

Polystyrenes: A Review of the Literature on the Products of Thermal Decomposition and Toxicity

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The current English literature through 1984 on the products of pyrolysis and combustion from polystyrenes and the toxicity of those products is reviewed. Among 57 compounds detected by chemical analyses of the thermal decomposition products produced under various atmospheric conditions (vacuum, inert and oxidative), the main volatile component is the styrene monomer. Evidence is provided that the mass fraction of styrene increases with furnace temperatures at least through 500°C. At 800°C and above, the concentration of styrene decreases. In oxidative atmospheres, carbon monoxide (CO), carbon dioxide (CO₂) and oxidative hydrocarbons are formed. The concentrations of CO and CO₂ are a function of temperature and combustion conditions, i.e. greater amounts are produced in the flaming than in the non-flaming mode. Eleven different test procedures were used to evaluate the toxicity of the pyrolysis and combustion atmospheres of polystyrenes. The more toxic environments produced under flaming conditions appear to be mainly attributed to CO and CO₂. Incapacitating effects observed during exposures to non-flaming effluents are not due to CO and CO₂ but rather to some other toxicant, probably the styrene monomer. When compared with other common materials used in buildings and residences, polystyrenes, in general, are among the least toxic.

Keywords: combustion products; fire data; literature reviews; polystyrene; pyrolysis products; test methods; toxicity.

INTRODUCTION

Polystyrenes, which constitute one of the major classes of synthetic polymers in use today, have a variety of applications, ranging from food and medical packaging to home insulation. They have also been commonly used to simulate wood for decorative purposes. 'Polystyrene' is a generic term, which denotes a number of forms, e.g. crystal, impact or expandable. Improvements designed to enhance the physical properties of this class of polymers have been in the areas of impact resistance, gloss levels, resistance to stress-cracking by fats and oils, flame resistance and purity. These improvements in material characteristics and the ease with which polystyrenes are processed have made commercial use of this synthetic material economically favorable.^{1,2}

Enhancing the physical properties of polystyrenes has not been the only concern facing manufacturers and consumers. For many years researchers have investigated the effects of heating polystyrenes under various conditions.³ The nature of the gaseous products produced when polystyrenes degrade during industrial processing and in fire situations and the toxicity of these gases have been a primary focus of many research studies. In this report the English literature published through 1984 on the volatile pyrolysis and combustion products of polystyrene and the toxicity of these products is reviewed.

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CHEMISTRY

Polymerization

Polystyrenes are amorphous, high molecular weight linear polymers. Unless modified with special additives, they are constituted of covalently bound units of the styrene monomer, which is composed solely of carbon and hydrogen and contains a benzene ring in its structure (Fig. 1).^{2,4}

Not all forms of polystyrenes, however, are simply homogeneous polymers of the styrene monomer. In order to enhance its physical properties, specific additives are incorporated into the polymer. For example, commercial impact polystyrenes have an elastomer, generally polybutadiene, incorporated as a block copolymer into the matrices in order to strengthen their mechanical properties.^{1,5} Expandable polystyrene beads or foams may contain 3-7% of a volatile blowing agent (e.g. pentane) which is used in processing this product. Fire resistant polystyrenes usually contain halogenated additives and antimony oxide which are incorporated during polymerization.^{1,5}

The polymerization of the styrene monomer is a thermodynamically favored reaction.² Most styrene-containing plastics are polymerized by a free radical mechanism, where polymerization of the styrene monomer is initiated either thermally or through the use of catalysts.

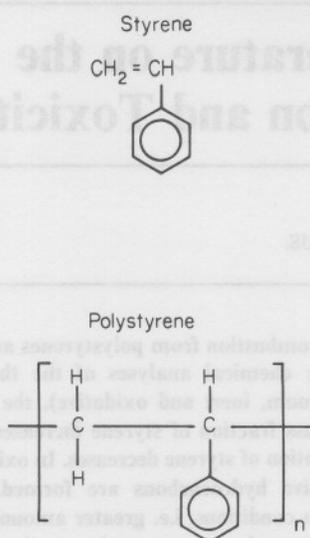


Figure 1. Structure of styrene and polystyrene.

Thermal decomposition processes

The thermal degradation of various polystyrenes has been studied under a wide range of temperatures. The temperatures quoted are those of the furnace or heating device and not necessarily those of the polystyrenes being heated. In most cases the temperature of the furnace increases faster than that of the material studied. The evolved products may or may not be directly related to the furnace temperature, depending on the apparatus design.

Michal⁶ studied the thermo-oxidative degradation of a polystyrene (standard polystyrene, Krasten 127^a) between 400° and 800°C. Parikh⁷ calculated from his studies that no degradation of a pure polystyrene would occur below 227°C, while 100% would decompose at 332°C when the material was exposed for 2 h. The mean temperature at which a sample of polystyrene (GM51⁸) spontaneously ignites was found by three laboratories who participated in an interlaboratory evaluation of the National Bureau of Standards (NBS) Toxicity Test Method to be 520° ± 62°C.⁹

While still not completely understood, the mechanism of the thermal degradation of polystyrenes is considered to be a radical chain reaction.¹⁰ This process is essentially a reverse of the polymerization process.

Thermal degradation products

Thermal decomposition of polystyrenes has been conducted under a variety of different atmospheric conditions, e.g. vacuum, inert and oxidative. It is generally agreed that the major volatile component produced from the thermal degradation of polystyrenes under these atmospheres is the styrene monomer.^{3,11-19,21-23} Other commonly detected products are oligomers of styrene, such as the dimer and trimer,^{13,15-17,19,20} toluene, benzene, ethylbenzene and α -methylstyrene and, under oxidative conditions, species such as benzaldehyde and benzoic acid.¹¹⁻¹⁹ Butadiene has also been identified as a degradation product of polystyrenes containing polybutadiene.^{18,21} A summary list of the identified degradation products is provided in Table 1.

Many problems were encountered in the evaluation of the literature on polystyrenes. First, a large variety of experimental systems and conditions have been used to degrade polystyrenes. Second, many types of polystyrenes, with and without additives, have been studied without adequate specification of the formulations. Third, tests have been run at temperatures ranging from those used for industrial processing (150–320°C)^{17,22} to those used to simulate fire scenarios (as high as 1200°C).³ The following sections will discuss the thermal degradation products that have been detected and identified when polystyrenes have been decomposed under the three different atmospheric environments: vacuum, inert and oxidative.^b

Vacuum degradation Straus and Madorsky²³ studied the decomposition of specially prepared laboratory samples of polystyrene under vacuum. These samples were either heated for 30 min at 400° and 500°C, or for 5 min at 800° and 1200°C in a platinum tube surrounded by a preheated moveable furnace. Ninety-eight per cent or greater volatilization of the samples occurred, regardless of the temperature. Using mass spectrometry, Straus and Madorsky identified styrene as the major decomposition product, but noted that the fractional per cent yield varied with temperature. An average of 48.3 and 53.9 wt% of the total volatiles was styrene at 400° and 500°C, respectively, whereas, at 800° and 1200°C, an average of 47.5 and 41.6 wt% of the total volatiles was styrene. Straus and Madorsky noted an increased fragmentation of the degradation products at 800° and 1200°C over that found at 400° and 500°C; this was probably due to secondary decomposition of the initial decomposition products. In other words, greater amounts of low molecular weight hydrocarbons (C_3 and below) and benzene were observed at the higher temperatures.

Degradation in inert atmospheres The thermal degradation of polystyrenes under inert atmospheres has been examined by a number of investigators.^{3,11-13,15-21,23-25,27} While nitrogen (N_2) was the gas most widely used to study polystyrene degradation under inert conditions,^{11,15,17-21,24,25} helium (He) and argon (Ar) atmospheres were also used.^{3,12,13,16,23,27} Different degradation systems as well as a variety of analytical techniques were employed; for example, pyrolysis–gas chromatography (pyrolysis–GC), thermo-gravimetric analysis–gas chromatography (TGA–GC), gas chromatography–mass spectrometry (GC–MS) and thermogravimetric analysis–gas chromatography–high resolution mass spectrometry (TGA–GC–HRMS). Many researchers have concentrated their efforts on measuring the styrene monomer even though many other gaseous components have also been detected and identified (Table 1).

Using pyrolysis–GC, Knight¹¹ investigated the influence of varying both sample size and pyrolysis temperature on the decomposition of a laboratory polymerized polystyrene. It is important to note that the flash pyrolysis of the ultra-thin, low mass samples needed for pyrolysis–GC may not be totally indicative of the decomposition of larger mass samples. (This comparison is discussed later and shown in Table 4.) These studies by Knight, plus others using this technique,^{12,18,20} were

Table 1. Volatile combustion products of polystyrenes under varying experimental conditions

Decomposition products	Atmosphere			References
	Vacuum	Inert ^a	Oxidative	
Acetaldehyde	—	—	x	14
Acetophenone	—	—	x	17, 22
Acetylene	x	He, N	x	3, 23, 28
Acrolein ^b	—	—	x	17
Acrylaldehyde	—	—	x	22
Allylbenzene	—	N	x	18, 22
Benzaldehyde	—	—	x	18, 19, 22
Benzene	x	Ar, He, N	x	3, 12–14, 17, 18, 21–23
Benzoic acid	—	—	x	17
Benzyl alcohol	—	—	x	17, 22
Butadiene ^b	—	He, N	—	18, 21
Butane	—	He	x	3, 23
1-butene	—	N	x	14, 18
Carbon dioxide	—	He	x	6, 13, 28, 30
Carbon monoxide	—	N	x	6, 22, 25, 28–30
Cinnamaldehyde	—	—	x	17, 22
Cumene	—	He	x	16, 22
1, 3-diphenylpropane	—	N	x	17
1, 3-diphenylpropene	—	N	x	17
Ethane	x	He, N	x	13, 14, 23
Ethylbenzene	x	He, N	x	3, 13, 14, 16–19, 22, 23
Ethylene	x	He, N	x	3, 14, 23, 28
Ethyl-methyl benzene	—	N	x	17
Formaldehyde	—	—	x	22
Formic acid	—	—	x	22
Hexane	—	He	—	13
Hexene	—	He	—	13
1-hexene, 2-methyl-1-pentene	—	N	—	18
Methane	x	N	x	3, 14, 28
Methanol	—	—	x	14
3-methyl-1-butene	—	N	—	18
4-methyl-2-hexene	—	N	—	18
2-methyl-3-pentene	—	N	—	18
Methyl phenol ^b	—	N	x	17
α -methylstyrene	—	He, N	x	13, 14, 16–19, 21
β -methylstyrene	—	N	x	14, 17, 21
Pentane	—	He, N	—	13, 18
1-pentene	—	N	—	18
Phenol	—	—	x	17, 22
1-phenylethanol	—	—	x	22
Propane	—	—	x	14
(Iso) propylbenzene	—	N	x	17, 18
(n) propylbenzene	—	N	x	17, 18, 22
Propylene	—	—	x	14
(α) styrene	—	—	x	22
Styrene-				
monomer	x	Ar, He, N	x	3, 11–19, 21–23
dimer	x	He, N	x	3, 13, 15–17, 19, 23
trimer	x	He, N	x	3, 15, 16, 19, 20, 23
tetramer	x	He	x	3, 15, 16, 19, 23
pentamer	—	—	x	19
hexamer	—	—	x	19
heptamer	—	—	x	19
Styrene oxide	—	—	x	22
Toluene	x	Ar, He, N	x	3, 12–14, 16–19, 21, 22
1, 1, 2 trichloroethane	—	N	—	18
Vinylcyclohexane ^b	—	N	—	18, 21
Vinylcyclohexene ^b	—	N	—	18, 21

^aDecomposed under inert atmospheres of argon, helium or nitrogen as specified.

^bProducts found when impact polystyrenes or polystyrenes with a polybutadiene additive were decomposed.

Ar: Argon; indicates product detected when decomposed in argon atmosphere.

He: Helium; indicates product detected when decomposed in helium atmosphere.

