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A Review of the Literature on the Gaseous Products and Toxicity Generated From the Pyrolysis and Combustion of Rigid Polyurethane Foams

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A REVIEW OF THE LITERATURE ON THE GASEOUS PRODUCTS AND TOXICITY GENERATED FROM THE PYROLYSIS AND COMBUSTION OF RIGID POLYURETHANE FOAMS

Maya Paabo and Barbara C. Levin

Abstract

The literature on rigid polyurethane foam has been reviewed with an emphasis on the gaseous products generated under various thermal decomposition conditions and the toxicity of those products. This review is limited to publications in English through 1984. Carbon monoxide (CO) and hydrogen cyanide (HCN) were the predominant toxicants found among more than 100 other gaseous products. The generation of CO and HCN was found to increase with increasing combustion temperatures. Many test methods were used to assess the acute inhalation toxicity of combustion products from various rigid polyurethane foams. Lethality, incapacitation, physiological, and biochemical parameters were employed as biological end points. In general, the combustion products generated from rigid polyurethane foam in the flaming mode appear to be more toxic than those produced in the non-flaming mode. The LC_{50} values for 30 minute exposures ranged from 10 to 17 mg/l in the flaming mode and were greater than 34 mg/l in the non-flaming mode. With the exception of one case in which a reactive type phosphorus containing fire retardant was used, the addition of fire retardants to rigid polyurethane foams does not appear to generate unusual toxic combustion products.

Key words: carbon monoxide, combustion products, fire retardants, hydrogen cyanide, literature reviews, polyurethane foams, rigid foams, thermal decomposition, toxicity.

1. INTRODUCTION

Rigid polyurethane foams have been in commercial production for about thirty years. In 1983, about 255,000 metric tons of rigid polyurethane were produced. Of this, the largest portion, 140,000 metric tons, was used for building insulation; the second greatest use, about 50,000 metric tons, was for thermal insulation in domestic and commercial refrigeration [1][1]. Rigid polyurethane also is used for structural portions of furniture and decorative paneling.

This report reviews the literature on rigid polyurethane foams with special emphasis on the gaseous products generated under various thermal decomposition conditions and the toxicity of those products. Only those papers which were published in English through 1984 and which specifically identified the foam studied as rigid polyurethane were used for this review.

The generic term polyurethane has been employed in the scientific and commercial literature to refer to those polymeric materials in which the repeated structural units are urethane linkages (see equation 1). The complete formulations, however, of these polyurethanes (both rigid and flexible) are proprietary and therefore unknown. When these materials are thermally decomposed under various conditions, specific gaseous products may be measured and the toxicity of the resultant atmospheres can be assessed. However, since the exact formulations of the foams are unknown, conclusions as to the toxicity of the gaseous thermal degradation products from a particular, different polyurethane can only be estimated.

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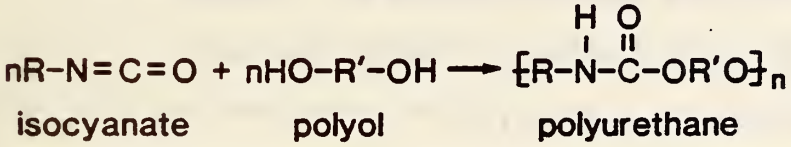
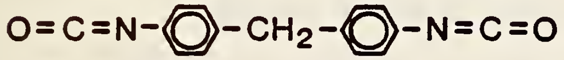
[1] Numbers in brackets refer to the literature references listed at the end of this review.

Rigid polyurethane foams are prepared primarily by the reaction of polyisocyanates with polyol compounds as follows:

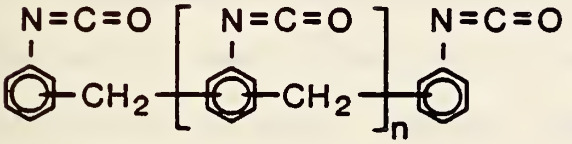


$$nR{-}N{=}C{=}O + nHO{-}R'{-}OH \longrightarrow \left[R{-}\overset{\overset{\displaystyle H}{|}}{N}{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OR'O\right]_n \qquad (1)$$

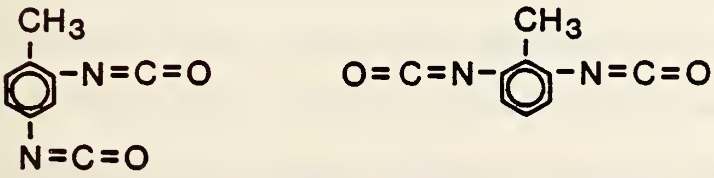
Further reaction of the urethane groups with isocyanates may take place to form allophanates. Common isocyanates shown below include 4,4'-diphenylmethane diisocyanate (MDI), its polymeric form - polymethylene polyphenylisocyanate (as typified by PAPI[2]), and to a lesser extent mixtures of 2,4 and 2,6 isomers of toluene diisocyanate (TDI).



MDI



PAPI



2,4 isomer

2,6 isomer

TDI

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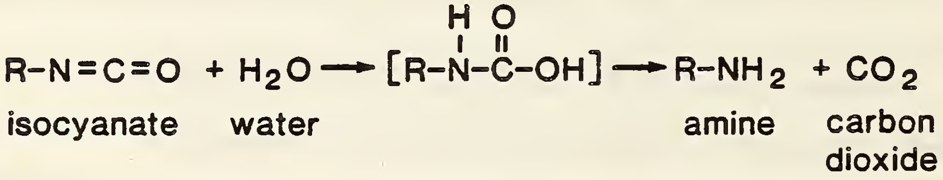
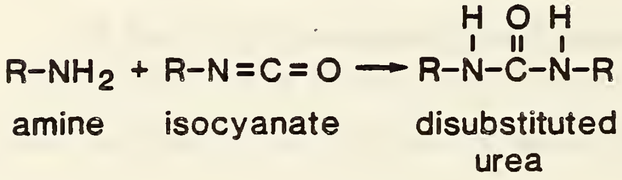
[2] Certain commercial materials are identified in this review in order to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material identified is necessarily the best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

The primary blowing agents for rigid polyurethane foams are (inert) chlorofluorocarbons. In addition, the isocyanates will also react in the presence of water to form carbon dioxide (CO_2) and amines (equation 2). The CO_2 performs as a blowing agent and the amines may react further with the isocyanates to form disubstituted ureas (equation 3).

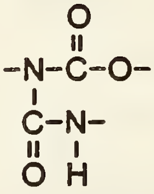


$$\underset{\text{isocyanate}}{R-N=C=O} + \underset{\text{water}}{H_2O} \longrightarrow [R-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-OH] \longrightarrow \underset{\text{amine}}{R-NH_2} + \underset{\text{carbon dioxide}}{CO_2} \qquad (2)$$

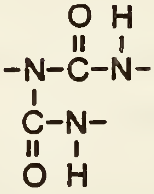


$$\underset{\text{amine}}{R-NH_2} + \underset{\text{isocyanate}}{R-N=C=O} \longrightarrow \underset{\text{disubstituted urea}}{R-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-R} \qquad (3)$$

In the presence of excess isocyanate, the above products undergo additional reactions yielding allophanate and biuret structures (see below) that may produce further crosslinking.



allophanate



biuret

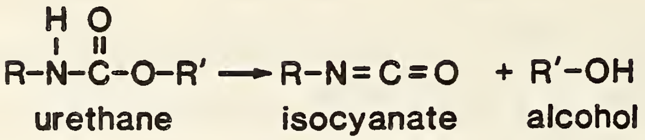
The source of the hydroxyl groups are polyols containing ether or ester linkages. The most common polyols are based on propoxylated sucrose, aromatic polyamines, pentaerythritol, and sorbitol. The numerous formulations of rigid polyurethane foam may also include surfactants, fire retardants, fillers, and catalysts, such as tertiary amines or organo-tin compounds [1a].

2. THERMAL DECOMPOSITION

The combustion of rigid polyurethane foams can produce numerous gaseous products. Many of the analytical studies to identify these volatile products have been performed under various controlled atmospheres ranging from completely inert to oxidative. Although real fires normally occur under oxidative environments, examination of the thermal decomposition products generated under controlled atmospheres provides information about the molecular mechanisms of degradation. This information is also important in understanding the thermal effects on materials which are decomposed in real fires under vitiated conditions. Table 1 presents a compilation of all the combustion products identified in the scientific papers reviewed for this report. The composition of the combustion products depends largely upon the formulation of the foam as well as the conditions of thermal degradation, i.e., temperature, oxygen availability, and ventilation. It should be noted that many of these products are the same regardless of whether the atmosphere was inert or oxidative. Complete combustion yields carbon dioxide (CO_2) and water (H_2O). However, during incomplete combustion in either a flaming or non-flaming mode, many other compounds, such as carbon monoxide (CO), oxides of nitrogen (NO_x), hydrogen cyanide (HCN), hydrocarbons, oxygenated organic compounds, and nitrogen-containing organic compounds, are produced.

