxicity).

(2) In order to maintain the extreme toxicity (or to produce it in the first place) there must be a secondary phase in which the primary particulate products are recirculated through a heated area or passed over a heated surface, and over a period of minutes are converted to extreme-toxicity products (the 'Icarus' effect). It is not certain at present whether these extreme-toxicity products once formed are stable, or whether their toxic potency lasts for only a short time (approximately 10–60 seconds), so that they are capable of causing a toxic effect only if they are inhaled very soon after formation. However, the current evidence points strongly towards the latter, particularly in the light of the particle aggregation findings.[14] There is a critical temperature range for the conversion of primary products to extreme-toxicity secondary products from approximately 400°C to 450°C (below which conversion to extreme toxicity as well as production of primary products is slow) and from approximately 600°C to 650°C (above which the extreme-toxicity product is not formed). Under non-flaming conditions there therefore appears to be a narrow temperature 'window' approximately 200°C wide, within which the formation of extreme-toxicity products is favoured, the product yield varying considerably, depending upon the exact decomposition conditions.

In all of our experiments shown in Table 2 where these conditions did not occur, we did not achieve extreme toxicity. The experiments that best satisfy these requirements are those shown at the bottom of Table 3, where PTFE falls into the range where its toxicity is up to 1000 times greater than that of most other materials. In these experiments the primary decomposition of small samples of PTFE was achieved by heating them under non-flaming conditions at between 540°C and 700°C in the NBS cup furnace. Once decomposition was achieved, these primary products were held within a closed chamber, and continually recirculated into the hot cup furnace for conversion to extreme-toxicity products. The hot cup was then either maintained at a relatively low temperature of around 575°C for the remainder of the 30-minute exposure (Table 3—Experiments 28–32) or allowed to cool at a rate of approximately 15°C per minute from approximately 700°C (Experiment 34). For Experiments 27 and 33, the primary decomposition was achieved over a methane flame at a temperature of approximately 700°C, and a gradually cooling cup furnace with, in one case, a somewhat hotter starting temperature being used for the secondary conversion process. For Experiment 26, a radiant heater achieved the same result as the cup furnace.[18]

When the decomposition conditions depart from this 'ideal' the yield of extreme-toxicity products and hence

the toxicity gradually decreases. Thus in a series of experiments by various workers (Experiments 24, 23, 21, 18, 16, 15, 12), standard NBS cup conditions were used with progressively higher temperatures maintained throughout the 30-minute run, and the toxicity decreases progressively. Similarly, in a series of experiments (Experiments 33, 27, 17, 14, 5, 2) Williams et al.[12] used a methane flame to obtain primary decomposition at a temperature of 700°C followed by a cup furnace gradually cooling from various starting temperatures for the secondary conversion. Ideal conditions were obtained when the cup furnace starting temperature was 700°C, but an increase or decreases in cup starting temperature from this point resulted in progressively lower toxic potency. When the cup starting temperature was less than 450°C, virtually no conversion to extreme-toxicity products took place. In another series of experiments Williams et al.[12] achieved primary decomposition in the cup furnace, and then, as in our experiments, removed it from the system after various times, thereby curtailing the period when secondary conversion reactions occurred (Experiments 34, 25, 22, 7, 3). This also reduced the toxicity of the atmosphere.

In other experiments where the primary products of decomposition pass through a flow-through system, so that the opportunity for secondary heating is greatly reduced, extreme toxicity does not occur. This is the case with our DIN furnace experiments (Experiment 8), the Coleman et al. tube furnace experiments (Experiment 9), and also, to a large extent, decomposition in the University of Pittsburgh apparatus (Experiment 11). In the University of Pittsburgh test, PTFE, with an LC_{50} of 1.07 mg l^{-1}, is really on the borderline of 'extreme' toxicity. However, due to the slow transit time of products through the furnace some extreme-toxicity products may be formed.

The effect of flaming conditions

Providing that the above conditions are satisfied, extreme-toxicity products can be generated by either non-flaming or flaming heat sources. The primary products have been generated at 700°C above a methane flame, and the conversion to extreme toxicity has been achieved by means of a small pilot methane flame[12] (Experiment 19). It would seem likely that under these conditions a proportion of the toxic particulate would be consumed in the secondary flame, while some would pass near enough to the flame for conversion to extreme toxicity to take place, but far enough from the flame hot zone to avoid decomposition. However, when PTFE is itself flaming, or when the sample of PTFE is enveloped in flame, extreme-toxicity products do not seem to be formed (Experiments 12 and 4). This is consistent with the finding that primary decomposition products of flaming decomposition are somewhat different from those of non-flaming decomposition.[12] It is likely that under these conditions, most of the precursors of extreme-toxicity products may be destroyed, but it is still possible that a proportion may escape the destructive zone of the flame. In our experiments when a small sample of PTFE was ignited at approximately 650°C (cup thermocouple temperature 700°C) ex-

treme toxicity was not observed (Experiment 12), and this has remained the case when samples of up to 20 g mass have been combusted in a current series of larger-scale experiments.

Effects of the presence of other materials on the toxicity of PTFE combustion products

In an early experiment (Experiment 13) a sample of PTFE was embedded in a sample of wood, which was decomposed under flaming conditions at a furnace temperature of 575°C. This reduced the toxicity of the products from the PTFE by approximately a factor for 10. When a sample of PTFE/glass-fibre roofing material was decomposed in the NBS cup furnace it was found to be less toxic than an equivalent sample of PTFE alone. When samples of Tefzel, a polymer containing both hydrogen and fluorine, were tested, extreme toxicity did not occur[17] (Experiments 1 and 6).

Intermediate-scale experiments

One factor that all these tests have in common is that they are all laboratory-scale experiments. Extreme toxicity from PTFE had not been observed in full-scale fires involving PTFE cable,[19] so that it was possible that, due to the special conditions required, extreme toxicity was a small-scale phenomenon. In order to test PTFE in conditions nearer to those in large-scale fires, a series of intermediate-scale experiments has been conducted at the Huntingdon Research Centre, in conjunction with scientists from the Fire Research Station and Thames Polytechnic.[20] For this work a 6 m³ volume Rochester type chamber is being used, initially with a scaled-up version of the NBS cup furnace and then using decomposition conditions more closely related to those in full-scale

fires.[20] In these experiments it has proved possible to reproduce the extreme-toxicity phenomenon at the intermediate scale, and to confirm the findings of the small-scale experiments that the extreme toxicity is greatly reduced, or lost, under flaming conditions, and also when the products are mixed with those from a burning wood crib.

FUTURE WORK AND IMPLICATIONS FOR BUILDING DESIGN

Apart from the need to discover the exact mechanism of extreme toxicity and the exact identity of the toxic product, it is important to continue intermediate- and large-scale experiments to determine whether extreme toxicity might occur in full-scale fires. In particular, it is important to measure how long the extreme-toxicity products remain potent once formed. If, as we suspect, the half life may be a matter of seconds or a few tens of seconds, then this finding, when taken into consideration with other mitigating factors, may have important implications for the in-use safety of PTFE-based products in a variety of applications, including roofing materials. It is likely that, providing certain design precautions are taken, PTFE roofing materials may be used safely on buildings. These design precautions could be set out in a code of practice for the use of the materials.

Acknowledgements

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