N: Nitrogen; indicates product detected when decomposed in nitrogen atmosphere.

x: Indicates product found.

—: Indicates product not found or no analyses performed.

Table 2. Flash pyrolysis of polystyrene at different temperatures in nitrogen atmospheres¹¹

Sample weight	Pyrolysis temperature (°C)	Styrene (%)
1–5 µg	550	63 ± 4
	600	64 ± 9
	650	84 ± 8
	700	101 ± 6
1–3 mg	700	75 ± 5

designed as an initial attempt to determine the primary products and mechanism(s) of decomposition. Knight determined from the flash pyrolysis of 1–5 µg samples at 550°, 600°, 650° and 700°C under a N₂ flow rate of 0.030 l min⁻¹ that styrene was the major decomposition product and that the styrene yield increased with increasing temperature (Table 2). Results from studies on 1–3 mg samples were compared with those with the 1–5 µg samples and demonstrated that at 700°C, the smaller sample size produced a larger percentage of styrene (Table 2).

Fuchs and Szepesy¹² also used pyrolysis–GC to examine the thermal decomposition products from various polymers, including several different polystyrenes. These polystyrene samples (0.1 mg) were initially dissolved in benzene which was evaporated before the sample was subjected to flash pyrolysis in an argon atmosphere (flow rate: 25 ml min⁻¹) for 0–15 s. The resulting pyrograms contained four major peaks which were identified as styrene, toluene, benzene and other light hydrocarbons. Styrene was the primary thermal decomposition product, constituting 97.3% of the total peak areas. Fuchs and Szepesy concluded from their study that only the styrene concentration could be accurately determined since the relative peak areas of the other pyrolysis products were not consistent or totally reproducible.

Two different samples of polystyrenes (Krasten 127, a standard polystyrene, and Krasten 336, a polystyrene with an unspecified percentage of polybutadiene) were degraded in a nitrogen atmosphere (flow rate of 0.25 ml min⁻¹) at 510°C by Pacakova *et al.*¹⁸ Pyrolysis–GC was used for the degradation and analysis of products in this study. Monomeric styrene comprised 73.5% and 79.1% of the total volatiles produced from the polystyrenes with and without polybutadiene, respectively. Butadiene monomers and dimers, as well as vinylcyclohexene, were also found in the degradation gases of the polybutadiene-containing polystyrene samples. A number of other saturated and unsaturated hydrocarbons were also detected.

Trojer²⁰ also used pyrolysis–GC to examine the decomposition products and the evolution of hydrogen from a special laboratory formulated polystyrene. The polystyrene samples were pyrolyzed under nitrogen atmospheres at temperatures which ranged from 510° to 980°C. The hydrogen yield was observed to increase with increasing temperature and pyrolysis time. The values ranged from 0.8% to 26%.

A number of other investigations of the thermal decomposition of polystyrenes in inert atmospheres were performed under more realistic degradation conditions,

i.e. at slower pyrolysis rates and using larger masses. These studies are described below.

The research efforts of Bouster *et al.*¹⁶ concentrated on the kinetics of decomposition of a commercial, expanded polystyrene sample. A qualitative identification of the thermal degradation products was made when this polystyrene was degraded in helium at temperatures ranging from 300° to 370°C. Styrene, toluene, ethylbenzene and α -methylstyrene were identified. Similar to the results of Knight, an increase in styrene evolution with an increase in temperature was noted.

A combustion system composed of a Pyrex tube with a movable furnace was used by Hoff *et al.*¹⁷ This apparatus permitted the degradation of small samples and the maintenance of a continuous flow of gas through the furnace. Two commercial polystyrenes and two impact polystyrenes in pellet form (additives unknown) were thermally degraded at temperatures within the industrial processing range (240–260°C) in nitrogen at flow rates of 20–30 ml min⁻¹. At these temperatures, only about 0.2–1.2% of the total sample mass was actually degraded. The gaseous products were analyzed by GC–MS. Styrene was identified as the main volatile product. The yields of styrene were 9.1% and 13% by weight of the commercial polystyrene samples volatilized and 3.1% and 3.3% by weight of the impact polystyrene volatilized.

Brauman¹⁵ heated 50 mg samples of a polystyrene at 350° and 450°C in a tube furnace under a dried nitrogen flow of 75 ml min⁻¹. Using GC analysis, she found that 18–19% of the total mass volatilized at 350°C was styrene, whereas at 450°C, styrene constituted 50–51% of the total mass volatilized. A 700 mg sample degraded at 350°C produced approximately 37% monomeric styrene; thus, at the same temperature, an increase in sample size resulted in an increase in the percentage monomer production. Although this result disagrees with that obtained by Knight,¹¹ who found that increasing the sample size decreased the yield of styrene, this difference may be related to the different decomposition conditions, namely, flash pyrolysis versus a slower thermal degradation method.

To determine the extent to which the addition of a fire retardant would affect volatiles generated, Brauman¹⁵ analyzed the products from 700 mg samples of a polystyrene with and without antimony trioxide and a chlorinated wax. When the fire retarded polystyrene was heated at 350°C in nitrogen, the organic volatiles contained 1.5% monomeric styrene, whereas the non-fire retarded polystyrene sample produced 37%. In a similar fashion, an overall reduction of other volatile organics (benzene, toluene and ethylbenzene) was observed for the fire retarded polystyrene sample. In contrast, the total tar content from the fire retarded sample was approximately five times greater than that from the non-fire retarded polystyrene.

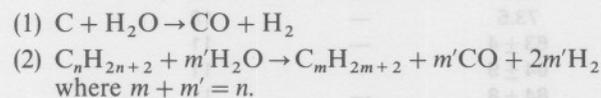
Using a radiant heating system in order to achieve a linear rate of degradation of a long polystyrene rod, Brauman *et al.*¹⁹ examined the pyrolysis products of this rod decomposed under a controlled nitrogen flow of 15 l min⁻¹ and a flux level of 56 kW m⁻². Low boiling point volatiles were analyzed by GC. Once again, styrene was found to be the major product, comprising 33.2 ± 3.1% of the total volatiles recovered (Table 3).

A decrease in styrene yield with an increase in

temperature was found by Straus and Madorsky²³ when a thermally prepared polystyrene was decomposed in a helium atmosphere. This result appears to disagree with those of Knight¹¹ and Bouster *et al.*,¹⁶ as discussed previously. However, the highest temperatures examined in either of these investigations was 700°C, whereas Straus and Madorsky used temperatures as high as 1200°C. In the work by Straus and Madorsky, polystyrene samples, ranging in mass from 13.4 to 20.4 mg, were heated either for 30 min at 500°C or for 5 min at 800°C or 1200°C. Ninety-five per cent or greater volatilization of the sample occurred at all temperatures. With MS, an average of 50.9 wt% of the total volatiles was detected as the styrene monomer at 500°C, while only an average of 10.7 and 0.6 wt% styrene monomer was detected at 800° and 1200°C, respectively. As previously mentioned, under vacuum pyrolysis, Straus and Madorsky detected an average of 53.9, 47.5 and 41.6 wt% styrene at 500°, 800° and 1200°C, respectively. Straus and Madorsky attributed this finding to a greater degree of fragmentation of the polystyrene decomposition products which occur at high temperatures in a helium atmosphere.

Chang and Mead¹³ carried out an extensive high-resolution mass spectrometry study designed to analyze and identify the products of thermal decomposition produced from a polystyrene foam degraded in an inert atmosphere. The authors heated 3 mg samples of the polystyrene foam in helium, starting at 200°C and increasing the temperature at a rate of 15°C min⁻¹ up to 500°C. In addition to the decomposition products identified and listed in Table 1, the authors detected several aromatic and aliphatic components which they were unable to identify. Although Chang and Mead conducted their experiments in an inert environment, three gaseous compounds containing oxygen were detected: CO₂, C₈H₈O, and C₉H₈O. The authors concluded that these compounds may have resulted from oxygen leakage into the degradation or analysis systems or from oxygen that was trapped or absorbed in the polystyrene foam during processing.

Morikawa²⁵ investigated the effect of water vapor on the thermal decomposition of a polystyrene in an inert atmosphere. In particular, he was concerned whether CO could be produced from the reaction of the water vapor with the polystyrene. Polystyrene samples of 0.5 g were heated in a tube furnace at temperatures ranging from 600° to 1000°C. Morikawa, using GC analysis, detected small amounts of CO when polystyrene was decomposed at 1000°C in the presence of water vapor. He hypothesized that CO evolution from the polystyrene in an inert atmosphere containing water vapor probably occurred as a result of one of the following two reactions:



Thermal decomposition in an oxidative environment Many investigators^{6,17,19,22,25,28-30} studied the thermal decomposition of polystyrene in air or other oxidative atmospheres. These studies have been conducted in a variety of combustion systems, e.g. tube furnaces, crucible furnaces and radiant furnaces. Although most of the studies were very methodically performed, it is difficult to

Table 3. The low-boiling point volatile products from radiant pyrolysis of a polystyrene in nitrogen or air atmospheres¹⁹

Product	Relative chromatogram peak	
	Nitrogen	Air
Toluene	0.8	1.2
Ethylbenzene	<0.2	0.2
Styrene	100.0 ^a	100.0 ^b
Benzaldehyde	0.0	0.9
α -methylstyrene	1.0	0.8

^aStyrene yield is 33.2 ± 3.1 wt %.

^bStyrene yield is 35.4 wt %.

compare the results because each investigator attempted to model what he believed to be the most relevant combustion scenario, and thermo-oxidative decomposition encompasses everything from simple oxidative pyrolysis to fully involved flaming combustion. Since polystyrene contains no oxygen in its molecular formulation, it is only in oxidative degradation that one would expect to find appreciable quantities of oxidized decomposition products, such as benzaldehyde, styrene oxide, CO and CO₂.

Hoff *et al.*,¹⁷ Morikawa²⁵ and Morimoto *et al.*²⁸ used tube furnaces to study the thermo-oxidative decomposition of polystyrenes. Hoff *et al.*, using temperatures within the industrial processing range, heated pellet-shaped samples of two commercial polystyrenes and two impact polystyrenes (additives unknown) for 10 min in a dry air flow of 0.025–0.030 l min⁻¹. Using GC and GC/MS techniques, 21 volatile products were identified from the degradation of the polystyrenes at 240° and 250°C. Twenty-two compounds were detected and identified in the gaseous products of the impact polystyrenes. Benzyl alcohol and cinnamaldehyde were identified as decomposition products of the polystyrene but were not detected among the decomposition products of impact polystyrenes. Methyl phenol, ethanol and acrolein were also detected among the volatiles produced by the impact polystyrenes, but were not found among the polystyrene degradation products.

The thermal degradation apparatus used by Pfaffli *et al.*²² consisted of a J-shaped glass tube inserted into a laboratory oven. Polystyrene samples without additives were heated at 200°, 350° and 500°C under a slight air flow rate (0.7 l min⁻¹). This experimental procedure was designed to simulate industrial processing conditions. High-pressure liquid chromatography (HPLC), GC, GC-MS and gas indicator tubes^c were used to identify the degradation products. At 200°C trace amounts of styrene, ethylbenzene and cumene were detected. Experiments conducted at 350° and 500°C produced about the same amounts of styrene, but the concentrations of the aromatic and aliphatic hydrocarbons and oxidized hydrocarbons were greater at 350°C than at 500°C. Pfaffli *et al.* hypothesized that the reason for these results was that at the higher temperature, a more rapid degradation and therefore less effective oxidation occurred. However, a greater amount of CO was evolved at 500°C (2.1%) than at 350°C (0.4%). The authors concluded that the most important thermal degradation products generated by this polystyrene from an industrial hygiene point of view

were the styrene monomer and oxidized aromatic compounds, such as benzaldehyde, styrene oxide, acetophenone and 1-phenylethanol.

Morikawa²⁵ examined the effect of water vapor and air supply rate on the evolution of CO. A 500 mg sample of a commercial polystyrene was heated at 600°C with air flow rates from 0.5 to 1.5 lmin⁻¹. At each air flow rate, tests were run with or without water vapor. In all cases, the evolution of CO increased as the water vapor supply rate increased.