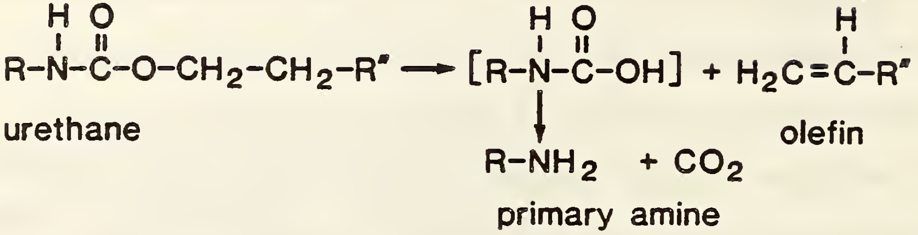
Thermal decomposition of polyurethanes can be represented by the following general types of reactions:

A. Dissociation to isocyanate and alcohol



$$R{-}\overset{H}{\underset{}{N}}{-}\overset{O}{\overset{\|}{C}}{-}O{-}R' \longrightarrow R{-}N{=}C{=}O + R'{-}OH \qquad (4)$$

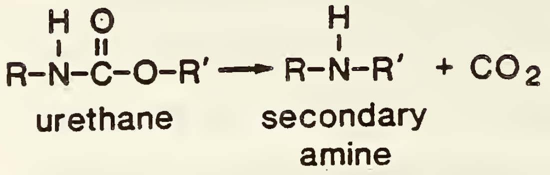
B. Formation of a primary amine and an olefin



$$R{-}\overset{H}{N}{-}\overset{O}{\overset{\|}{C}}{-}O{-}CH_2{-}CH_2{-}R'' \longrightarrow [R{-}\overset{H}{N}{-}\overset{O}{\overset{\|}{C}}{-}OH] + H_2C{=}\overset{H}{C}{-}R'' \qquad (5)$$

$$[R{-}\overset{H}{N}{-}\overset{O}{\overset{\|}{C}}{-}OH] \longrightarrow R{-}NH_2 + CO_2$$

C. Formation of a secondary amine



$$R{-}\overset{H}{N}{-}\overset{O}{\overset{\|}{C}}{-}O{-}R' \longrightarrow R{-}\overset{H}{N}{-}R' + CO_2 \qquad (6)$$

Much of the early work to identify these initial degradation steps has been reviewed by Saunders et al. [2,3]. Many of these papers involved differential thermal analysis (DTA) and thermogravimetric analysis (TGA) along with the identification of functional groups to indicate those reactions that may have occurred. One of these studies includes the work by Backus et al. [4], the results of which agree, in general, with degradation reactions 4, 5, and 6 shown above. Backus et al., using TGA, degraded several formulations of rigid polyurethane foam in helium and air and identified the functional groups in the residual chars and the volatile gases by infrared spectroscopy. The volatile products detected included CO_2, CO, alkenes, mixtures of organic compounds characterized by -NH, -OH, -COC-, and monosubstituted phenyl groups. Although further work has been published on several mechanistic aspects, the detailed degradation reactions have not yet been fully elucidated [5,6,7]. The following sections of this review cover the more recent experimental studies and are separated according to the atmospheric conditions under which the experiments were performed.

2.1 Degradation in Inert Atmospheres

2.1.1 General Decomposition Studies

When rigid polyurethane foam is exposed to elevated temperatures under real fire conditions, even more extensive degradation occurs than indicated by the reactions in equations 4 to 6. In an attempt to determine the detailed mechanism of degradation and to identify the further breakdown products which may be of toxicological concern, several studies have been performed in helium or nitrogen atmospheres under pyrolytic conditions at controlled temperatures. Bott et al. [8] found that small quantities of CO, HCN, and ammonia (NH_3) were generated when a sample of a highly crosslinked polyurethane (formulated from diphenyl diisocyanate and polyethylene oxide alcohol) was decomposed under either nitrogen or air atmospheres in a tube furnace over a temperature range of 300 to 750°C. The volatile gases were analyzed by Draeger tubes[3], infrared (IR), and mass spectrometric (MS) techniques. The generation of CO, HCN, and

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[3] It should be noted that the use of colorimetric tubes, such as Draeger tubes, provides unreliable and, at best, semiquantitative results, primarily because other combustion gases may interfere in the analysis. The temperature of the gas being sampled also has been noted to have an effect on the results [9].

NH_3 was shown to be temperature dependent. In nitrogen atmospheres, rapid evolution of CO was detected at the lowest temperature (400°C), followed by HCN at 550°C and NH_3 at 600°C. At 500°C, the relative concentrations of CO, NH_3, and HCN were 500, 250, and 20 ppm, respectively. When the foam was heated at high enough temperatures (>500°C) to ensure complete decomposition, the yield of HCN was 14 mg/g of foam. Since HCN was detected before NH_3, Bott et al. postulated that HCN is not produced as a secondary reaction from NH_3 and carbon, but is produced from the relatively stable carbon-nitrogen groups in the foam.

Napier and Wong [10] evaluated the generation of phosphorus-containing compounds from fire retarded polyurethanes thermally decomposed in atmospheres of different oxygen concentrations or in nitrogen. Two rigid polyester polyurethane foams treated with FYROL 6[4] or trichloroethyl phosphate[5] were decomposed in a glass reaction vessel over a temperature range of 220 to 400°C. The degradation products were analyzed by elemental analysis, wet chemical techniques, and infrared spectroscopy. In experiments with both fire retarded foams, CO_2 and alkenes were produced and the infrared spectra indicated the presence of functional groups corresponding to C-F and C-Cl in the gaseous products and to -OH, C-O-, $-NH_2$, -NCO, and urea in the liquid products. The type of fire retardant appeared to influence the degradation

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[4] The chemical name for FYROL 6 is O,O-diethyl-N,N-bis(2-hydroxyethyl)-aminomethyl phosphonate. FYROL 6 is a reactive fire retardant, i.e., it is chemically incorporated into the foam by reacting like a polyol and replacing a portion of the polyether in the formulation.

[5] Trichloroethyl phosphate is the fire retardant name that was used in the paper being reviewed. It is highly probable that the authors were referring to tris(2-chloroethyl) phosphate, a commonly used fire retardant. Tris(2-chloroethyl) phosphate is an additive fire retardant, i.e., it is physically added to the foam during formulation.

mechanism. For example, the foam containing FYROL 6 produced compounds which corresponded to equations 4 and 5; whereas, in the case of the foam containing trichloroethyl phosphate[5], depolymerization according to equation 4 seemed to constitute the main reaction. Phosphorus-containing compounds were observed when the foam treated with trichloroethyl phosphate[5] was decomposed at each tested temperature or when the foam with FYROL 6 was thermally degraded at temperatures greater than 320°C. In addition to the phosphorus compounds, chlorine was also generated from the foam containing trichloroethyl phosphate[5].

Woolley et al. [5,11,12,13] have conducted a major investigation of the general mechanism of thermal degradation of polyurethane foams and identified the nitrogen-containing combustion products. They suggested that flexible and rigid polyurethane foams decompose by different mechanisms. Using elemental ultramicroanalysis, Woolley et al. monitored the nitrogen content of the residues of several flexible and rigid foam samples decomposed under inert (nitrogen) pyrolytic conditions in a tube furnace. The flexible foams exhibited a rapid loss of most of their nitrogen at low temperatures (about 300°C) while losing only aproximately one third of their mass; whereas with the rigid foams, the higher the temperature (200 to 500°C), the greater the nitrogen and weight loss. This suggests that in rigid foams the nature of the fragmentation process is temperature dependent [11].

Other studies showed that at relatively low temperatures (300°C) the flexible foams decompose by the depolymerization reaction (equation 4) into a "yellow smoke" (mainly polymeric isocyanates) and a residue (mainly polyol). When subsequently heated at elevated temperatures (over 800°C), the "yellow smoke" condensates form HCN and various other nitrogen-containing compounds. When the yellow smoke or the foam was heated at 1000°C, about 70% of the nitrogen in the original foam was converted to HCN [12].

In contrast, rigid polyurethane foams release some polyol at low temperatures (200-300°C) and then, as the temperature increases, undergo uniform fragmentation and produce both isocyanate and polyol in about equal proportions [5,13]. In these studies, four MDI/polyester and polyether type rigid foams (two of which contained phosphorous fire retardants) as well as samples of the component compounds, polyols and isocyanate, were thermally decomposed at degradation temperatures up to 1000°C. Volatile decomposition products were collected in traps and analyzed by gas chromatographic (GC) and gas chromotographic/mass spectrometric (GC/MS) techniques. These studies also showed that most of the volatile phosphorus compounds were generated below 200°C and the majority of the gaseous products from the polyol were produced between 300 and 600°C. In addition, they found that the particulates in the smoke were primarily fragmented polyurethanes [13].

Chambers et al. [7] also studied the mechanism of both flexible and rigid polyurethane decomposition. By using an array of model compounds and analyzing the residues and volatiles by various analytical techniques [IR, nuclear magnetic resonance (NMR), GC, and MS], they showed that, at 300°C, the degradation mechanism involves o-acyl fission of the urethane linkage with the formation of volatile polyureas (TDI-type flexible foam) or non-volatile polycarbodiimides (MDI-type rigid foam). Above 600°C, both the polyureas and polycarbodiimides decompose further to yield nitriles and olefinic and aromatic compounds. With a ^{13}C labelling technique, HCN and nitriles were shown to originate from the breakdown of the aromatic ring of MDI.

Another major investigation to establish the decomposition mechanism as well as to identify toxic products formed during thermal degradation of rigid polyurethane in an inert atmosphere was conducted by Voorhees et al. [6]. They studied the thermal decomposition of a laboratory formulated rigid foam based on polymethylene polyphenyl isocyanate (PAPI) and propoxylated trimethylol propane (TMP). The pyrolysis of the samples was performed with a commercial pyrolysis probe or in a glass reaction tube at 500, 750, and 1000°C. The volatile products were identified by GC/MS, gas chromatography with chemical ionization mass spectrometry (GC/CIMS), and IR analytical techniques. The finding of thermal degradation products, such as low molecular weight alkenes, aldehydes, methanol, and aniline, supports the dissociation steps depicted in equations 4 and 5. In contrast, the secondary amines suggested in equation 6 were not detected in either the volatile products or in the non-volatile particulate matter. The results of Voorhees et al. suggest that the two pathways (equations 4 and 5) proceed through common intermediates involving allyl ether and methyl substituted vinyl ether. In addition, they found that the polyol fraction decomposes by a systematic sequence rather than a random breakdown [6,14].