Morimoto *et al.*²⁸ used a quartz degradation tube placed vertically in an electric furnace rather than horizontally (as in the conventional tube furnace). The main gaseous hydrocarbons produced from 0.1 g samples

of a polystyrene under flaming combustion at 700°C with an air flow rate of 0.83 or 1.7 lmin⁻¹ were methane, ethylene and acetylene. These compounds were identified by infrared spectrophotometry. The quantity of acetylene increased with the increase in air flow rate. In other experiments Morimoto *et al.* showed that acetylene could be produced from the combustion of methane and ethylene. Therefore they hypothesized that the acetylene in these polystyrene decomposition experiments was probably due to the further combustion of methane and ethylene. Among the oxidative products, CO and CO₂ were identified as major gaseous components.

Using a crucible furnace in the bottom of a 4.2 l combustion chamber, Michal²⁹ degraded 20–25 mg

Table 4. Styrene evolution during thermal decomposition of polystyrenes

Sample	Temperature (°C)	Mass volatilized (w%)	Styrene evolved (w% of mass volatilized)			Reference
			Vacuum	Inert	Oxidative	
PS	200	—	—	—	Trace	22
IPS	224	1.0	—	—	3.4	17
IPS	240	1.1	—	3.3	—	17
PS	240	0.6	—	—	8.0	17
IPS	250	0.9	—	—	3.8	17
PS	250	0.7	—	—	7.0	17
PS	255	0.3	—	9.1	—	17
IPS	260	0.3	—	3.1	—	17
PS	260	0.6	—	13.0	—	17
PS	350	5–20	—	18–19	—	15
PS	350	7	—	37	—	15
PS	350	43–87	—	—	14–22	15
PS	350	35	—	—	18.5	15
PS/FR	350	40	—	1.5	—	15
PS/FR	350	40	—	—	9.0 ^a	15
PS	350	—	—	—	5.2 ^a	22
PS	362	83	40.9	—	—	27
PS	362	83	—	31.4	—	27
PS	400	99	47–50	—	—	23
PS	437	67	—	—	35.4	19
PS	447	46	—	33.2	—	19
PS	450	100	—	50–51	—	15
PS	450	100	—	—	42–47	15
PS	500	—	—	—	5.8 ^a	22
PS	500	100	51–56	—	—	23
PS	500	100	—	49–53	—	23
PS	800	100	47–48	—	—	23
PS	800	99	—	9–13	—	23
PS	850	100	27.8	—	—	27
PS	850	98	—	17.2	—	27
PS	1200	98	41–42	—	—	23
PS	1200	95	—	0.6	—	23
Flash-pyrolyzed Samples						
PS	—	—	—	93.7	—	12
PS	510	—	—	79.1	—	18
PS/PB	510	—	—	73.5	—	18
PS	550	—	—	63 ± 4	—	11
PS	600	—	—	64 ± 9	—	11
PS	650	—	—	84 ± 8	—	11
PS	700	—	—	101 ± 6	—	11
PS	700	—	—	75 ± 5	—	11

PS: Polystyrene.

PS/FR: Polystyrene with flame retardants.

IPS: Impact polystyrene.

PB: Polybutadiene.

—: No data provided.

^aBased on weight per cent of total sample.

samples of a polystyrene foam (Krasten 336) under a limited supply of oxygen. These experiments were designed to closely simulate actual fire conditions in which the oxygen supply may become depleted. Carbon monoxide, the main concern of the author in these studies, was analyzed by GC. The average weight per cent of CO, which evolved during the vitiated flaming combustion of the polystyrene samples, was $9.86 \pm 4.40\%$. From these results Michal concluded that laboratory tests demonstrate a high degree of variance and may only be considered an approximation of the actual combustion of a material in real fire situations.

In later studies, Michal⁶ degraded 0.1–0.5 g samples of polystyrene granules (Krasten 127) in a crucible furnace located in the bottom of a 4.5 l combustion chamber at temperatures of 500°C (non-flaming) and 600°C (flaming). Michal's results indicated that as the sample size of the polystyrene increased, the concentrations of CO and CO₂ increased. He also showed that flaming conditions produced greater concentrations of CO and CO₂ than non-flaming conditions.

Further work by Michal³⁰ on polystyrenes examined the effect of using a larger combustion chamber, which consisted of an oval chamber with a total capacity of 650 l. In this larger chamber, where the ratio of sample weight to chamber capacity is lower than in the 4.5 l chamber, non-flaming conditions exist at 600°C and flaming combustion occurs at 800° and at 1000°C. Michal compared the gaseous concentrations of CO and CO₂ from the degradation of the polystyrene samples (Krasten 127) in both combustion chambers. Greater quantities of CO₂ and H₂O but very low CO concentrations were observed in the larger chamber when compared with the smaller chamber. Michal suggested that these results were indicative of a more complete thermo-oxidation of the polystyrene in the larger chamber.

Brauman *et al.*¹⁹ used a radiant heat source to examine the degradation of a polystyrene sample (Styron 666U) under simulated fire conditions, i.e. non-flaming radiant pyrolysis with a flux level of 5.6 W cm^{-2} in a controlled air atmosphere with a flow rate of 15 l min^{-1} . The low boiling-point volatiles were analyzed by GC. As in many of the previous studies cited, the principal decomposition product was the styrene monomer, comprising 35.4 wt% of the total weight loss. A comparison of the low boiling point volatiles produced during oxidative pyrolysis and those from inert pyrolysis (i.e. nitrogen, 15 l min^{-1}) showed a qualitative as well as quantitative similarity in the products (Table 3). Benzaldehyde and trace amounts of CO₂ were the only compounds not also found in a nitrogen atmosphere. Yields of CO were not determined.

Summary on thermal degradation products Studies on the thermal decomposition products of polystyrenes have been conducted under a variety of atmospheric and experimental conditions. The major volatile product, regardless of conditions, is the styrene monomer. The fractional percentage yield of the evolved styrene depends on the combustion mode (flaming or non-flaming), furnace temperature, sample size, amount and types of additives, concentration of water vapor and air supply rates to the furnaces. The many other chemical components that have been detected are listed in Table 1.

TOXICITY OF THERMAL DECOMPOSITION PRODUCTS

Toxicological evaluations of the thermal decomposition products from various polystyrenes have been reported in a total of 11 different experimental test systems. These protocols are briefly summarized in Table 5, and have been described in greater detail by Kaplan *et al.*²⁶

Although each test system was designed to assess the toxicity of the thermal decomposition products of various materials, the apparatus, experimental conditions and measured endpoints vary substantially and generate results that are not readily comparable. For example, some of the endpoints measured were:

- (1) The mass of material that is loaded or consumed in the furnace and which is necessary to produce a specific biological effect (i.e. incapacitation, death or other physiological change);
- (2) The concentration of material (mass loaded or consumed divided by the exposure chamber volume or air dilution factor) which is needed to produce the above biological effects; and
- (3) The time necessary to develop or exhibit a given biological effect.

As a result, for specified exposure times, data may be reported as the 'lethal loading' (LL_{50}) or 'lethal concentration' (LC_{50}) necessary to kill 50% of the exposed animals, or the 'effective loading' (EL_{50}) or 'effective concentration' (EC_{50}) needed to produce some other biological effect in 50% of the test animals. When the endpoint is based on the time needed to produce some biological effect, such as death or incapacitation, the data have been reported as T_d or T_i values, respectively.

The numerous test methods can also be classified in a variety of different manners (e.g. static versus dynamic atmospheres; isothermal versus ramped temperatures, head-only versus whole-body animal exposures, etc.). For the purposes of this report, the results from the various test methods will be discussed in sections distinguished by the type of combustion system used to generate the exposure atmosphere. A total of three general combustion systems have been used to evaluate polystyrene toxicity. They are the cup furnace (used in test methods 1–3 as noted in Table 5), the tube furnace (used in test methods 4–8a), and various combustion ovens (used in test methods 8b–11). Of the test systems described in Table 5, only one (No. 3) has undergone a formal interlaboratory evaluation. In addition, another test (No. 9) has been accepted by the State of New York for use in establishing a data base on the combustion toxicity of materials.

The cup furnace

Dow Chemical Company test method Potts and Lederer³¹ designed a method for testing smoke toxicity for the Dow Chemical Company. This test method consisted of a 160 l cubic exposure chamber that contained a furnace in which a quartz beaker was placed. The test materials were exposed to both flaming and non-flaming degradation conditions. In each test, seven male Sprague–Dawley rats were placed in a cage set on the floor of the exposure

Table 5. Summary of toxicity protocols

Test no.	Protocol	Animal species	Duration (min)	Biological endpoint	Type of exposure	Combustion system	Airflow system
1 ^a	Dow	Rats	30	Death	WB	Cup furnace	Static
2 ^a	Univ. of Utah	Rats	30	(1) Incapacitation (2) Death	HO	Cup furnace	Static
3 ^a	NBS	Rats	30	(1) Incapacitation (2) Death	HO	Cup furnace	Static
4 ^a	DIN	Rats	30	(1) Death (2) Respiratory frequency	NO WB	Tube furnace	Dynamic
5 ^a	FAA/CAMI	Rats ^b	30	(1) Incapacitation (2) Death	WB	Tube furnace	Recirculatory
6 ^a	NASA/USF	Mice	30	(1) Incapacitation (2) Death	WB	Tube furnace	(1) Static (2) Dynamic
7 ^a	Japanese	Mice ^b	15	(1) Incapacitation (2) Cardiovascular (3) Death	WB	Tube furnace	Dynamic
8a ^a	Univ. of Michigan	Rats	240	Death	WB	Tube furnace	Static
8b ^a	Univ. of Michigan	Rabbits	140	Death	HO	Combustion furnace	Dynamic
9a ^a	Univ. of Pittsburgh	Mice	30	(1) Incapacitation (2) Death (3) Respiratory frequency	HO	Combustion furnace	Dynamic
9b	Univ. of Pittsburgh	Mice	3	Respiratory frequency	HO	Direct flaming ignition	Static
10 ^a	GE/SRI	Rats	120	Death	WB	Combustion furnace	Recirculating
11 ^a	Harvard	Rats	20	(1) Incapacitation (2) Death	WB	Combustion furnace	Recirculating

^aDescribed by Kaplan *et al.*²⁶

^bAnimals in an activity wheel during exposure.

WB: Whole-body exposure.

NO: Nose-only exposure.

HO: Head-only exposure.

chamber. The whole bodies of the rats were exposed to the gaseous products for 30 min after which the chamber was vented with fresh air for 15 min. Animal mortality was the principal toxicological endpoint noted during the exposure and the 14 day post-exposure observation period, although a gross pathological examination was also used to assess the toxic effects of smoke inhalation. During the exposure, the concentrations of various gases (e.g. O₂, CO, CO₂, NO_x, formaldehyde (H₂CO), acrolein and styrene) present in the chamber were monitored.

Potts and Lederer evaluated the toxicity of many synthetic and natural materials, including polystyrenes and Douglas fir.^d Three different samples of polystyrenes were tested: (1) a polystyrene without additives (Styron 492U), (2) a polystyrene with an additive designed to reduce flaming tendency and decrease ease of ignition (Styron 6021.01) and (3) a polystyrene foam (Styrofoam). Table 6 lists the animal fatalities and levels of gases present in the chamber when approximately 40 mg l⁻¹ of the polystyrenes or Douglas fir samples were degraded in the flaming and non-flaming modes in this test. The data presented by Potts and Lederer demonstrate that these polystyrenes were less toxic than wood (Douglas fir) in the non-flaming mode in this test. Under flaming conditions, the toxicities of the polystyrene samples and the wood were comparable. Of the gases monitored, CO, CO₂, H₂CO, acrolein and styrene were noted to evolve during

the non-flaming degradation of Styron 492 and Styron 6021.01, while only CO and CO₂ were detected from the Styrofoam. Flaming degradation of all the polystyrene samples resulted in significantly greater quantities of CO and CO₂ than in the non-flaming mode. Low quantities of NO_x were also produced during the flaming exposures, whereas H₂CO was produced from the polystyrenes in both modes except for Styrofoam in the non-flaming mode. Degradation of Styron 6021.01, which contained a flame retardant, produced greater amounts of CO in both combustion modes than the other two polystyrene samples.

All deaths from polystyrene occurred during exposure and only from the flaming combustion products. Due to the high concentrations of CO (> 2700 ppm), Potts and Lederer concluded that the dominant cause of death in the flaming mode was CO intoxication. They also suggested that the low O₂ (< 15%) levels produced during the flaming combustion of Styron 492U and Styrofoam SM contributed to the cause of the lethality. Recent results by Levin *et al.*³² indicate that 4600 ppm of CO in air are necessary to produce death in rats in 30 min. Examination of Potts and Lederer's data show that only the flaming Styron 6021.01 produced enough CO to account for the deaths. However, other data by Levin *et al.* have shown that CO₂ will potentiate the toxicity of the CO, such that in the presence of 5% CO₂ (50 000 ppm), the animals will

Table 6. Results from the Dow Chemical Company test^{a,1}

Temp. (°C)	Material	During exposure	Animal fatalities		O ₂ (%)	CO ^c (ppm)	CO ₂ (ppm)	Gas concentrations			
			Post-exposure	Total				NO _x (ppm)	H ₂ CO (ppm)	Acrolein (ppm)	Styrene (ppm)
Flaming											
475	Styron 492U	5/7; 7/7	0/7	5/7; 7/7	13	3700	58 800	4.5	100		
675	Styron 6021.01	7/7	0/7	7/7	17	5700	21 700	10	250		
550	Styrofoam SM	7/7	0/7	7/7	14	3800	50 900	15	150		
475	Douglas fir	2/7; 6/7	0/7	2/7; 6/7	16	3900	38 600	5	< 2	20	
Non-flaming											
475	Styron 492U	0/7	0/7	0/7	20	300	6 500		> 300	14	> 400
550	Styron 6021.01	0/7	0/7	0/7	19	2100	7 400		> 300	3	> 400
550	Styrofoam SM	0/7	0/7	0/7	19	500	6 400				
450	Douglas fir	1/7; 1/7	3/7; 5/7	4/7; 6/7	19	5800	15 100	< 2	5	30	27

^a40 mg l⁻¹ samples.^bAverage values of which only the minimum is presented here.^cAverage values of which only the maximum is presented here.**Table 7. Results from the NBS test⁹**

Materials	Mode	Temp. (°C)	Laboratory ^a number	EC ₅₀ (mg l ⁻¹)	Animal measurements			
					LC ₅₀ (30 min) (mg l ⁻¹)	LC ₅₀ (30 min + 14 days) (mg l ⁻¹)	COHb (%) at 30 min LC ₅₀	CO (ppm) at 30 min LC ₅₀
Polystyrene (GM51)	NF	425	2	> 50.0	> 50.0	> 50.0	> 6	> 100
		525	4	—	> 46.2	> 46.2	—	> 600
		465	6	> 40.0	> 40.0	> 40.0	> 6	> 70
	F	475	2	~ 30.0	53.5	53.5	77	2500
		550	4	—	33.0	32.6	67	2300
		540	6	~ 28.7	38.9	38.9	78	1300
Douglas fir	NF	445	2	10.1	42.9	27.6	ID.	4900
		460	4	22.0	24.9	24.0	79	3100
		440	6	13.5	29.0	22.8	86	3400
	F	510	2	18.4	50.1	45.3	I.D.	3400
		525	4	—	30.6	29.6	65	2700
		490	6	~ 23.5	39.8	39.8	83	3400

^aThree different laboratories tested polystyrene. Laboratory 6 was NBS.

NF: Non-flaming.

F: Flaming.

ID: Insufficient data.

die from 2500 ppm of CO.³² Thus, the data in Table 6 indicate that the combination of CO and CO₂ is sufficient to account for the deaths that occurred. A pathological examination of animals exposed to the non-flaming gaseous products of polystyrene showed no specific adverse effects.

The National Bureau of Standards toxicity test method The development and interlaboratory comparison of the National Bureau of Standards (NBS) toxicity test method was described by Levin *et al.*^{9,33} Natural and synthetic materials, including a rigid polystyrene foam (GM51), were examined by different laboratories using the NBS protocol. This toxicity test method consists of a combustion system, an animal exposure chamber and a chemical analytical system. Materials are thermally decomposed, at both non-flaming and flaming temperatures, in a quartz beaker inserted into a cup furnace located below a 200 l exposure chamber. All of the gaseous products are circulated through analytical equipment, which continuously monitors CO, CO₂ and

O₂, and back to the exposure chamber. In each test, the heads of six rats are exposed to the gaseous combustion products for 30 min, at which time the surviving animals are withdrawn and held for 14 days of observation. LC₅₀ values, based on deaths which occur during the 30 min exposures plus the 14 day post-exposure period, are currently used as the biological endpoint for the NBS protocol. However, incapacitation based on 30 min EC₅₀ values and blood carboxyhemoglobin (COHb) levels were also monitored and used to evaluate the toxicity of a material.

The results for the toxicity of a polystyrene and Douglas fir obtained from three of the laboratories who participated in the interlaboratory evaluation of the NBS test method are listed in Table 7. As reported by Levin *et al.*, the polystyrene tested appeared to be more toxic in the flaming mode than in the non-flaming one.⁹ EC₅₀ and LC₅₀ values for the flaming mode were less than those values for the non-flaming mode. The CO concentration for flaming polystyrene combustion at the 30 min LC₅₀ was much greater than that for non-flaming conditions

and, consequently, the percentage COHb at the 30 min LC_{50} value was much greater for the flaming mode (67–78%) than the non-flaming mode (at the highest concentration tested (50 mg l⁻¹) the COHb was 6%). Based on pure CO-in-air studies at NBS, the concentration of CO in the flaming mode was still too low to solely account for the deaths that occurred.⁹ Since CO₂ potentiates the toxic effect of CO, as mentioned earlier, the CO₂ may have played a role in these deaths. However, the CO₂ concentrations were not provided in reference 9.

The University of Utah test method The NBS test method was based to a large extent upon the University of Utah test method.²⁶ The main differences between the two test protocols are as follows:

- (1) In the University of Utah test method, a polytetrafluoroethylene (PTFE) covered aluminum cone is placed over the mouth of the cup furnace in the belief that it will shield the animals from the generated radiant heat and aid in the distribution and mixing of the combustion products;
- (2) The University of Utah uses a 60 l exposure chamber, not the 200 l chamber described in the NBS test method;
- (3) Four rats are exposed in the head-only mode instead of the six rats exposed in the NBS procedure; and
- (4) In the University of Utah test method, all animal deaths that occur during the 30 min exposures and the first 30 min following exposure are recorded as within-exposure deaths. In the NBS protocol, any deaths occurring after the 30 min exposure were considered post-exposure deaths.

Farrar *et al.*,³⁴ using the University of Utah test method, assessed the toxicities of the combustion products from fifteen plastics and compared the results with those of Douglas fir (used as a reference material in this test method). Among these materials were three samples of polystyrene foam. Farrar *et al.* reported that the toxicity of the polystyrene foams was very low for the non-flaming mode of combustion. EC_{50} and LC_{50} (30 min plus 14 days) values, percentage COHb and CO concentrations in both the non-flaming and flaming modes for the tested polystyrene foams are presented in

Table 8. Low CO levels (< 360 ppm) and low COHb levels (< 7%) were observed in the non-flaming mode. Farrar *et al.* stated that incapacitation under the non-flaming conditions could not be attributed to CO, but may be due to the presence of styrene in the exposure atmospheres.

The flaming combustion of polystyrene was shown to be more toxic than the non-flaming mode. The flaming EC_{50} and LC_{50} values for the polystyrene materials were comparable with those of Douglas fir. Higher CO and COHb levels were observed for the flaming mode than for the non-flaming mode for both the polystyrenes and the wood. Farrar *et al.* state that CO is probably the lethal agent in the flaming combustion of the polystyrene foams since high COHb levels (66–75%) were observed at death. However, work at NBS on CO in air has shown that COHb levels exceeded 80% before deaths occurred from 30 min exposures to CO alone.³²

One of the polystyrene foam samples, GM49, contained a fire retardant. Farrar *et al.* did not find any significant difference in the measured toxicity parameters which could be attributed to the fire retardant.

Tube furnace combustion systems

DIN 53436 toxicity test protocol The DIN 53436 test method was developed in the Federal Republic of Germany. In this system, a moving horizontal tube furnace thermally decomposes the sample in a flowing air stream to provide a 'steady-state' concentration of combustion products. The combustion air stream is diluted with room air prior to introduction into the animal exposure chamber. The diluted effluent is drawn past the animals and exhausted from the exposure chamber. Materials, thermally decomposed in this system, are toxicologically evaluated based on either an equal specimen volume or an equal mass per unit length.

Hofmann and Oettel³⁵ evaluated the toxicity of a variety of synthetic as well as natural products, including seven different cellular polystyrenes (i.e. Styropors P, F200, F210, KR2180, KR2180/1, KR2180/2 and F220). In each test, the noses of six rats were exposed to the thermal decomposition products of the polystyrenes for a total of 30 min. In order to compare material results, tests were conducted using either samples of equal mass (5g)

Table 8. Results from the University of Utah test³⁴

Material	Mode	Temp. (°C)	LC_{50}		COHb		CO	
			30 min (mg l ⁻¹)	30 min + 14 days (mg l ⁻¹)	at EC_{50} (%)	at LC_{50} (%)	at EC_{50} (ppm)	at LC_{50} (ppm)
GM47	F	540	15.4	27.8	31.6	—	1120	2030
GM49		500	17.9	35.8	35.8	(66–75) ^a	1180	2360
GM51		500	12.7	33.8	45.1	—	840	2230
Douglas fir		490	13.3	24.6	32.7	92	1840	3390
GM47	NF	480	27.2	> 40	6.6	—	240	—
GM49		440	30.9	> 40	4.1	—	250	—
GM51		420	> 40	> 40	1.7	—	< 360	—
Douglas fir		465	4.8	14.6	14.9	84	980	2980

^aThis is the range of values for the three polystyrene foams.

—: Values not given.

F: Flaming.

NF: Non-flaming.

or equal volume (300 min × 15 mm × 10 mm). Thermal decomposition of the samples was conducted at several isothermal furnace temperatures, ranging in 100-degree increments from 300° to 600°C. In these experiments, the furnace traveled at a rate of 10 mm min⁻¹ over the tube containing the sample, while an airflow of 100 l h⁻¹ was directed counter-current to the motion of the furnace through the tube. The decomposition gases were subsequently diluted with an additional airflow of 100 l h⁻¹ before entering the animal exposure chamber. Experimental results for the various polystyrenes and pine wood, including average levels of COHb developed in the blood of test animals, along with corresponding death ratios, are presented in Table 9. Experiments conducted with 5 g samples (a nominal exposure concentration of 50 mg l⁻¹) showed low COHb levels (<15%) in animals exposed to the polystyrenes decomposed at or below 400°C. These results would suggest that little, if any, CO was produced at these temperatures. For Styropor P, little CO was observed even at temperatures of 500°C. Styropor P did not ignite and undergo open burning until the samples were heated at 600°C. At this temperature, CO concentrations were reported to reach levels ranging from 5000 to 10 000 ppm. These exposures produced an average 92% mortality. In general, for these polystyrenes, when ignition and open burning did not occur, comparatively little CO was produced (<100 ppm) and all animals survived. In those tests where the material ignited, high COHb levels (>70%) were observed and animals died. At temperatures below the auto-ignition point of the samples (≤500°C), little CO (<100 ppm) was measured, COHb levels were observed to be low (<15%) and no lethality was observed. At and above the auto-ignition temperature (generally about 500°C for most of these polystyrene samples), the specimens burned, large quantities of CO were produced (>2000 ppm), the COHb levels were greater than 70% and deaths occurred.