2.1.2 Volatile Products

The number and type of volatile compounds detected as decomposition products of rigid polyurethane foam in inert atmospheres depend on the degradation conditions and the analytical techniques employed. Voorhees decomposed a rigid polyurethane foam at 500, 750, and 1000°C and identified 51 compounds by GC/MS including saturated and unsaturated hydrocarbons, oxygenated compounds, aromatics, nitrogen-containing compounds, CO, CO_2, and water. Of these, 18 GC peaks were ascribed to propoxylated trimethylol propanes. In addition to the 51 compounds mentioned above, seven peaks were not identified. The major volatile decomposition products that were identified and their concentrations are listed in Table 2. Decomposition at 1000°C produced three times more volatiles than at 500°C [6,14]. However, no HCN was detected under these experimental conditions.

Mumford et al. [15] pyrolyzed samples of an unknown rigid polyurethane foam with a commercial pyrolysis probe and analyzed the volatile products by GC/MS. In addition to detecting 20 compounds similar to those listed in Table 2, they also identified aromatic amines, an indication that the unknown foam was probably an MDI-based polyurethane.

With GC/MS and IR techniques, Woolley and his co-workers identified low molecular weight hydrocarbons, aromatic compounds, HCN, and aliphatic and aromatic nitriles as the combustion products of several rigid polyurethane foams that were thermally decomposed above 700°C [13]. The results of a quantitative analysis of eight major combustion products obtained from four different types of rigid foams, two of which were flame retarded, are shown in Table 3.

Even though the degradation mechanisms at low temperatures are different for rigid and flexible foams [5,11,12,13,16], both types of foams yield similar products at elevated temperatures. For example, all of the major products listed in Table 3, except naphthalene, were also found among the degradation products of TDI formulated polyester and polyether type flexible foams which were decomposed at 800°C [12]. Similarity of the high temperature degradation products between rigid and flexible foams was also observed by Chambers and Reese [16]. Specially formulated foams based on 2,4- and 2,6-TDI were degraded over a temperature range of 800 to 1000°C (these temperatures are higher than those typically found in fires). The volatiles from the decomposition of the smoke were analyzed by GC. The yields of the major nitrogen-containing products, namely HCN, acrylonitrile, acetonitrile, benzonitrile, and pyridine from the rigid foams were very close to those found when the flexible foams were decomposed under similar conditions (Table 4) [16].

2.1.3 HCN and CO Generation

HCN appears to be the predominant nitrogen-containing compound produced when rigid polyurethane foam is decomposed at high temperatures [13,16]. At 1000°C, the yield of HCN from four rigid foams varied between 38 and 73 mg/g which indicated that 27.8 to 42.8% of the nitrogen was recovered as HCN [13]. The increase in evolution of HCN with increasing temperature was also observed by Michal when he degraded nitrogen-containing polymers in a tube furnace [17]. An ultraviolet spectrophotometric method was used for measuring the HCN in the volatile products of a commercial polyurethane insulation foam. HCN increased from 0.5 to 60.7 mg/g as the temperature increased from 600 to 1200°C. These results and those of several other studies which indicate the temperature dependence of HCN generation are summarized in Table 5.

CO is produced under inert conditions from polyurethane foam since it contains oxygen in its molecular structure. Voorhees et al. [6] in a study on a flame retarded rigid foam showed that the production of CO increases with increasing temperature. The evolution of CO from the rigid polyurethane foam increased from 0.29 mg/g at 500°C to 2.8 mg/g at 750°C to 26.5 mg/g at 1000°C. Therefore, the generation of both CO and HCN from rigid polyurethane increases with increasing temperature.

2.2 Degradation in Oxidative Atmospheres

In order to evaluate the toxic atmosphere produced by rigid polyurethane foams under flaming or smoldering conditions similar to those found in real fire situations, the evolution of combustion products has been studied under oxidative conditions. Most of the studies have been performed in small-scale laboratory experiments, although large-scale burns would probably simulate real fire atmospheres more accurately.

Small-scale tests performed under non-flaming oxidative pyrolysis are representative of the early stages of a fire in which oxygen levels are relatively high (>16%) and the heat flux is relatively low. Under such conditions, volatile product profiles are very complex and may contain many different types of chemical species, such as hydrocarbons, aldehydes, ketones, and nitrogen-containing compounds. Flaming tests represent fires close to or following flashover during which the oxygen levels would drop rapidly and the heat flux would be high. In these tests, the profile of combustion products is relatively less complex consisting of more thermally stable compounds, such as aromatics. In both the flaming and non-flaming oxidative cases, CO and CO_2 are the predominant products produced, but HCN has also been found in toxicologically significant quantities under these conditions.

Many of the papers surveyed in this section did not distinguish between oxidative pyrolysis and flaming combustion. In many cases, the sample size was limited and the emphasis was on the temperature of decomposition rather than on the occurrence of flaming. Whenever possible, this distinction will be made in this review.

2.2.1 Volatile Combustion Products

2.2.1.1 Common Toxicants

Although the production of volatile combustion products from rigid polyurethane foam in air has been studied over a wide range of temperature and ventilation conditions, few detailed analyses of the products have been done. In most cases, interest has centered on the common toxicants, such as HCN and CO. However, in many flaming experiments, NO_x generation has also been measured.

Michal [18] evaluated the generation of CO from a number of polymeric materials, including rigid polyurethane foam, under different oxygen (O_2) concentrations in order to simulate real-fire conditions in which the O_2 concentration in the atmosphere can vary widely. Using GC, he determined the amount of CO generated from rigid polyurethane foam decomposed in the flaming mode under limited O_2 conditions in a combustion chamber (CAB 4.2) set at temperatures between 500 and 800°C. The CO concentration varied from 121 to 154 mg/g with an average of 141 mg/g. The CO content in the combustion products of the polymeric materials studied, including rigid polyurethane, was shown to increase with increasing temperature.

Evolution of CO, HCN, and NH_3 from a highly crosslinked isocyanate-based rigid polyurethane foam decomposed in nitrogen and in air was studied by Bott et al. [8]. At 500°C, the relative concentrations of CO, HCN, and NH_3 generated from one gram samples in air were 5000, 200, and 500 ppm, respectively. When samples of the foam were completely degraded at temperatures greater than 500°C, 13.5 mg/g of the foam was recovered as HCN. Comparison of the results obtained in air and in nitrogen (see Section 2.1.1) shows that CO, HCN, and NH_3 evolve at lower temperatures in air than in nitrogen. That is, CO, HCN, and NH_3 start to evolve rapidly in air at 300, 400, and 450°C and in nitrogen at 400, 550, and 600°C, respectively. CO, however, evolves at a slightly lower temperature than HCN in both atmospheres. As the calculated apparent activation energies for HCN and CO production were not found to be greatly different in air and in nitrogen (95 vs 73 kJ/mole for HCN and 76 vs 74 kJ/mole for CO), Bott et al. concluded that the presence of oxygen does not affect the mechanism of HCN and CO generation.

The generation of HCN from polyurethane foams also appears to be dependent on the specific chemical formulation [19]. Specially prepared polyurethane (rigid and flexible) and isocyanurate foams based on TDI and PAPI formulations (some with phosphorus-containing fire retardants) were pyrolyzed in both air and nitrogen atmospheres in a tube furnace at 500°C, the temperature at which maximum evolution of HCN was found to occur in air. The evolved HCN was measured by a colorimetric technique using a spectrophotometer. Amounts of HCN generated from ten different rigid foams decomposed in air are listed in Table 6.

With the PAPI-based foams, the quantity of HCN evolved during decomposition in air appeared to be related to the nitrogen content of the foam. This was not found in the TDI-based foams, which produced much less HCN than the PAPI type foams except in the case of the foam prepared with crude, undistilled TDI. The presence of a phosphorus-containing fire retardant (FYROL 6) was found to reduce the HCN evolution [19].

After comparison of HCN generation data from rigid polyurethane foam decomposed in air and in nitrogen, Ashida concluded that oxygen may be necessary for the generation of HCN [19]. The effect of oxygen on the amount of HCN generated was demonstrated with a modified isocyanurate foam which produced about thirty times more HCN in air than in nitrogen and with one of the PAPI based foams which produced 11.5 mg/g HCN when decomposed in air and only 0.23 mg/g HCN when decomposed in nitrogen. TDI-based foams, however, did not follow this pattern, i.e., about the same amount of HCN (0.5 mg/g) was generated in air and in nitrogen [19].

The dependence of HCN generation on the chemical formulation of the foam is also suggested by the results of Gaskill [20], who evaluated smoke development from four rigid polyurethanes decomposed under flaming (2.5 W/cm^2), non-ventilated conditions in the NBS Smoke Chamber. Colorimetric tubes[3] were used to determine the approximate quantities of HCN and CO produced (Table 7). The highest levels of HCN, 100 ppm, were generated from the non-fire retarded PAPI-ester based foam and the fire retarded MDI-sucrose based foam. Similar to the results of Ashida, Gaskill observed that two other fire retarded PAPI foams produced considerably less HCN (10 and 32 ppm) than the non-fire retarded PAPI foam. The production of CO followed the general pattern of HCN evolution. In one case, involving the fire retarded PAPI-ether/fluorocarbon foam, HCl was detected, an indication that the blowing agent and possibly the fire retardant was halogenated [20].

Evolution of HCN does not only depend on the atmosphere and the chemical formulation but also on the temperature of decomposition. Michal [17] conducted a systematic study of HCN concentrations generated from commercial polymeric materials (including a rigid polyurethane insulation foam) which were pyrolyzed under oxidative conditions at controlled temperatures ranging from 600 to 1200°C. The results in nitrogen atmospheres were described in Section 2.1.3. In air, the yields of HCN were as follows: 15.8 mg/g at 600°C, 7.4 mg/g at 800°C, 33.9 mg/g at 1000°C, and 48.1 mg/g at 1200°C. With the exception of 800°C, it appears that increasing temperatures produce increasing amounts of HCN. However, when compared to the results in nitrogen atmospheres, more HCN is generated in air at 600°C, about the same amount is produced at 800°C, and less is found at the higher temperatures. These results at 600°C showing an increased evolution of HCN in air than in nitrogen agree with results of Ashida et al. at 500°C [19].

Michal's results [17] indicate that the HCN evolution in air increases as the temperature increases from 800 to 1200°C, whereas Ashida found that the HCN evolution in air peaked at 500°C. However, since the highest decomposition temperature examined by Ashida et al. was 700°C, they would not have observed the increase in HCN evolution shown by Michal at the higher temperatures.

NO_x, in addition to HCN, CO, and CO_2, has been detected in experiments involving the flaming combustion of rigid polyurethane foam. The change from pyrolysis to flaming combustion may convert the nitrogen-containing decomposition products to nitrogen oxides. This reaction, which occurs especially under high O_2 conditions, has been demonstrated in combustion studies on HCN, acetonitrile, and acrylonitrile using a hydrogen diffusion flame [23]. To evaluate the thermal performance of rigid polyurethane foam, Herrington [24] used the Ohio State University heat release rate apparatus, (this instrument was not designed to simulate a real fire but rather to generate data for illustration and comparison purposes only). The generation rates of NO_x, HCN, CO, and total hydrocarbons and the times to the maximum generation rate were measured when a rigid polyurethane boardstock was exposed to a heat flux of 1 W/cm^2 and a 0.18 kW ignition source (Table 8). During these experiments, this foam ignited about 9 seconds after exposure. This was approximately the time of the maximum generation rate of the volatile organic compounds. The maximum rate of generation of the CO and CO_2 came later during the flaming combustion. The maximum generation rate for NO_x was about three times more than that for HCN, both of which occurred during flaming mode about 12 to 13 seconds into the test.

Ball et al. [25,26] compared the production of the toxicants, NO_x, CO, and HCN, in both room and building tests in which an isocyanate based rigid foam was thermally decomposed. The room tests were conducted by burning paper-covered foam slabs in a 25 m^3 room. Volatile gases were measured with Draeger tubes[3]. The average gas concentrations found in the room after 20 minutes were 225 ppm for CO, 20 ppm for HCN, and 5 ppm for NO_x. These concentrations were similar to those measured during large-scale tests conducted in buildings constructed with panels in which rigid polyurethane foam was sandwiched between steel facings. In these tests, the average concentrations were 100 ppm for CO, 7 ppm for HCN, and 8 ppm for NO_x. Ball et al. compared these results to concentrations designated by Sax [27] as dangerous to man in 30 to 60 minutes (CO:1000-1200 ppm, HCN:100-200 ppm, NO_x:100-150 ppm) and concluded, in spite of the fact that none of these gases reached dangerous levels, that CO is probably the only toxic combustion product of concern from rigid polyurethane foam.

2.2.1.2 Detailed Chemical Profiles

The thermal degradation of rigid polyurethane generates a great variety of compounds, in addition to the commonly recognized toxicants HCN, CO, and NO_x. Because of the known complexity of these other combustion products, the analytical techniques and sampling procedures are more sophisticated than the required routine instrumentation used to collect the information on the more common toxic combustion products.

A flame-retarded rigid polyurethane foam was burned under flaming conditions in a 23 m^3 room and the combustion products were analyzed by MS and IR [26]. The following organic compounds were detected: aniline, toluidine, dichlorobenzene, trichlorofluoromethane, carbon tetrachloride, ethanol, acetamide, and ammonia. The presence of toluene, benzene, methane, and acetone was also suggested by these analytical techniques. The concentration of the primary amines in the combustion atmosphere was estimated to be 4 ppm; the amounts of the other gases were not quantified.

During their studies of hazards generated in underground mines, Paciorek et al. [28] and Hartstein and Forshey [29] analyzed the toxic products produced when synthetic materials overheat or burn. In their first series of experiments, commercial samples of rigid polyurethane were decomposed in a "stagnation" burner arrangement through which preheated air was passed. These conditions were designed to simulate oxidative pyrolysis and combustion. Gas samples were collected and analyzed by GC, MS, and IR. Because of condensation in the ampoules during sampling, only a few volatiles, such as CO_2, CO, HCl, trichlorofluoromethane, ethylene, propylene, propane, and acetylene were detected [28,29].

In a second series of experiments, Hartstein and Forshey decomposed two MDI type rigid polyurethane samples under static conditions in a glass reaction vessel at 365 to 370°C [30]. The sampling technique was improved to include analyses of condensible compounds. In addition to GC, MS, and IR techniques, wet chemical procedures were used for measuring Cl^-, CN^- and NH_3. With these sampling techniques, no CO and only traces of HCN were detected. The major fractions of the detected volatiles were oxygenated and halogenated compounds. The main toxic component was aniline. Also found were the toxic compounds chloroethanol and chloroisopropanol. The other products identified in these experiments are listed in Table 1 in conjunction with reference 30.

2.2.1.3 Effects of Blowing Agents

Evidence of the blowing agent used in the formulation of the foam is usually observed in the degradation products [6,14,15,26,28,29,30]. In some studies, the blowing agent, such as trichlorofluoromethane (FREON 11), was detected unchanged. In other cases, thermal degradation products of the blowing agent itself, such as -CF and HCl have also been detected [10,20,30].

In the course of evaluating the fire performance of structural foam materials, Lee et al. decomposed a specially fabricated rigid polyurethane foam in which 1,2-dibromotetrafluoroethane (HALON 2402) was used as the blowing agent [31]. In the NBS smoke chamber, the rigid polyurethane foam was subjected to a heat flux of 2.5 W/cm^2 with and without a pilot flame for flaming and non-flaming degradation, respectively. Colorimetric tubes[3] were used for measuring the primary toxic combustion products - CO, HCN, NO_x, HBr, and HF. The average concentration of all the products was higher in the flaming mode than in the non-flaming mode. For example, in one case, the average concentrations of HBr and HF were 40 ppm and 30 ppm in the flaming mode and 22 ppm and 3 ppm in the non-flaming mode. As HBr and HF are compounds of toxicological concern, the contribution of the blowing agent to the toxicity of the fire atmosphere generated by the thermal degradation of rigid polyurethane foam must be considered.

2.2.1.4 Fire Retardants

The addition of fire retardants to the polyurethane formulations will also influence the composition of the thermal degradation products. An untreated foam produced more HCN than a PAPI foam treated with either a reactive fire retardant (FYROL 6[4]) or an additive fire retardant [tris-(2-chloroethyl)phosphate] when thermally decomposed [19]. Phosphorus compounds were detected in the combustion products of fire retarded rigid polyurethane foams decomposed in air or in nitrogen [10]. The additive type fire retardant, trichloroethyl phosphate[5], evolved unchanged from the foam when heated at low temperatures (160 to 180°C) [10].

The research which is probably most responsible for the inception of the field of fire toxicology as known today concerned the acute inhalation toxicity of the nonflaming combustion products from a laboratory-formulated PAPI/propoxylated trimethylolpropane rigid foam containing the reactive fire retardant 0,0-diethyl-N,N-bis-(2-hydroxyethyl)aminomethyl phosphonate [32]. Convulsions were observed in rats exposed to these combustion products. After extensive analytical studies using GC, NMR, and CIMS techniques, a highly toxic bicyclic phosphate ester was detected and identified as 4-ethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2] octane-1-oxide. It was postulated that this bicyclic phosphate ester was formed by the reaction of the fire retardant and trimethylolpropane, one of the thermal degradation products [33]. The formation of this bicyclic phosphate ester was also observed by Woolley and Fardell in the combustion products from flexible and rigid polyurethane foams and from isocyanurates commercially produced in England until 1974/75 [34]. They found that decomposition of the foams in a tube furnace at 500°C produced up to 0.03 mg of the highly toxic bicyclic phosphate ester per gram of foam. Foams of this composition are no longer manufactured in England. (For additional details on the toxicity of this fire retarded foam, see section 3.7.3.)

2.2.2 Particulate Combustion Products

Some of the complex organic compounds generated during flaming or non-flaming combustion do not remain as gaseous products in the fire atmosphere but condense onto smoke particulates. Because of their potential toxic nature, the identity of these compounds is also important. However, only one study has been performed on smoke particulates from a rigid polyurethane foam [35]. Joseph and Browner thermally decomposed a foam under smoldering conditions and identified many compounds in the particulate fraction of the smoke. They used a complex scheme of chemical extractions and washes of the smoke particulates, separations by liquid chromatography, and analysis by GC/MS. They found many compounds not usually observed in the volatile fraction, e.g., aromatic amines and urethanes (expected from the basic decomposition steps shown in equations 4 and 5), 4,4-diaminodiphenylmethane compounds and benzoquinolines, polycyclic hydrocarbons, nitrogen-containing five-membered ring compounds, including indoles, isoxazole, indazole and carbazoles, diphenylamine and its alkyl derivatives, phthalate esters, glycol homologues, and trimethylindole (Table 1). This study indicates the importance of the particulate fraction of the smoke in the examination of the thermal decomposition products from materials and points out the extremely complex nature of those products.