For those experiments performed using equal volumes of test material (i.e. 300 mm × 15 mm × 10 mm), auto-ignition of the polystyrene samples was not observed below 600°C. Although greater quantities of CO were produced in the flaming mode than in the non-flaming one, COHb levels did not exceed 41% and no mortalities were observed. This low toxicity was attributed to the small polystyrene sample mass actually charged in the tube furnace (i.e. approximately 1 g, resulting in nominal exposure concentrations ranging from 16 to 27.7 mg l⁻¹). Conclusions reached from these tests, run with samples of equal volume were:

- (1) This size polystyrene samples did not ignite below 600°C;
- (2) COHb levels were elevated only after exposure to the flaming combustion products; and
- (3) No mortalities were observed because of the low sample mass tested.

Hofmann and Sand³⁶ examined the toxicity of the thermal decomposition products of a number of synthetic materials, including a rigid expanded and a non-cellular polystyrene. The test conditions were similar to those previously described by Hofmann and Oettel. The results found with the rigid expanded polystyrene closely paralleled that previously reported by Hofmann and Oettel for Styropor P. In addition, the atmospheres produced by both polystyrenes, when decomposed under similar non-flaming conditions, at temperatures not exceeding 500°C, caused no animal deaths and low COHb (<15%) blood levels. At 600°C, where ignition and flaming were observed for both polystyrenes, the COHb levels were substantially elevated (rigid expanded polystyrene: 80%; non-cellular polystyrene: 75%) and 92–100% of the animals died.

Herpol and Minne³⁷ used the DIN apparatus to evaluate the toxicity of 15 different synthetic and natural materials. Two different expanded polystyrene samples

Table 9. Results from the DIN 53436 test³⁵

Material	COHb blood content (%) and death ratio ^a of rats at decomposition temperatures of							
	300°C		400°C		500°C		600°C	
	(%)	(ratio)	(%)	(ratio)	(%)	(ratio)	(%)	(ratio)
Specimens of equal weight (5 g)								
Styropor P	<15	0/12	<15	0/12	<15	0/18	80	11/12
Styropor F 200	<15	0/12	<15	0/12	19	0/12 ^b	81	12/12
					75	12/12 ^c		
Styropor F 210	<15	0/12	<15	0/12	72	13/18	81	12/12
Styropor KR 2180	<15	0/12	<15	0/12	85	12/12	74	12/12
Styropor KR 2180/1	<15	0/12	<15	0/12	79	12/12	78	12/12
Styropor KR 2180/2	<15	0/12	<15	0/12	74	12/12	78	12/12
Styropor F 220	<15	0/12	<15	0/12	82	12/12	78	12/12
Pinewood	32	3/12	86	12/12	85	12/12	85	12/12
Specimens of equal volume (300 × 15 × 10 mm)								
Styropor P	<15	0/12	<15	0/12	<15	0/12	29	0/12
Styropor F 200	<15	0/12	<15	0/12	<15	0/12	26	0/12
Styropor F 210	<15	0/12	<15	0/12	<15	0/12	26	0/12
Styropor KR 2180	<15	0/12	<15	0/12	<15	0/12	40	0/12
Styropor KR 2180/1	<15	0/12	<15	0/12	20	0/12	41	0/12
Styropor KR 2180/2	<15	0/12	<15	0/12	<15	0/12	33	0/12
Styropor F 220	<15	0/12	<15	0/12	<15	0/12	34	0/12
Pinewood	<15	0/12	88	12/12	87	12/12	89	12/12
Spruce	<15	0/6	88	6/6	88	6/6	92	6/6

^aThe ratio of dead rats to the total number of rats exposed to the fumes.

^bNon-flaming.

^cFlaming.

(normal and self-extinguishing) were evaluated. In each experiment, the whole bodies of six Wistar rats (three males and three females) were exposed for 30 min to the thermal decomposition products from 2 g samples placed in the tube furnace and heated to 600°C. The furnace was adjusted to move over the sample in 30 min. Airflow through the combustion system and the dilution air were adjusted to 200 l h⁻¹ producing a nominal exposure concentration of 10 mg l⁻¹. No animal deaths were observed in any of these experiments. These findings are, however, consistent with those observed by Hofmann and Oettel for the polystyrene samples tested at equivalent volumes.

Herpol³⁸ evaluated the acute toxic effects of exposures to the thermal decomposition products of 35 materials, of which one was a sheet-type, chlorinated fire-retarded polystyrene. Ten gram samples were evaluated at furnace temperatures of 400°, 600° and 800°C. Animals were monitored for changes in respiratory rate (monitored for 30 s at 6 min intervals), COHb levels and lethality. Carbon monoxide concentrations in the exposure atmosphere were also measured. Flaming combustion of the polystyrene samples was observed at 600° and 800°C. At 400°C, no lethality was observed, COHb concentrations did not exceed background levels (i.e. < 15%) and the respiratory rate was only slightly perturbed (i.e. it gradually decreased 20% during the first 18 min but then increased such that there was only a 10% decrease by the end of the exposure). At 600°C all the exposed animals died, the average COHb level was 68 ± 1.8% and the respiratory rate decreased almost linearly to zero by the end of the 30 min exposure period. At 800°C only 72% of the exposed animals died and the average COHb levels obtained were 50 ± 6.9% (surviving animals) and 53 ± 5% (dead animals). In contrast with the experiments run at the lower temperatures, the respiratory rates initially increased slightly, i.e. about 10% above pre-exposure rates; however, by 14 min, the rates had started to decrease reaching 50% of the control rate by the end of the exposure period. These toxicological findings are consistent with the average CO concentrations observed at 600° (~ 8000 ppm) and 800°C (~ 2500 ppm).

Herpol and Vandeveld^{39,40} also tested polystyrenes according to the procedure outlined above for Herpol.³⁸ They did not report their raw data, but only gave results corresponding to their own 'Toxicity Index'. The 'index' values calculated using this approach range from $TX = 0$, when all animals survive the exposure, to $TX = 100$, when all animals die within the first 6 min of exposure. To compare materials, the highest TX values obtained for each material were used, irrespective of the temperature of decomposition. The toxicity 'index' value calculated for the sheet-type chlorinated fire retarded polystyrene was 56.7 and when compared with the other materials tested by Herpol, indicated that this polystyrene was one of the top four toxic materials, only surpassed by a polyamide-polyester blend carpet with foam backing, a plasticized PVC cable and a 100% acryl-type jacquard upholstery material. No direct correlation was made by the authors between the level of CO produced and the extent of toxic effects.

FAA/CAMI toxicity protocol Crane *et al.*⁴¹ at the Federal Aviation Administration's Civil Aeromedical Institute

(FAA/CAMI) developed a laboratory small-scale inhalation test which used rats to assess the toxicity of commercial materials designed for aircraft interiors. In this test system, 750 mg samples of materials are thermally decomposed in a tube furnace at an isothermal temperature of 600°C. The combustion atmosphere is recirculated at a rate of 4 l min⁻¹ through the combustion and animal exposure chamber (total chamber volume equals 12.6 l). In each experiment, three Sprague-Dawley rats are placed in separate motorized rotary cages and exposed in the whole-body mode to the decomposition products for a maximum of 30 min. This mass loading is equivalent to a nominal exposure concentration of approximately 60 mg l⁻¹. Times-to-incapacitation (T_i) (the time which animals were unable to walk in the rotary cages) and times-to-death (T_d) were monitored and recorded.

Using the FAA/CAMI test method, Hilado *et al.*^{42,43} evaluated the toxicity of four different synthetic materials, one of which was a polystyrene (Styron 402 D). The thermal decomposition atmosphere generated from this polystyrene did not incapacitate or kill any of the test animals. Compared with the combustion atmospheres generated from the other three materials, the decomposition products from this polystyrene were the least toxic.

NASA/USF toxicity protocol The NASA/USF toxicity protocol was developed by Hilado at the University of San Francisco (USF)⁴⁴ for the National Aeronautics and Space Administration (NASA). In this test, four Swiss-Webster male mice are allowed to move freely in a 4.2 l chamber while being exposed to thermal degradation products from 1 g samples of materials heated in a horizontal tube furnace. The exposure chamber is connected to the furnace by a glass tube. Materials are decomposed in the furnace set at either a fixed temperature or ramped at a rate of 40°C min⁻¹. The system is designed such that either static or dynamic combustion conditions may be generated. In the static mode, movement of the combustion products into the exposure chamber is primarily due to thermal expansion, while in the dynamic mode, a pump moves the decomposition products through the system at flow rates of either 1 or 3 l min⁻¹. The nominal calculated chamber concentration, based on a 1 g mass loading and 30 min exposure, would be 240 mg l⁻¹ in the static mode and 33 or 11 mg l⁻¹ in the dynamic mode, depending of whether the air flow is 1 or 3 l min⁻¹.

Hilado and his coworkers concentrated their efforts on measuring the exposure time necessary to produce a specific biological effect, such as incapacitation (T_i) or death (T_d). These values were examined as a function of the total amount of material consumed.

Hilado and coworkers in a series of studies^{42,45-48} evaluated the toxicity of several different commercially available polystyrene materials (i.e. styrofoam pellets, rigid foam slabs, solid transparent sheet). Using static flow conditions and ramped furnace temperatures (200-800°C at 40°C min⁻¹), they found that the decomposition products from these polystyrenes caused mean times to incapacitation (based on the observed times of staggering by the animals) ranging from 13.6 to 20.7 min and mean times to death ranging from 20.0 to 27.5 min.

Table 10. Concentration-response data from a polystyrene decomposed via the NASA/USF toxicity test method⁴⁹

Mass loaded (g)	Number of tests	Time to death (min)	Mortality (%)	CO (ppm)	CH ₄ (ppm)
0.1	1	26.6 ± 4.1	75	900	
0.2	1	25.2 ± 2.4	100	4000	
0.5	2	28.1 ± 1.2	38 ± 18	4600 ± 1130	
1.0	5	27.5 ± 1.3	100 ± 0	6900 ± 2000	760 ± 160
2.0	4	28.0 ± 4.5	62 ± 43	4650 ± 2250	1450 ± 740
5.0	2	24.8 ± 6.5	100 ± 0	3500	

^aRising temperature program (200–800°C at 40°C min⁻¹).

Hilado and Huttlinger⁴⁹ also attempted to determine the quantity of a polystyrene (Styron 402 D) which, when thermally decomposed, produced 50% lethality in the exposed animals. Using the static flow conditions and the ramped temperature mode, 0.1 to 5 g samples were decomposed in the furnace. In all experiments better than 99% of the mass charged in the furnace was pyrolyzed. No correlation, however, was obtained between sample mass decomposed and percentage lethality or time to death (Table 10). Concentrations of CO and CH₄ also did not show any correlation with the mass of sample loaded in the furnace or with death. These experiments highlight the variability in results obtained with this test method.

Hilado and coworkers^{42,45,46,47,50} also investigated the effect temperature and heating rate had upon the toxicity of the thermal decomposition products of various types of polystyrenes. Results from tests performed isothermally at 800°C were compared with those from thermally ramped tests. Mean T_i for the polystyrene materials ranged from 6.0 to 12.5 min and the mean T_d death from 15.4 to 22.1 mins. The thermal degradation products from the polystyrene decomposed at the higher isothermal conditions resulted in shorter mean times to incapacitation and death. These results were attributed to a more rapid and higher generation of CO at 800°C.

Hilado and coworkers^{42,47,51} also examined the effects of air flow rates through the furnace. Hilado and Huttlinger⁵¹ tested a rigid polystyrene foam under both ramped and isothermal temperature conditions (800°C) and under both static and dynamic chamber conditions (airflow rate of 1 l min⁻¹). Results under the various test conditions are presented in Table 11. Regardless of whether air flowed through the chamber or not, the mean

times to effect were shorter when the polystyrene was decomposed isothermally at 800°C than under the ramped furnace conditions. The experiments conducted with an airflow of 1 l min⁻¹ did, however, produce slightly shorter mean times to incapacitation than those without any airflow. However, the main difference between the static and dynamic exposure modes was that no animal deaths were observed under the dynamic conditions. It is unclear why no deaths occurred when there appears to be sufficient toxicant(s) generated under the dynamic exposure conditions to produce incapacitation even earlier than under the static conditions.

The toxicity of the thermal decomposition products from a polystyrene foam was examined along with that of three other materials (i.e. ABS, polycarbonate and polyethylene) under ramped temperature conditions (200–800°C at 40°C min⁻¹) and under both static and dynamic exposure chamber conditions (airflow rates of 1 and 3 l min⁻¹).⁴² A summary of the mean times to incapacitation and death, along with their standard deviations, and percentage mortality obtained under these various conditions are presented in Table 12. The results obtained with no air flow suggest that the effluent produced by polystyrene at the isothermal temperatures of 600° and 800°C was more incapacitating than that produced by the ramped temperature condition. The effluents at 800°C were more toxic than at 600°C. Only slight differences in the mean time to death were seen for polystyrene under static conditions, regardless of the temperature of decomposition. Mortality, on the other hand, was lower at 600°C. With air flow through the system, at 600°C, times to incapacitation and death were lower than with no air flow. At 800°C and 1 l min⁻¹ air

Table 11. Toxicity of pyrolysis gases from a polystyrene rigid foam insulation decomposed under the NASA/USF toxicity test method⁵¹

Exposure mode	Temperature mode (°C)	Sample weight (g)	Staggering (min)	Mean time ^a ± standard deviation T_o			
				Convulsion (min)	Collapse (min)	Death (min)	
Static	Ramped ^b	1.0	13.6 ± 6.4	20.4 ± 2.6	21.1 ± 0.3	26.2 ± 0.1	
Static	800	1.0	6.4 ± 6.3	9.8 ± 0.2	10.6 ± 0.4	15.4 ± 0.0	
Dynamic	Ramped ^b	1.0	6.2 ± 1.5	8.0 ^c	—	No deaths	
Dynamic	800	1.0	3.5 ^c	7.9 ^c	9.9 ± 2.9	No deaths	

Static: No forced air flow.

Dynamic: 1 l min⁻¹ air flow.

^aMean of two tests.

^bTemperature is ramped from 200° to 800°C at 40°C min⁻¹.

^cResults from only one test.

Table 12. Toxicity of pyrolysis gases from a polystyrene foam decomposed under the NASA/USF toxicity test method⁴²

Airflow rate (l min ⁻¹)	Temperature mode (°C)	Mean time ^a ± standard deviation T ₀		Mortality
		Incapacitation (min)	Death (min)	
0	ramped	19.0 ± 0.4	26.2 ± 0.1	8/8
0	600	10.3 ± 6.7	26.0 ± 0.7	5/8
0	800	6.0 ± 4.2	21.8 ± 6.6	11/12
1	600	4.1 ± 0.9	12.0 ± 1.4	3/8
3	600	3.1 ± 0.3	7.0 ± 1.5	4/8
1	800	3.9 ± 2.3	n.d.	0/12
3	800	6.1 ± 2.9	n.d.	0/8

^aMean of two of three tests.

flow, times to incapacitation were lower than in the static mode but no deaths were observed. Considering the large difference in exposure concentrations tested (11, 33 and 240 mg l⁻¹), remarkably little differences in the mean times to incapacitation or death were observed. In the majority of cases polystyrene appeared to be slightly less toxic than ABS, polycarbonate and polyethylene.

These observations were supported by results reported by Hilado and coworkers^{52,53} for tests where a polystyrene, as well as six other materials (polypropylene, polyethylene, polycarbonate, polyoxymethylene, polyether sulfone and Douglas fir) were decomposed isothermally from 200° to 800°C, at 100°C intervals under static as well as dynamic air flow conditions (1 l min⁻¹). For all seven materials under the static chamber conditions, increasing furnace temperature generally resulted in increased CO concentration, shorter mean times to death and increased mortality. For polystyrene, no deaths were observed below 400°C, whereas at 800°C, 95% of the animals died. With an air flow of 1 l min⁻¹, mortalities were only observed when the polystyrene was decomposed at 600° and 700°C. No deaths were seen below 600°C or at 800°C. The authors concluded that, at lower temperatures, insufficient amounts of toxicants were produced to cause death, while at higher temperatures the toxicants were apparently produced so rapidly that they were not present in the exposure atmosphere long enough to cause death.

Japanese toxicity test protocols Japanese researchers have developed several different methods to evaluate and compare the toxicity of combustion products from building and furnishing materials. Three different studies have been reported⁵⁴⁻⁵⁶ in which the toxicities of the thermal degradation products of rigid polystyrene foams were compared with those of other commonly used materials. In all three studies neither the exact type nor the supplier of the materials was specified. Although the experimental protocols were different, some similarities were noted. The sample materials were heated in a quartz tube under dynamic airflow conditions. In all cases, mice were exposed in a separate chamber through which the gaseous effluents passed.

Kishitani⁵⁴ studied the toxicity of the thermal decomposition products of ten building materials, including two different polystyrene foams. Three grams of the foams were heated in a tube furnace in which the temperature was raised from ambient to 740°C in 15 min.

The heating rate was selected to simulate the temperature increase expected in the initial stages of a fire. Heat was provided to the test material by four propane burners placed under the quartz tube through which air flowed at a rate 2 l min⁻¹. For each material, a total of five mice were exposed, one at a time, in a 56 l glass chamber for 15 min. Measurements of T_d, COHb, 3-day post-exposure observation of surviving animals, electrocardiograms (ECG) and necropsy examinations of the mice exposed to the polystyrene combustion products were recorded.

No mice died either during the exposures or the post-exposure observation periods. However, the combustion products of these polystyrene foams were not totally innocuous. Carboxyhemoglobin levels ranged from 17.5% to 34.5% and the mucous membranes of the eyes and nasal passages of some of the mice were injured. In addition, irregular pulses were observed in the ECGs. Kishitani concluded that one or more irritant gases were present in the thermal decomposition products of these polystyrenes and were responsible for the effect on the ECGs and the mucous membranes of the animals. No attempt was made to identify or speculate on the nature of the noxious gas(es).

Kishitani and Yusa⁵⁵ evaluated the toxicity of the thermal degradation products of 15 different materials, one of which was a rigid polystyrene foam. This study differed from the one of Kishitani, described above, in that the mice were exposed to the combustion effluents produced when the materials were isothermally heated at either 550° or 850°C. The test apparatus consisted of a quartz combustion tube which was suspended in an electrically heated tubular furnace and connected to a 55 l glass exposure chamber. A 5 cm layer of alumina marbles was placed in the combustion tube in order to dry the air and increase gas dispersion. An airflow of 4 l min⁻¹ supplied through the combustion tube went into the exposure chamber. Temperatures in the exposure chamber did not increase more than 2°C above ambient. The mass of material placed in the tube furnace was varied in order to obtain a concentration-response relationship. The problem of loading of a large enough sample of foam in the tube furnace to produce incapacitation was overcome by thermally preconditioning the samples in an oven at 150°C for 20 min to reduce their volumes and increase their densities. The weight reduction, 7.4%, was attributed to the loss of blowing agent and was not believed by the authors to affect the resultant composition or toxicity of the combustion products. The toxicologic

Table 13. Relative toxicological comparisons of a polystyrene foam and other materials in the test of Kishitani and Yusa⁵⁵

Heating temp. (°C)	Sample	W(g)
850	Japanese cedar	3.72–5.83
	Luan	3.47–5.21
	Hardboard	3.09–4.46
	Untreated plywood	1.31–2.19
	Fire retardant-treated plywood	2.20–3.55
	Melamine resin-impregnated sheet # 1	0.60–1.00
	Melamine resin-impregnated sheet # 2	0.64–0.97
	Polyacrylonitrile	0.24–0.33
	Polyamide	0.17–0.25
	Wool	0.41–0.60
	Urea resin foam	0.24–0.33
	Polystyrene foam	17.7–24.6
	Polyurethane foam	0.58–0.87
	Polyvinyl chloride foam	2.61–4.02
Polyvinyl chloride A	34.5–48.6	
550	Japanese cedar	5.50–8.32
	Luan	6.13–9.11
	Untreated plywood	4.35–6.98
	Fire retardant-treated plywood	3.42–4.91
	Melamine resin-impregnated sheet # 2	2.47–3.72
	Polyacrylonitrile	0.61–0.88
	Polyamide	0.38–0.55
	Urea resin foam	0.25–0.39
	Polystyrene foam	10.7–15.2
	Polyvinyl chloride foam	3.45–5.45

W: Specimen weight which produced an average time to incapacitation between 2.5 and 3.5 min.

Note: Heating at 550°C of untreated plywood polystyrene and polyvinyl chloride A were compared at a time of 3.5–4.5 min.

endpoint, incapacitation, was based on the time necessary for collapse of the animals. The exposure chamber contained five revolving cages which electrically monitored the activity of each mouse. Routine visual observations were also made. The time when a mouse could no longer make the cage revolve was considered the time of incapacitation. The total test exposure was 15 min.

Kishitani and Yusa attempted to develop a relationship between the sample mass loaded in the tube furnace and the average T_i obtained in each test. The following empirical formula was derived:

$$W = kT_i^p$$

where W = sample mass (in grams), T_i = time to incapacitation (in minutes) and k and p are empirically derived regression coefficients. Various materials were compared by ranking the total mass of material, W , which, when heated in the tube furnace, produced an average collapse time of between 2.5–3.5 min (Table 13). With the exception of polyvinyl chloride-A (PVC-A), polystyrene produced combustion products which were less toxic than those of any other material tested. (The unexpectedly low toxicity rating for PVC-A was suggested by the authors to be due to the extremely large amount of inorganic filler used in its formulation.)

Nishimaru *et al.*⁵⁶ evaluated the relative acute toxicities produced by the inhalation of smoke and gases from pyrolyzing or burning plastics used for insulation. Five different foams, two of which were polystyrenes, and a wood (luan) sample were tested at four different temperatures; 350°, 450°, 550° and 750°C. Temperatures were selected to simulate the early stages of fire development. The test specimen was placed into a quartz tube and heated in an electric furnace. Dry air flowed through the tube furnace and into the animal exposure chamber at a rate of 5 l min⁻¹. In most tests, eight male mice were placed in individual revolving activity wheels, which were rotated solely by the movement of the mice and were electronically monitored. The time to incapacitation (T_i), i.e. the time at which the mouse stopped rotating the cage, was then used as the measure of acute toxicity. Each test ended when all the animals had collapsed. In a few experiments, materials were heated at 550°C for 10 min and a hybrid, male rabbit was exposed to the thermal decomposition products along with the six mice. Measurements performed on the rabbits included ECGs and respiratory tracings.

Gas concentrations (CO, CO₂ and O₂) in the exposure chamber and the incapacitation times calculated for both polystyrene foams at each temperature are presented in Table 14. The greatest toxicity, as indicated by the shortest average time to incapacitation, occurred at 550°C for both polystyrenes. This temperature produced the highest concentration of both CO and CO₂ and the lowest concentration of O₂. The flaming which occurred at 550°C was also longer than that at the other temperatures and it was noted that polystyrene was more toxic in the flaming mode.