3. TOXICOLOGY

Bioassay methods, which expose animals to smoke and toxic gases from the thermal decomposition of materials, have been used most frequently for assessing the acute toxicity of fire atmospheres. In most of these tests, lethality or incapacitation serve as the biological endpoints; however, more elaborate methods involving various physiological and biochemical parameters have also been used. Most procedures include the chemical analyses of specific toxicants of interest in addition to the animal exposures. Some early approaches have suggested the use of only the results from the chemical analyses of specific toxicants. For example, Tsuchiya and Sumi have proposed a "maximum toxicity index" (T_m) to evaluate the potential danger from toxic gases produced by combustion of materials [22]. The mathematical model proposed is $T = \Sigma \frac{C_e}{C_f}$ where T = toxicity index, C_e = experimental concentration from a 1 g sample in a 1 m^3 volume, and C_f = concentration dangerous or fatal to humans in 30 minutes. T_m is the maximum value of T (toxicity index) obtained from experimental data. When samples of rigid polyurethane foam were burned at 800°C in a glass flask, the production of HCN was found to be constant (8 mg/g) for sample sizes ranging from 0.4 to 2.4 g, whereas CO and CO_2 concentrations decreased with increasing sample size from 210 to 90 mg/g and 1400 to 280 mg/g, respectively [21]. Using their toxicity index model, Sumi and Tsuchiya found that the maximum toxicity indexes were 0.05 for HCN and CO, and < 0.01 for CO_2 at 800°C. Based on these calculations, they estimated that when rigid polyurethane was burned, the same level of toxicity resulted from HCN and CO. Toxicity due to CO_2 was considered negligible. By Sumi's model, rigid polyurethane has a total toxicity index of 0.10, which is several times smaller than that of other nitrogen-containing materials such as acrylic, nylon, wool, and urea-formaldehyde, but is very close to that of polystyrene and white pine. Such an approach has been considered less reliable than animal data because of the potential additive or synergistic effects of the toxicants and/or the possibility that unusual toxic products could be generated and would not be measured with routine chemical analyses.

The various toxicity test methods have been reviewed in detail by Kaplan et al. [36]. The main approaches employed to evaluate the acute inhalation toxicity of combustion products generated from rigid polyurethane foam are summarized below.

Biological Endpoints

	Lethality			Incapacitation		Physiological and Biochemical Parameters
Method	LC_{50}	No. Animals Affected	Time to Death	EC_{50}	Time to Incapacitation	
NBS[a]	x			x		
UTAH[b]	x			x		
PITT[c]	x	x	x	x		x
DIN[d]	x	x			x	x
JAPAN[e]			x		x	
USF[f]			x		x	

[a] National Bureau of Standards
[b] University of Utah
[c] University of Pittsburgh
[d] Method developed in response to the German Commission of Standards
[e] Methods used by Japanese workers
[f] University of San Francisco

3.1 National Bureau of Standards (NBS) Toxicity Test Method

The toxicities of the thermal degradation products from polymeric materials, including rigid polyurethane foams, have been evaluated by a number of laboratories using the NBS toxicity test method [37, 38]. This test method consists of three components: a combustion system, a chemical analytical system, and an animal exposure system. The material in question is thermally decomposed in a 1000 ml cup furnace which is preheated to a temperature either

25°C below the material's autoignition temperature (non-flaming decompostion) or 25°C above the material's autoignition temperature (flaming combustion). These two conditions, the non-flaming and flaming modes at temperatures close to the autoignition temperature, are considered worst cases but still realistic fire conditions. Testing materials under worst case conditions prevents false negative data. In this case, a false negative result would be one where the conditions are not optimized to produce the maximum quantity of toxic materials.

All of the combustion products generated in the cup furnace go directly into the 200 liter rectangular exposure chamber and remain there (static exposure) for the duration of the exposure. Carbon monoxide, carbon dioxide, and oxygen concentrations are monitored continuously, as are the furnace and chamber temperatures. If the material contains nitrogen, hydrogen cyanide may also be measured.

Six rats are exposed head-only to the combustion atmospheres in each experiment. Blood samples are taken from two of the six animals to monitor the amount of carbon monoxide adsorbed in the blood. Animals are exposed to the combustion atmospheres for 30 minutes and then observed during a 14 day post-exposure period. The biological endpoint is the determination of the LC_{50} - the concentration of material in mg/ℓ that causes 50% of the animals to die in the 30 minute exposure and 14 day post-exposure observation period. In this case, concentration is defined as the mass of material (grams) placed in the cup furnace divided by the volume of the exposure chamber (liters). The LC_{50} may also be calculated based on mass consumed per chamber volume. The amount of material consumed is obtained simply by weighing the cup before and after the 30 minute exposure. The post-exposure observation period is a very important feature of the NBS toxicity test method since the combustion products from many of the tested materials have been found to cause extensive animal weight loss and death during this post-exposure period.

The toxicity of the combustion products from the rigid polyurethane foam designated GM 29 or GM 30 obtained from the Products Research Committee (PRC) [39] has been studied by NBS and two other laboratories which participated in an interlaboratory evaluation (ILE) of the NBS toxicity test method (Table 9) [38]. GM 30 is based on a polymeric isocyanate formulation and differs from GM 29 (samples of which were used by Alarie et al. [45,49,50] and Farrar et al. [43] in their toxicological studies, Section 3.2 and 3.3) only in the sample sizes distributed for testing.

GM 30 appears to be more toxic in the flaming mode with LC_{50} (30 min + 14 day) values averaging about 12 mg/ℓ compared to more than 34 mg/ℓ found in the non-flaming mode. (The results of the flaming experiments by Lab 4 shown in Table 9 did not agree with those of the other laboratories.) In the non-flaming mode, no deaths were observed at the highest sample loadings tested (more than 39 mg/ℓ).

When compared to Douglas fir and flexible polyurethane foam tested by the NBS test method (see table below), flaming rigid polyurethane foam GM 30 was the most toxic [i.e., the LC_{50} (30 min + 14 day) value of rigid polyurethane is 13.3 mg/ℓ, whereas, the LC_{50} of Douglas fir is 40 mg/ℓ and that of flexible polyurethane foam GM 21 is greater than 40 mg/ℓ]. In the non-flaming mode, the pyrolysis products of rigid polyurethane foam are less toxic than those of

Douglas fir or flexible polyurethane foam whose LC_{50} (30 min + 14 day) values are 23 and 27 mg/ℓ, respectively. These values are, however, less than an order of magnitude different which is not considered toxicologically significant.

	LC_{50} (30 min + 14 days)	
	Flaming (mg/ℓ)	Non-Flaming (mg/ℓ)
GM 30	13.3	>39.6
Douglas Fir	39.8	22.8
GM 21	>39.6	26.6

One of the ILE participating laboratories (No. 8) also used the hind-leg flexion behavioral avoidance response model [37,40] to monitor incapacitation and determined EC_{50} values (the concentration necessary to incapacitate 50% of the rats during the 30 minute exposures). The results shown in Table 9 indicate that this form of incapacitation occurs at only slightly lower sample loadings of GM 30 than that necessary to cause lethality [37,38].

Table 10 shows that the percent carboxyhemoglobin (COHb) from exposures to 30 minute LC_{50} concentrations of flaming GM 30 was 64% and the average concentrations of CO and HCN in the exposure chamber atmosphere were 1800 ppm and 140 ppm, respectively. In the non-flaming mode, the LC_{50} value was greater than 40 mg/ℓ (i.e., no animals died at concentrations $\leq$ 40 mg/ℓ) and therefore, the LC_{50} gas concentrations are listed as greater than 1700 ppm and 44 ppm for CO and HCN, respectively. Experiments at NBS on the toxicity of CO in air have shown that 4600 ppm of CO are necessary to kill 50% of the rats in

30 minutes [41]. This atmospheric CO concentration results in an average blood concentration of 84% COHb. In the case of rigid polyurethane foam GM 30 in the flaming mode, deaths were observed during the exposure at less than lethal levels of CO (i.e., the CO concentration was only 1800 ppm and the COHb was 64%). These results suggest that CO was not the sole cause of death.

Levin et al. have observed that a mixture of CO and HCN act in an additive fashion, such that if $\frac{[CO]}{LC_{50}\ CO} + \frac{[HCN]}{LC_{50}\ HCN} \geq 1$, the animals will die [41]. This formula indicates that the CO and HCN concentrations generated at the LC_{50} value of flaming rigid polyurethane (i.e., $\frac{1800\text{ ppm CO}}{4600\text{ ppm CO}} + \frac{140\text{ ppm HCN}}{160\text{ ppm HCN}}$), would be sufficient to account for the deaths. Therefore, these results strongly suggest that the deaths that occurred from flaming rigid polyurethane GM 30 were due to the combination of CO and HCN.

The toxicity of combustion products generated in the flaming mode from a sample of rigid polyurethane foam of unknown composition originating from a jail fire in which 27 people died of smoke inhalation has been tested by Levin et al. [42]. The LC_{50} (30 min + 14 days) value for this material decomposed under flaming conditions was 11 mg/ℓ with 95% confidence limits of 10 to 12 mg/ℓ. This LC_{50} value is comparable to that found for rigid polyurethane foam GM 30 (14.3 mg/ℓ) exposed to the same conditions [37]. When a sample loading of the jail material equivalent to a concentration of 11 mg/ℓ was tested, the average concentrations of CO and HCN were 1160 ppm and 115 ppm, respectively. The concentrations of these two toxicants are similar to those found in the GM 30 experiments [37]. According to the NBS studies quoted above [41] on the interaction of CO and HCN, these two gases were produced in concentrations sufficient to account for the lethalities observed in the jail fire.

3.2 University of Utah Toxicity Test Method

During the development of a protocol to assess the toxicity of combustion products, Farrar et al. evaluated a series of cellular plastics including the rigid polyurethane foams GM 29, GM 31, GM 35, GM 37, and GM 39 from the PRC collection [43]. This toxicity test method and apparatus upon which the NBS method was largely based differed from that of NBS in that the University of Utah test utilized a 60 liter instead of the 200 liter NBS exposure chamber and used an aluminum cone coated with polytetrafluoroethylene above the cup furnace to aid in the mixing of gases in the exposure chamber.