When compared with the other three foams (i.e. PVC, urea resin and polyurethane) and luan wood decomposed at 550°C, the thermal decomposition products from polystyrene foam appeared to be the least

Table 14. Results from the Nishimaru test⁵⁶

Material	Temp (°C)	Sample mass (g)		Test duration (min)	Flaming duration (min)	Gas concentration in exposure chamber (%)			Mean time to incapacitation ± S.D. (8 mice) (min)
		Before test	After test			CO (max)	CO ₂ (max)	O ₂ (min)	
Polystyrene Foam 1	750	15	0.1	60	0.20–1.63	0.17	0.69	19.8	12.80 ± 2.81
	550	15	0.1	60	0.83–3.50	0.21	1.45	18.6	12.49 ± 4.10
	450	15	0.1	40	None	0.09	0.35	20.5	15.06 ± 2.70
	350	15	0.9	70	None	0.02	0.20	20.6	32.83 ± 10.28
Polystyrene Foam 2	750	15	0.1	60	0.18–1.60	0.16	0.79	19.8	14.51 ± 8.20
	550	15	0.1	60	1.03–3.40	0.21	1.45	18.6	13.41 ± 2.62
	450	15	0.1	45	None	0.09	0.30	20.5	15.89 ± 3.24
	350	15	5.1	60	None	0.01	0.05	20.7	25.98 ± 5.23

Table 15. Comparison of results from various materials under the Nishimaru test⁵⁶

Material	Temperature (°C)	Sample mass (g)		Test duration (min)	Flaming duration (min)	Mean time to incapacitation ± S.D. (min)
		Before test	After test			
Polystyrene foam 1	550	15	0.1	10	0.90–3.83	4/6 NI
Polyvinyl chloride foam	550	7.5	1.9	10	1.93–NR	4.62 ± 1.94
Urea resin foam	550	1	0.1	10	0.43–0.75	3.18 ± 0.81
Polyurethane foam	550	5	0.3	10.5	None	5/6 NI
Lauan	550	15	3.1	10	0.50–3.50	5.60 ± 1.17

S.D.: Standard deviation of average time to incapacitation of 6 mice.

NI: Not incapacitated.

NR: Not reported.

toxic (Table 15), especially since a larger mass loading of polystyrene foam was degraded than for any of the other foams. More animals were incapacitated and at shorter times from the decomposition products of the lauan wood, which was the only material with a mass loading equivalent to that of the polystyrene. However, abnormalities were observed in the ECG wave patterns and the pneumatograms of a rabbit exposed to the polystyrene combustion products. In particular, anoxia with deep breathing was evident.

Since the polystyrene, when decomposed in the non-flaming modes, produced relatively low levels of CO and CO₂, the incapacitating effects are probably caused by something other than CO and CO₂. Styrene, one of the major pyrolysis products of polystyrene and a known irritant, was considered by the authors to be a likely cause.

Combustion ovens

University of Pittsburgh toxicity protocol Prior to the establishment of the current version of the University of Pittsburgh Test Method (to be described later), Alarie *et al.*⁵⁷ developed a test procedure to evaluate the degree of sensory irritation evoked by exposure to plastic decomposition products. In a 12 l combustion chamber a known amount of material was ignited with a bunsen burner, which was removed after ignition so that the continued combustion was self-propagating. Samples were configured so as to burn like tapers from the top down. A constant airflow of 17 l min⁻¹ was maintained through the combustion chamber. The thermal decomposition products were further diluted by mixing them with varying amounts of fresh air (i.e. 0, 17, 51, and 96 l min⁻¹) to produce different exposure concentrations of gaseous products in order to develop a concentration–response relationship. In each test four mice were placed in individual body-plethysmographs such that only their heads were exposed to the various dilutions of the gaseous effluents which were directed through the 2.3 l glass exposure chamber. Since sensory irritation was correlated with a reduction in respiratory rate,⁵⁸ Alarie *et al.* determined the concentration of the gaseous products which reduced the respiratory rate by 50%; that concentration was designated the RD₅₀. The respiratory rates of the mice were monitored before each test (control

rates), during the 3 min exposures to the combustion products, and following the exposures to establish recovery times. Concentration–response relationships were developed based on the amount of material loaded in the combustion chamber and the total exposure airflow (i.e. combustion air and dilution air).

Two polystyrene materials (i.e. a sheet and a foam) were evaluated by this procedure and compared with a polycarbonate sheet.⁵⁷ The calculated RD₅₀ values for the polystyrene sheet was 6.0 mg l⁻¹ and that for the polystyrene foam was 9.6 mg l⁻¹. These RD₅₀ values indicated that the irritant potencies of the combustion products of these materials were as follows: polystyrene sheet > polystyrene foam > polycarbonate sheet. The authors concluded that the sensory irritancy was not due to the elevated CO or CO₂ or decreased O₂, but was probably due to small amounts of styrene monomer or some other styrene derivatives produced during combustion.

The current version of the University of Pittsburgh toxicity test method is a dynamic flow-through system that uses a Lindberg furnace which is programmed to heat the sample at a ramped heating rate of 20°C min⁻¹. Air and combustion products are flushed through the oven and diluted with cooled air, such that a total airflow of 20 l min⁻¹ passes through the animal exposure chamber. In each experiment, four male mice are exposed in the head-only mode. Typical endpoints are the LL₅₀, the amount of material loaded in the furnace that kills 50% of the animals during a fixed exposure time (usually 30 min); the LT₅₀, the time needed to kill 50% of the animals when exposed to the LL₅₀; and the RD₅₀, the loading of material in the furnace that reduces the average respiratory rate of the animals to 50% of their pre-exposure control values. Although continuous mass loss is measured throughout the experiments in the University of Pittsburgh method, all biologic endpoints are based on the mass of material initially loaded in the furnace, not the total mass consumed.

Alarie and Barrow⁶⁰ used respiratory rate depression (i.e. RD₅₀) as a measurement endpoint to assess the relative toxicity of the thermal decomposition products of polymeric materials, including polystyrene. The RD₅₀ level reported for the oxidative pyrolysis of a polystyrene was 0.18 mg l⁻¹ with 95% confidence limits of 0.08–

0.42 mg l⁻¹. This value may be compared with the RD_{50} value (6.0 mg l⁻¹ with a 95% confidence limit of 4.4–8.4 mg l⁻¹) for the same material examined with the earlier method under flaming combustion. The conclusion made by these investigators was that biologically significant differences existed between the irritant effects produced by non-flaming oxidative pyrolysis and open-flaming of polystyrene.

Anderson and Alarie⁶¹ evaluated the toxicity of the thermal decomposition products of three different polystyrenes, two of which were specially formulated rigid polystyrene foams (GM47 and GM49⁸) and one was a commercially available polystyrene film. The formulations of GM 47 and GM 49 were alike except that GM 49 contained an undefined fire retardant. The LL_{50} values for these polystyrenes were 5.8, 9.8 and 10.0 g, respectively. Although Alarie provided values based only on the mass loading, a nominal LC_{50} value in mg l⁻¹ may be estimated based on the exposure duration (30 min) and the flow rate of the dilution air (20 l min⁻¹) through the animal exposure chamber. These nominal LC_{50} values for GM47, GM49 and the polystyrene film would be 9.7, 16.3 and 16.7 mg l⁻¹, respectively. Although this is a possible way to define a nominal LC_{50} , a more valid approach in a dynamic system, when materials undergo rapid thermal decomposition, is to actually account for the gas concentration which passes by the animals and the time period that the animals are exposed. This latter time period is related to the time of total mass loss. Based upon the information provided by Alarie and Anderson,⁶² GM47 totally decomposed in approximately 6 min and GM49 took 8 min. The LC_{50} values based on the times of total mass loss for each sample would then be 48.3 mg l⁻¹ for GM47 and 62.5 mg l⁻¹ for GM49. These LC_{50} values are approximately four to five times larger than those calculated based on the assumption that decomposition occurred uniformly over the total exposure period and more nearly resemble values reported with other test methods.

In addition to the LL_{50} values, Alarie and Anderson^{62,63} also measured and calculated LT_{50} (the time necessary to kill 50% of the animals exposed to the 30 min LL_{50}), LLT_{50} (i.e. LL_{50} times LT_{50}) and RD_{50} values for GM47 and GM49 (Table 16). Along with these toxicity data, the authors also provided information on the mass loss and the CO production that occurred during the decomposition of the polystyrenes. Both polystyrenes, i.e. GM47 and GM49, decomposed rapidly, with the initial mass loss starting to occur at about 300°C and the major portion of the mass being lost between 400° and 500°C. Although CO was released by both GM47 and GM49, the concentration produced by the fire-retarded

sample, GM49, was substantially greater (about 5000 ppm) than that produced by GM47 (about 1500 ppm). The toxicity of the various materials evaluated was compared with that of Douglas fir. Regardless of the endpoint used for comparison, these polystyrenes, i.e. GM47 and GM49, were ranked by the authors as more toxic than wood. (This test method is one of a few in which polystyrene products are ranked as being more toxic than wood.)

Harvard Medical School toxicity test method This test method was developed and used by Dressler⁶⁴ in the evaluation of the toxicity of combustion effluents from consumer products. In this method the combustion system consists of a modified self-cleaning oven and is connected to an animal exposure chamber which contains ten revolving, animal exercise wheels. The time-of-useful-function (TUF) is the biological endpoint and is defined as the time from the start of exposure to when the animal is unable to move voluntarily in the exercise wheel. The combustion products are recirculated through the furnace and exposure chamber.

With this test procedure Robinson *et al.*⁶⁵ assessed the acute toxicity of the combustion products from three polymeric materials commonly used to manufacture television cabinets. These materials consisted of two different polystyrenes, one of which was designated PS-SB-BR and contained a brominated flame retardant and the other, designated PS, was not flame retarded. The third material was a polyphenylene oxide (PPOP). Two sample loadings were tested; the first (128 mg l⁻¹) was considered equivalent to the concentration produced by an 8 lb television cabinet being burned in a 100 ft³ room. This mass loading was heated at 350°, 400° and 450°C. The second loading was equivalent to a nominal animal exposure concentration of 32 mg l⁻¹ and was only tested at 450°C. In each test, a total of 28 rats (i.e. 10 in exercise wheels, 18 in wire-mesh cages) were placed inside the exposure chamber and exposed to the pyrolysis products from these materials for 20 min. Both the TUF and the number of animal deaths were recorded during each experiment. Surviving animals were observed for 21 days to determine if the thermal decomposition products resulted in post-exposure deaths.

The results of the mortality study⁶⁵ are presented in Table 17. When fuel loads equivalent to 32 mg l⁻¹ were decomposed at 450°C, the flame retarded materials produced no mortalities, while the non-flame retarded polystyrene caused 10% of the animals to die. At the 128 mg l⁻¹ loadings, no deaths were noted at 350°C, 0 and 82% deaths were observed when the flame retarded and non-flame retarded materials were heated at 400°C,

Table 16. Toxicological evaluation of GM 47 and GM 49 polystyrene foams under the University of Pittsburgh toxicity test method⁶²

Material	RD_{50} (mg l ⁻¹)	LL_{50} (g)	LT_{50} (min)	LLT_{50} (g. min)	LC_{50}^a (mg l ⁻¹)	LC_{50}^b (mg l ⁻¹)
GM47	22	5.8	11	64	9.7	48.3
GM49/FR	14	10.0	9	90	16.7	62.5

FR: Fire retardant.

^aBased on a 30 min concentration average.

^bBased on the actual time to complete loss of sample mass.

Table 17. Results from polystyrene television cabinets tested under the Harvard Medical School test⁶⁵

Loading (mg l ⁻¹)	Temp. (°C)	Flame retarded	Mortality (%)	TUF ^a (min)
32	450	Yes	0	20
		No	10	20
128	350	Yes	0	20
		No	0	20
	400	Yes	0	20
		No	82	2
450	Yes	51	12	
	No	93	5	

^aTUF = Time of useful function.

respectively; whereas at 450°C, 51 and 93% of the animals died from exposure to the thermal decomposition products from the flame retarded and non-flame retarded polystyrenes, respectively. These results indicate that the non-flame retarded polystyrene was more toxic than the flame retarded one. Additional results presented by the authors showed that the flame retarded polystyrene was more toxic under non-flaming decomposition at 450°C than when flaming occurred. These findings are contradictory to the already discussed polystyrene results, in which the flaming mode of combustion was observed to be more toxic.

The results of the TUF measurements showed the same trend as the mortality data (Table 17). Animals exposed to the higher concentration of non-flame retarded smoke produced at both 400° and 450°C had the shortest TUF, 2 and 5 min, respectively. Compared with the other television cabinet material, polyphenylene oxide, polystyrene appeared to be more toxic at the higher loading.