The toxicological endpoints were death and incapacitation (determined by monitoring the hind-leg flexion behavioral avoidance response [37, 40]). EC_{50} values were calculated for the 30 minute exposures and LC_{50} values were calculated from the deaths that occurred during the 30 minute exposures and 14 day post-exposure periods (Table 11).

Most of these rigid polyurethane foams were more toxic in the flaming mode [LC_{50} (30 min + 14 day values) ranged from 10.9 to 16.6 mg/ℓ] than in the non-flaming mode [LC_{50} (30 min + 14 day values) were greater than 36.7 mg/ℓ in all cases except for the rigid spray foam formulation GM 39 which had an LC_{50} value of 10.9 mg/ℓ]. The presence of an unspecified fire retardant (GM 31) did not affect the LC_{50} values. Total mortality, which included the 14 day post-exposure deaths, was very close to the exposure lethality for the rigid polyurethanes studied.

According to the data of Farrar et al., incapacitation (EC_{50}) occurred at about the same mass loading per chamber volume (mg/ℓ) for all the tested rigid polyurethane foams regardless of the combustion mode (flaming or non-flaming) (Table 11). However, in the interlaboratory evaluation of the NBS toxicity test method in which seven laboratories examined twelve materials, the EC_{50} results from the University of Utah were always lower than those found by the other laboratories who examined the same materials [38]. This may indicate that another factor in addition to the toxic insult was affecting the incapacitation data. One possible explanation is that the intensity of the shock to which the animals would respond was set too low. When the animals became stressed by low concentrations of toxic atmospheres, they would fail to respond to the electrical shock and appeared incapacitated when, in actuality, they were not.

Comparison of the LC_{50} values of these rigid polyurethanes with the corresponding values found by Farrar et al. for Douglas fir reveals that the rigid polyurethanes are about twice as toxic in the flaming mode and less toxic in the non-flaming mode than Douglas fir [43] (see below). In the same study, LC_{50} (30 min and 14 day) values for various flexible polyurethane foams indicate that they were similar or less toxic than the Douglas fir.

Material	LC_{50} (30 min + 14 days) Flaming (mg/ℓ)	 Non-Flaming (mg/ℓ)
Rigid Polyurethane		
GM 21	11.2	>40
GM 31/FR	14.2	>40
GM 35	12.1	>36.7
GM 37	10.9	>36.7
GM 39*	16.6	10.9
Douglas Fir	24.6	14.6
Flexible Polyurethane		
GM 21	43.2	13.4
GM 23/FR	34.5	12.6
GM 25	>37.5	36.9
GM 27/FR	33.1	30.5

*foam spray on asbestos cement board
FR: fire retardant

To evaluate the extent to which the CO and HCN concentrations in the combustion atmospheres generated from the rigid polyurethane foams contributed to the toxicity of the combustion products, the calculated levels of CO and HCN at the EC_{50} and LC_{50} (30 min + 14 days) concentrations in the flaming mode (the most toxic conditions) are shown in Table 12. Based on the studies at NBS on the toxic interactions of CO and HCN, the LC_{50}'s observed with all the foams can be attributed to the toxic interaction of CO and HCN [41].

At the University of Utah, Hartzell et al. showed that exposure of rats to CO alone at concentrations greater than 1500 ppm for 30 minutes caused incapacitation as indicated by the loss of the hind-leg flexion behavioral avoidance response [44]. Corresponding studies have shown that HCN alone at concentrations greater than 60 ppm for 30 minutes will also produce incapacitation. The CO and HCN levels in Table 12 range from 610 to 910 ppm and 40 to

70 ppm, respectively, at the EC_{50} concentrations. With three of the five rigid polyurethane foams, GM 29, 31 and 35, the HCN levels alone were sufficient to explain the incapacitation. In the other two cases, the CO probably played a contributory role.

At the EC_{50} concentrations, the CO and HCN levels in the non-flaming mode (690 to 850 ppm and 40 to 75 ppm, respectively) are similar to the levels in the flaming mode (Table 12) [43]. This is reflected in the closeness of the EC_{50} values in the two modes of combustion.

3.3 University of Pittsburgh Toxicity Test Method

The toxicity of the thermal degradation products from eight different rigid polyurethane foams have been evaluated with the University of Pittsburgh test method [45,47,48,49]. This method is described in detail by both Alarie et al. [45] and Kaplan et al. [36]. Briefly, this method uses a dynamic flow system in which materials are decomposed at a steadily increasing temperature of 20°C/min in a Lindberg furnace. The material is allowed to decompose initially in a non-flaming mode and to flame when the ignition temperature is reached. The decomposition products are fed into a glass exposure chamber (2.3 ℓ) in which four mice are exposed in the head-only mode. An airflow of 11 ℓ/min which is maintained through the furnace is further diluted with cold air resulting in a 20 ℓ/min air flow through the exposure chamber. Whole body plethysmographs are used to measure the respiration rate of the mice. For determination of sensory irritation, 10-minute exposures are used; for all other biological endpoint determinations, 10 or 30-minute exposures are used.

This method proposes the use of any of three biological endpoints, all of which are based on the amount of material placed into the furnace:

(1) Sensory irritation from which an RD_{50} is calculated. The RD_{50} corresponds to the concentration of smoke which produces a 50% decrease in the respiration rate of the animals.

(2) Lethality from which the LC_{50} (the concentration of smoke which causes 50% of the animals to die during the 30 minute exposure and a 10 minute post-exposure period) is calculated.

(3) Physiological stress from which a "Sensory Irritation Stress Index" (SI) is calculated [46]. SI values are calculated by a mathematical approximation which represents the onset, recovery, and degree of depression of the respiratory rate and includes the corresponding physiological adjustments, e.g. blood pressure and heart rate. The SI 100 corresponds to a sample size which produces a 50% decrease in the stress index (maximum value for SI in these experiments was found to be about 200).

The sensory irritation produced by the combustion products from two rigid polyurethane foams, based on polymeric isocyanate and polyether polyol (from sucrose) formulations was examined by Alarie et al. [47]. One of the two samples contained the fire retardant tris (beta chloroethyl) phosphate. In this early version of the University of Pittsburgh test method, the furnace was heated at 25°C/min and the combustion products generated in the furnace were pumped through the exposure chamber with an air flow rate that could be varied from 2 to 100 ℓ/min. The concentration of the decomposition products was changed by varying the amount of dilution air. The respiratory rates of the mice were monitored during the exposures which lasted five minutes beyond the time that the visible smoke from degradation of the samples disappeared. The calculated RD_{50} values for the two rigid polyurethane foams were 408 mg (not fire retarded) and 588 mg (fire retarded). These two RD_{50} values were not considered statistically different at a 0.05 level of significance. However, when compared to the the RD_{50} values found in the same study for a flexible polyurethane foam with and without a fire retardant, the rigid polyurethane foams were found to be significantly higher and, therefore, considerably less irritating than the flexible foams (data shown below).

	RD_{50} (mg)	
Polyurethane	FR[a]	NFR[b]
Rigid	588	408
Flexible	17	27

[a] Fire retarded.
[b] Non-fire retarded.

The combustion atmospheres from both of these rigid foams were examined by GC and MS and the following volatile compounds were identified: acetaldehyde, HCN, ethane, propylene, toluene monoisocyanate, propane, ethylene oxide, propylene oxide, acetone, and formamide. The fire-retarded foam also produced butyraldehyde. These decomposition products represent chemical asphyxiants and sensory irritants. Toluene monoisocyanate was believed to be one of the major irritants [47].

The effect of another type of additive, zinc ferrocyanide, on the toxicity of a rigid polyurethane foam was studied using the version of the University of Pittsburgh test method described on p. 34 [48]. LC_{50} values were determined for a 10 minute exposure plus a 5 minute post-exposure period. Two samples of rigid polyurethane foam ("PU", untreated; "PU-A", 5% zinc ferrocyanide) were examined. The LC_{50} values (10 min + 5 min post-exposure) were found to be greater than 64 grams (> 320 mg/ℓ)[6] for the "PU" sample and 26.2 grams (131 mg/ℓ) with 95% confidence limits of 22.1 to 31.1 grams for sample "PU-A". These LC_{50} values suggest that the foam treated with zinc ferrocyanide was more than twice as toxic as the untreated foam. When compared to other materials tested under these experimental conditions, the rigid polyurethane foams were significantly more toxic than Douglas fir, which had a 10 minute LC_{50} value greater than 460 g (> 2300 mg/ℓ), and less toxic by at least an order of magnitude than a polychloroprene containing 5% zinc ferrocyanide, which had a 10 minute LC_{50} value of 2.5 grams (12.5 mg/ℓ). A flexible polyurethane foam tested under the same conditions was found to have a 10 minute LC_{50} value of greater than 100 grams (> 500 mg/ℓ) indicating a lower toxicity than the untreated rigid polyurethane.

Using the University of Pittsburgh test method, Anderson et al. also evaluated the sensory irritant properties and the stress index of four rigid polyurethane foam samples from the PRC collection (GM 29, GM 31, GM 35, and GM 37) [49]. All these foams were based on polymeric isocyanate formulations.

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[6] Alarie reports his toxicological results in grams of material. For comparison purposes the gram units have been converted to mg/ℓ units by the following equation:

$$\frac{\text{wt (g)}}{\text{chamber air flow rate } (\ell/\text{min}) \times \text{exposure time (min)}} \times 1000 \text{ mg/g}$$

Fluorocarbons were used as blowing agents except for GM 37, in which the blowing agent was CO_2. GM 31 contained an unspecified fire retardant.

In these experiments, the air flow through the furnace was 7.5 ℓ/min through the furnace. Dilution air was added at a rate of 12.5 ℓ/min to maintain an overall air flow of 20 ℓ/min through the exposure chamber. RD_{50} values were based on the respiratory rates of mice exposed for 10 minutes and followed by a 5 minute recovery period. Stress index determinations were based on mice exposed for 30 minutes followed by a 10 minute recovery period. The RD_{50} values, summarized in Table 13, show no difference in the rigid polyurethane foams studied. The sensory irritant quality of these foams based on their RD_{50} values is comparable to that of Douglas fir (RD_{50}, 0.14 mg/ℓ). However, the RD_{50} values of four flexible polyurethane foams decomposed under the same conditions were in the range of 0.018 to 0.044 mg/ℓ, an order of magnitude more toxic and a difference of considerable importance. Evaluation of the materials based on the stress index measure placed the four rigid foams into a high stress index category, whereas Douglas fir was considered moderate and the flexible polyurethanes were considered low [49].

Further experimental work on the same rigid polyurethane foams, GM 29, GM 31, GM 35, and GM 37, used a slightly higher ventilating condition (an air flow of 11 ℓ/min through the furnace) although the total air flow through the system was still the same (20 ℓ/min) [45]. In addition to sensory irritation and evaluation of the stress index, acute mortality (as determined by LC_{50} values for 30 minute exposures followed by 10 minute recovery times), asphyxiation, and histopathology were also examined. Under these experimental conditions, the rigid polyurethane foams started to decompose at about 200°C.

Foams GM 29, GM 31, and GM 35 never flamed, whereas foam GM 37 ignited for a short duration in the 450 to 500°C range. The CO and HCN were released monophasically with peaks occurring about 500 to 525°C.

The RD_{50} values for the four rigid foams ranged between 0.085 and 0.124 grams (0.42 - 0.62 mg/ℓ) (Table 14) [45]. When compared to the corresponding RD_{50} values obtained by Anderson et al. [49] (Table 13), it appears that all the foams are about half as irritating (based on respiratory rate depression) when thermally decomposed with increased ventilation. The RD_{50} value for Douglas fir under the same conditions of increased ventilation was 0.034 g or 0.17 mg/ℓ which was 2.5 to 3.5 times more toxic than those observed for the four rigid foams [45]. The RD_{50} values for flexible polyurethane foams were an order of magnitude lower than the rigid foams. However, the sensory irritating effects occurred faster for rigid polyurethane foams than for Douglas fir and the flexible polyurethane foams. The resulting stress index values in rigid foams were in the SI 100 = 0.5 to 0.9 grams or 0.83 to 1.5 mg/ℓ range, which indicates more stress than that found for Douglas fir (SI 100 = 4.0 g or 6.7 mg/ℓ or for flexible polyurethane foams (SI 100 = 1.3 to 2 g or 2.16 mg/ℓ to 3.3 mg/ℓ) [45].

The LC_{50} values calculated from the lethality results following a 30 minute exposure to the combustion products from these rigid polyurethane foams and a 10 minute recovery period ranged from 7.5 to 10.4 grams (12.5 to 17.3 mg/ℓ) (Table 14). These LC_{50} values were comparable to those found for flexible polyurethane foams [LC_{50} = 8.3 to 14.4 g (13.8 to 24.0 mg/ℓ)] [45]. Douglas fir, in comparison, was considerably less toxic with an LC_{50} value of 63.8 grams (106.3 mg/ℓ) [45]. Asphyxiation due to rigid polyurethane foams occurred at concentrations which ranged from 2 to 8 g (3.3 to 13.3 mg/ℓ).

Histopathological studies, conducted on the animals 24 hours after the 30 minute exposures to the thermal decomposition products of these rigid polyurethane foams showed various degrees of tissue damage in the noses, corneas, lungs, and hearts.

In summary, the results of these University of Pittsburgh studies showed that the thermal decomposition products from the rigid polyurethane foams, GM 29, GM 31, GM 35, and GM 37, were more toxic than wood on the basis of acute mortality (LC_{50} values) and physiological stress (SI 100), and less toxic than wood on the basis of sensory irritation (RD_{50}).

Alarie [45] has also attempted to address the acute lethal hazard (ALH) of materials by taking into consideration LC_{50} values, physical properties, such as the thermal conductivity and density, and the temperature at which the materials lose 1% of their weight. Although through this mathematical approach Alarie recognizes that the evaluation of the fire safety of any material must consider other factors in addition to acute toxicity, this approach does not address many of the other chemical and environmental factors which are necessary to consider in a hazard assessment. Using his simple ALH, Alarie compared rigid polyurethane foams to a glass fiber used for insulation purposes. Rigid foams GM 35 and GM 37 were classified as more hazardous than the glass fiber and foams GM 29 and GM 31 as similar to this glass fiber [45].

Alarie has also proposed a classification of materials based on time-response and concentration-response relationships. The calculated LT_{50} values (the time at which 50% of the animals die after being exposed to concentrations equivalent to the LC_{50} value for 30 minutes) for the four rigid polyurethane foams were as follows: 28 minutes (GM 29), 23 minutes (GM 31), 17 minutes (GM 35), and 15 minutes (GM 37) [50]. Using this combination of concentration- and time-response (LCT_{50}), Alarie et al. showed that all four of these rigid foams fall into the "more toxic than wood" category [50].

3.4 DIN Toxicity Test Method

The toxicity of combustion products from many materials, including rigid polyurethane foams, has been evaluated by a number of investigators using several variations of the DIN method. This toxicity test method (designated as DIN-Draft 53436) is based on dynamic exposure of rats to decomposition products generated in the pyrolysis mode in a quartz tube which is heated by an externally moving (10 mm/min) electric oven. Samples of equal volume or equal weight per unit length are heated at constant temperatures between 200°C and 600°C in an air stream, which flows countercurrent to the movement of the oven. The decomposition products are diluted with air and introduced into the animal exposure chamber (of various designs) to permit head-only or whole body exposures. Rats usually are exposed for 30 minutes. Toxicity is expressed as mortality (number of animals affected) which in turn can be related to temperature, airflow, and mass loss, which either fail to produce lethal concentrations or produce an animal mortality of 50 percent (LC_{50}). The endpoints used to interpret mortality data under the stated test conditions are:

T_c(°C): the temperature which just fails to produce lethalities (critical temperature)

$C_c(g/\ell)$: the decomposition gas concentration which just fails to be lethal (critical concentration)

$D_c(\ell)$: the air dilution factor which just fails to provide a lethal concentration (critical dilution)

$T(LC_{50})(°C)$: the temperature at which 50 percent mortality occurs

$D_{600}(LC_{50})(\ell/h)$: the decomposition product dilution which produces 50 percent mortality at 600°C

$C_{600}(LC_{50})(g/\ell)$: the decomposition product concentration which produces 50 percent mortality at 600°C

A detailed description of the apparatus and the application of various endpoints has been summarized by Kaplan et al. [36].

Kimmerle has evaluated the results from toxicity studies of various materials including rigid polyurethanes using the DIN toxicity test method - Draft 53436 version [51]. In one of these studies, Effenberg measured the acute toxicity of the thermal degradation products of a fire retarded rigid polyurethane foam which was decomposed at 500°C in a specified tube furnace supplied with air at a rate of 300 ℓ/h. The biological endpoints used to assess the toxicity of the combustion products were death of the rats, which were exposed for 30 minutes in a whole body mode, the COHb at death, and the amount of time that the rats were able to swim before drowning. The pyrolysis gases from the thermal decomposition of a rigid polyurethane (sample size:

100 x 15 x 2 mm) contained 650 ppm CO and 48 ppm HCN. Ten percent (5/50) of the rats died during the exposure. The COHb level was found to be 24.3%. The swimming time corresponded to 47 minutes for the rats that survived the exposure as compared to 93 minutes for the control rats. In similar tests with spruce wood which produced 5125 ppm CO and no HCN, 69/75 of the animals died during the exposure, average COHb levels were 47%, and the average time to drown was 4.2 minutes. The fire retarded polyurethane tested appeared to be less toxic than the spruce wood [51].

The toxicity of pyrolysis products from two fire retarded (reactive and additive type fire retardants) and one non-fire retarded commercial rigid MDI polyurethane foams were evaluated by Kimmerle [51] using the DIN Draft 53436 apparatus. The rigid foam samples were decomposed at temperatures from 300 to 600°C, a temperature range in which mortalities of animals could be expected. Strips of foam, either 300 x 10 x 5 mm in size or 1.2 g per 100 mm in weight, were pyrolyzed in the tube furnace which had an air flow of 100 ℓ/h. The pyrolysis products were further diluted with a 100 ℓ/h air supply. Rats were exposed in a head-only mode for 30 minutes.

Table 15 shows that when standard size strips were pyrolyzed, no mortalities occurred, except in one experiment with sample 3 at 600°C in which 2/20 rats died. In the series of tests in which samples of equal weight were pyrolyzed, deaths were not observed below 400°C. In experiments which produced lethalities, the CO concentrations ranged from 1900 to 4400 ppm and HCN concentrations ranged from 75 to 100 ppm. The lethalities were attributed by Kimmerle mainly to concentrations of CO or HCN or both.

The toxicity produced by the thermal degradation of rigid polyurethane foams was compared to that from a conventional material (spruce wood) tested under equal surface area conditions. The lowest decomposition temperatures at which deaths were observed were 600°C and 350°C for standard size strips of rigid polyurethane (No. 3) and spruce wood, respectively. Based on these results, Kimmerle concluded that the pyrolysis products from these rigid polyurethane foams were less toxic than those of wood [51].