The average concentrations of CO, CO₂ and O₂ generated in the exposure chamber when the flame retarded and non-flame retarded polystyrenes were decomposed at 450°C are displayed in Table 18 for the 3

Table 18. Analysis of gases in the animal chamber from thermal decomposition of polystyrene in the Harvard Medical School test⁶⁵

Flame retarded	Time (min)	Gas concentration (%)		
		CO	O ₂	CO ₂
Yes	3	0	14.5	2.25
	12	0	17.5	1.00
No	3	0.45	11.5	4.00
	12	0.40	15.0	2.50

Fuel load: 128 mg l⁻¹.

Decomposition temperature: 450°C.

and 12 min sampling times. The lowest oxygen and highest CO and CO₂ levels were obtained when the non-fire retarded polystyrene sample was decomposed. These findings appear to be consistent with the higher mortality and more rapid incapacitation caused by exposure to this polystyrene.

General Electric/Southern Research Institute test method
Nelson *et al.*⁶⁶ developed a test procedure to determine the relative acute toxicities of the thermal degradation products from a variety of materials. In this method, different mass loadings of materials are placed in a combustion furnace (i.e. a nominal 10 l Electric Multiple Unit Furnace, type 66, or Lindberg Model 51442-S Box Furnace) and decomposed at temperatures which varied between 805° and 880°C. The smoke generated in the combustion furnace was drawn through a laminated rubber tube into a 740 l acrylic animal exposure chamber by an exhaust fan. As the smoke started to fill the exposure chamber, the exhaust fan was turned off and the exhaust port was sealed. Additional gaseous products and smoke were then transported and mixed in the exposure chamber by natural convection. When the thermal degradation of the material was complete (as determined by visual

Table 19. Amount of material necessary to produce mortality in 50% of the rats under the GE/SRI test⁶⁶

Material	FR	ALC ₅₀ values						Gas concentration	
		Loaded		Consumed		CO (ppm)	CO ₂ (ppm)		
		g	(95% CL)	mg l ⁻¹	g			(95% CL)	mg l ⁻¹
Polycarbonate III	+	8.6	7.3–9.8	11.6	6.8	5.7–7.8	9.2	2690	10300
High impact polystyrene	–	8.9	—	12.0	8.9	—	12.0	2530	12700
Wool	–	9.4	8.4–10.4	12.7	9.0	8.6–9.6	12.2	319	14000
Polyphenylene oxide	–	11.2	—	15.1	9.2	—	12.4	1900	14000
Poly(butylene terephthalate)	+	12.3	10.6–14.0	16.6	11.3	9.7–13.1	15.3	2390	13400
Polycarbonate II	+	13.8	8.9–16.9	18.6	11.3	7.6–13.4	15.3	2490	11600
Polycarbonate	–	14.0	—	18.9	10.9	—	14.7	1740	11900
Polycarbonate I	+	15.5	12.3–22.3	20.9	12.4	10.0–17.7	16.8	2220	13900
Red oak	–	16.8	15.6–19.7	22.7	16.3	15.1–17.9	22.0	2550	11700
Poly(butylene terephthalate)	–	16.9	14.1–19.8	22.8	16.5	13.5–19.3	22.3	2100	15500
Polyphenylene oxide	+	17.4	15.5–18.8	23.5	13.8	12.2–14.9	18.6	1960	18400
Polycarbonate (glass filled)	+	31.9	30.6–33.4	43.1	23.4	22.4–24.5	31.6	1420	35500
Phenolic (mineral filled)	–	43.3	36.8–48.6	58.5	19.8	16.9–22.2	26.8	1780	15600
Phenolic (general purpose)	–	47.5	41.8–53.3	64.2	25.5	22.5–28.7	34.5	1700	21900

ALC₅₀: Amount of test material needed to cause death of 50% of the animals.

FR: Fire retardant.

CL: Confidence limits.

observation of the sample), the furnace was disconnected and the animal chamber was sealed. In each test, ten Sprague-Dawley rats (five males and five females) were placed into five cages located inside the animal exposure chamber and exposed to the gaseous atmosphere produced. The timed animal exposure of 120 min officially began when the combustion furnace was disconnected and the exposure chamber was sealed. The apparent lethal concentrations (ALC_{50}) (i.e. the amount of test material which, when decomposed under the specified test conditions, produced mortality in 50% of the exposed animals) were determined for twelve synthetic (including one high-impact polystyrene sample) and two natural materials. The concentrations of CO, CO₂ and O₂ in the exposure chamber were analyzed and the blood COHb levels of a minimum of four animals per test were measured following removal of the animals from the exposure chamber. The ALC_{50} data, which are based either on the amount of material loaded or the amount of material actually consumed, are presented in Table 19. These values are presented (based on the ALC_{50} values for the amount of material loaded in the furnace) from the most toxic to the least toxic. When the ALC_{50} values of all 14 materials were compared, the high impact polystyrene was determined to be the second most toxic material with an ALC_{50} of 12.0 mg l⁻¹. However, none of the ALC_{50} values differed by more than a factor of 6 (based on the amount of sample loaded) and the high-impact polystyrene was determined to be about twice as toxic as red oak.

Table 19 lists the concentrations of CO and CO₂ in the exposure chamber atmospheres at the ALC_{50} values for each material. The CO₂ levels were noted to increase during the exposure period; this can be attributed to the respiration of the animals. The authors concluded that, with the exception of wool, CO, in conjunction with the elevated CO₂ levels, was the primary cause of the observed toxicities produced by these materials. All animals that died within the 2 h exposure period (except those exposed to wool products) were found to have blood

COHb levels in excess of 60%, mostly in the 70–80% range. Surviving animals also exhibited elevated COHb levels, which, in some instances, approached levels of 60%.

University of Michigan toxicity protocol Two different test procedures, one static and the other dynamic, were developed at the University of Michigan to study the toxicity of thermal decomposition products of various combustible materials.⁶⁷ In the static method the test sample is rapidly decomposed by heating for a period of 6–10 min at 700°C in a Vycor tube wrapped with resistance wiring. In each test, a group of Sprague-Dawley rats (usually 15 per test) is exposed for a period of 4 h to the combustion products which are generated directly into a 1500 l stainless steel chamber.

The dynamic method involves slowly heating a sample material placed in a furnace programmed to increase the temperature at a rate of either 3 or 5°C min⁻¹. An airstream of 1 l min⁻¹ flows through the furnace and is cooled and further diluted with air flowing at a rate of 2 l min⁻¹ prior to passage through the animal exposure system. After 140 min, the furnace temperature reaches about 700–800°C and the decomposition process is considered essentially complete. At this time, all exposed animals are removed. In each test, five rats are exposed to the thermal decomposition products from different mass loadings. The chamber used for exposing the rats to the thermal degradation products is a Pyrex glass column with side tubes attached so that only the rats' noses extend into the decomposition effluent airstream.

In both test methods, the primary biological endpoint is lethality. The LL_{50} values determined for the various materials tested are presented in Table 20. The LL_{50} value for the polystyrene sample decomposed under static conditions was 29 g whereas, under the dynamic conditions, it was 4.3 g. In the static mode, polystyrene ranked as the sixth most toxic material among eleven evaluated materials while in the dynamic mode, it seemed to be the least toxic material. The nominally calculated LC_{50} value for polystyrene in the static exposure tests was

Table 20. Results from the University of Michigan test⁶⁷

Material	Static chamber ^a			Relative toxicity ranking	Material	Dynamic chamber ^b	
	LL_{50} (g)	LC_{50} (mg l ⁻¹)				LL_{50} (g)	LC_{50} (mg l ⁻¹)
Polyurethane foam (FR)	18	12.0		1	Polypropylene	1.0	2.4
ABS	18	12.0		2	Polyurethane foam (FR)	1.4	3.3
ABS (FR)	20	13.3		3	Polyurethane foam	1.5	3.6
SAN 760	23	15.3		4	PVC	1.7	4.1
Polypropylene	26	17.3		5	ABS	1.7	4.1
Polystyrene	29	19.3		6	SAN 760	2.1	5.0
Nylon knit	33	22.0		7	ABS (FR)	2.2	5.2
Nylon	43	28.7		8	Nylon	2.6	6.2
Polyurethane foam	44	29.3		9	Nylon knit	3.0	7.1
Nylon Yarn	47	31.3		10	Nylon yarn	4.3	10.2
PVC	54	36.0		11	Polystyrene	4.3	10.2

LL_{50} : Amount of material loaded in the furnace that causes 50% of the rats to die in 4 h in the static system and 140 min in the dynamic system.

LC_{50} : The LL_{50} divided by the volume of the exposure chamber or the total airflow.

FR: Fire retarded.

^aTemperature approximately 700°C.

^bTemperature ramped from ambient to 700–800°C at 3–5°C min⁻¹.

19.3 mg l⁻¹, while in the dynamic exposure tests it was 10.2 mg l⁻¹.

Cornish *et al.*⁶⁸ also investigated whether different animal species would respond differently to thermal decomposition products from various materials. Both rats and rabbits were exposed to the thermal decomposition effluents generated when 20 g of a material were decomposed under static conditions. The results of this study were inconclusive with regard to polystyrene since no mortalities were observed in either rats or rabbits at this loading.

The two exposure systems described above are obviously quite different. Under the static conditions the animals are exposed to the total products resulting from the thermal degradation for a period of 4 h. In the dynamic system animals are exposed to the thermal decomposition products only during the time in which they are being generated. Thus in the dynamic system animals are exposed to specific decomposition products for only relatively short times. Based on the actual LC₅₀ values calculated, this polystyrene appeared to be more toxic under dynamic than under the static exposure conditions. This observation, that the LC₅₀ values are lower under dynamic than under static conditions (i.e. more toxic), was also noted for the other test materials. On the other hand, under the dynamic conditions the polystyrene was the least toxic of all the tested materials.

CONCLUSIONS

- (1) In general, the main volatile product regardless of atmospheric conditions is the styrene monomer. The concentrations ranged from 0.6% to 100% of the mass evolved.

- (2) The composition and quantity of other evolved products depend greatly upon the chemical formulations (mostly unspecified) and experimental conditions.
- (3) The evolution of styrene is temperature dependent—increasing with furnace temperatures up to 500°C and decreasing above 800°C.
- (4) In oxidative atmospheres, CO and CO₂ were formed and appeared to be responsible for the animal deaths that occurred during the flaming decomposition of polystyrenes.
- (5) Effluents produced during flaming degradation of polystyrenes were generally found to be more toxic than those produced under non-flaming conditions.
- (6) Animal incapacitation occurred during non-flaming decomposition of polystyrenes and could not be attributed to CO and CO₂ since their concentrations were too low. Some other toxicant, perhaps styrene, was responsible.
- (7) When compared with other common natural and synthetic building materials, the thermal decomposition products of polystyrene appear to be among the least toxic.

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NOTES

^aCertain commercial equipment, instruments or materials are identified in this paper in order to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the equipment or material identified is necessarily the best available for the purpose.

^bExamination of materials under oxygen-free conditions does not simulate real fire situations. However, such studies provide information on the generation of thermal decomposition products under controlled experimental conditions and possible effects of vitiated atmospheres which are common in fires. In actuality, many of the products produced under inert atmospheres were also detected in oxidative environments.

^cThe use of colorimetric tubes, such as Draeger tubes provides

unreliable and, at best, semiquantitative results.⁶⁹

^dDouglas fir data are shown to allow a comparison of relative toxicity within a test system. Wood is not a substitute for polystyrene in most commercial products.

^eThe published literature uses the term LC₅₀ rather than LL₅₀. The authors of this review, however, have decided to use LL₅₀ to point out that in this test method the endpoint is actually based on the amount of material loaded into the furnace and is not the exposure concentration which has to include some measure of atmospheric volume. In fact, it is somewhat difficult to determine the actual exposure concentration over time, which depends on the mass loss rate and dispersion of thermal decomposition products in the airflow through the oven.

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