The extent to which rigid polyurethane foams can pose a toxic threat in real fires was further examined by Kimmerle and Prager [52]. In this second study, the effects of variable characteristics of a fire were estimated by varying the concentration of decomposition gases with different air dilutions as well as varying the pyrolysis temperature between 300 and 600°C. Two MDI type polyurethanes ("PUR 1" - non-fire retarded and "PUR 2" - treated with a reactive flame retardant) were used. For "PUR 1", the following toxicological values were determined:

T_c = 400-450°C
T (LC_{50}) = 425°C
D_{600} (LC_{50}) = 1100 ℓ/h
LC_{50} (600°C) = 6.6 mg/ℓ
LC_{50} (500°C) = 7.5 mg/ℓ
LC_{50} (400°C) = 29 mg/ℓ

A comparison of these T_c and T(LC_{50}) values to those of spruce wood [T_c = 350-400°C; T(LC_{50}) = 375°C] suggests that the relative toxicity of decomposition products from "PUR 1" is less than that of wood. However, the

$D_{600}(LC_{50})$ and LC_{50}(600°C) values show that "PUR-1" products produce greater toxicity than those of wood [$D_{600}(LC_{50})$ = 250 ℓ/h; LC_{50}(600°C) = 29 mg/ℓ). The limited amount of toxicity data for the fire retarded polyurethane sample, "PUR-2", did not show conclusively whether the toxicity was influenced by the presence of the fire retardants.

By comparing the toxicological results of rigid polyurethane to those of other nitrogen-containing materials under the same test conditions, Kimmerle and Prager also demonstrated that toxicity is not necessarily dependent on the nitrogen content of the material. For example, both flexible and rigid polyurethane contain about the same amount of nitrogen in the formulations (3 to 6%), but the T (LC_{50}) and $D_{600}(LC_{50})$ values for flexible polyurethanes were found to be about 600°C and 100-300 ℓ/h, respectively, which makes them appear slightly less toxic than rigid polyurethanes. Whereas nylon and wool, which contain about twice as much nitrogen as polyurethanes (11 to 12% and 13 to 14%, respectively) have T (LC_{50}) and $D_{600}(LC_{50})$ values of 500 to 600°C and 100-200 ℓ/h (nylon) and 450 to 500°C and 900 ℓ/h (wool). Thus the hazard based on toxicity of combustion products cannot be evaluated on the basis of chemical composition alone.

Herpol used the DIN method to evaluate the toxicity of the combustion products from fire retarded and non-fire retarded materials, including rigid polyurethane foams [53,55]. These studies were designed to estimate the contribution of toxicity to total fire hazard. In one study, samples of a self-extinguishing rigid polyurethane foam (K14), coated with asbestos on both sides, were degraded at three different temperatures, 400, 600, and 800°C [53]. An air flow of 200 ℓ/h was maintained through the furnace and the combustion products in the exposure chamber were further diluted with an additional air flow of 200 ℓ/h. Rats were exposed in a whole body mode for 30 minutes and lethality (as measured by the cessation of respiration) was the biological endpoint. In the second study, a pair of polyether type polyurethane foams (K5 - not fire retarded and K6 - structurally self-extinguishing) were decomposed at 500, 600, and 700°C [55].

The results from both studies are shown in Table 16. The only lethalities noted for sample K14 occurred at 600°C. For sample K5, deaths occurred at 500 and 700°C, and for sample K6, deaths occurred at all three temperatures. For sample K14, the CO and CO_2 indexes (i.e., integrated concentrations for the test period) at 600°C were 143,430 ppm-min and 30.8 percent-min, respectively. (These values correspond to average concentrations of 4780 ppm CO and 1.03% CO_2 [53].) These results are in agreement with earlier work [54] on mixtures of CO and CO_2 in which Herpol et al. noted that deaths first occurred at a CO index of 120,000 ppm-min and 100% mortality occurred at 210,000 ppm-min. They also found that at a CO_2 index of 75 percent-min, respiration rate increased and reached a maximum at 150 percent-min; at 300 percent-min, inhibition of respiration occurred.

For samples K5 and K6, the CO and CO_2 indexes in experiments causing deaths ranged from 27,300 to 124,800 ppm-min and 57.0 to 162.0 percent-min, respectively. The wide scatter in the production of CO and CO_2 was thought to be caused by the heterogeneous flaming behavior of these materials.

According to Herpol, COHb levels in the blood of the dead animals exposed to the decomposition products from these samples of rigid polyurethane foam appear to be insufficient (42 to 64%) to be the sole cause of the deaths [53,55]. Other toxicants are also contributing to these deaths. Although CO_2, at the levels produced in these experiments, generally acts to increase respiration rates, the effect seen in these studies was an inhibition of respiration, an additional indication of the presence of other toxicants.

To estimate the hazard to life of a material, Herpol proposed the use of the "toxicity index" (TX), which is derived by the mathematical expression:

$$TX = \frac{\Sigma\, k_i m_i}{\Sigma\, k_i}$$

where m_i = observed mortality at time i and k_i = "penalization" factor. A good correlation was shown to exist between TX and LT_{50} values (the time necessary to cause 50% mortality). The TX value for the self-extinguishing rigid polyurethane foam (K14) was 18.00 at 600°C, which places it in the lower 50% of the range of values found for the materials studied [53]. The maximum TX values for the untreated (K5) and self-extinguishing polyurethane foam (K6) were 75.7 (700°C) and 44.4 (500°C), respectively, which are in the upper 50% of the range of values [55]. Foam (K6), however, appeared to be less dangerous than the non-fire retarded polyurethane foam (K5) based on a "global toxicity index" (an expanded mathematical model of the TX developed by Herpol).

A modified version of the DIN 53436 was used by Purser and coworkers to study the incapacitation effects from the thermal decomposition products of a rigid polyurethane foam (whose formulation was based on MDI) [56,57]. The rigid foam was introduced into the tube furnace at a constant rate of

3.2 mm/min and was decomposed in non-flaming mode at 600°C under flow of air (1 ℓ/min). The combustion products were diluted further with air in a mixing chamber. Cynamolgus monkeys were exposed for 30 minutes to various sublethal atmospheric concentrations (supplied to the monkey's face mask via a pneumotachograph). Respiration, electrocardiography (ECG), blood levels of toxic gases, electroencephalography (EEG), and peripheral nerve conduction were monitored. Onset of incapacitation was estimated by changes in various physiological signs. Atmospheres containing concentrations of HCN first caused an increase in respiration followed by a decrease and ultimately semi-consciousness. This was accompanied by a depression of EEG signs, a decrease in heart rate and a change in the ECG waveform.

When 1.83 mg/ℓ of the rigid polyurethane foam was degraded under non-flaming oxidative conditions at 600°C, 1187 ppm CO, 2467 ppm CO_2 and 108 ppm HCN were generated. The average incapacitation time was 23 minutes. The venous blood COHb levels at the end of the 30 minute exposures were in the 17 to 28% range and the blood cyanide levels ranged from 71 to 81 μmol/ℓ (1.8 to 2.1 μg/mℓ) range. A statistically significant relationship was found between the HCN concentration and the time of incapacitation. By comparing the toxicological results produced by the combustion products of rigid polyurethane with those of other materials studied, Purser noted that the toxicological signs were very similar to those produced by pure HCN in air or by the combustion of flexible polyurethane or polyacrylonitrile. Therefore, Purser and coworkers attributed the narcotic and toxic effects produced by the pyrolysis of the rigid polyurethane foam to HCN despite the fact that many other chemical species were also generated.

3.5 Japanese Combustion Toxicity Tests

The Japanese research groups have used various test methods to evaluate the toxicity of combustion products. In most cases, these tests are characterized by dynamic systems and time-based biological endpoints. In this section, the methodology and the results of the experiments that have been used in the evaluation of rigid polyurethane foams will be described.

The toxicity of fire gases from building insulation materials, including rigid polyurethane foams (some of which were fire retarded), was evaluated by Saito [58]. A burning wood crib was used as the ignition source in his combustion chamber. The system was designed to simulate actual fire conditions in a semi-closed room. Three rigid polyurethane PAPI based foams (RF-A, untreated; RF-B, treated with a reactive phosphorus-containing polyol fire retardant; and RF-C, treated with a nonreactive fire retardant tris-2-chloroethyl phosphate), were mounted on one wall and the ceiling and were subjected to the flames and radiation from the burning wood crib. Air was supplied to the combustion chamber at 12 ℓ/min for the first 6 minutes of the experiment. After 6 minutes, the rate of gas evolution from the burning material decreased considerably and the air flow was decreased to prevent dilution of the gas concentrations in the exposure chamber. Mice were placed in rotary cages in a separate exposure chamber and were exposed in the whole body mode to the combustion products for 20 minutes.

The toxicity of the fire gases was evaluated by three indexes: (1) the LT_{50}, the time for 50% of the test animals to become incapacitated as indicated by collapse of the mice, (2) the arithmetic mean incapacitation time

(X), and (3) T_S, the specific gas toxicity which is based on the weight of sample consumed and the collapse time of the animals.

Two sets of experiments were done. In the first series of experiments samples weighed 27 to 28 g and had a surface area of 300 cm^2 and the volume of the exposure chamber was 125 ℓ. The CO concentrations in the exposure box exceeded 10,000 ppm for all three foams. Replicate experiments showed that the evolution rate and maximum concentration of HCN (as measured in the connecting pipe between the combustion and exposure chambers) varied for the three materials: sample RF-A generated 72 to 96 ppm in the first two minutes after which the concentration decreased until it could not be detected at 6 minutes; sample RF-B generated 72 to 130 ppm at 4 minutes; and sample RF-C generated 121 to 138 ppm at the end of the 6 minute period.

In the second series of experiments, only samples RF-A and RF-B were used. The specimen area was increased 1.5 times and the exposure chamber 4.8 times. CO concentrations decreased to 4100 ppm and 3700 ppm for rigid polyurethane samples RF-A and RF-B, respectively. The maximum HCN concentrations, 328 ppm (RF-A) and 710 ppm (RF-B), were generated in the first 2 minutes.

The animal results, mean incapacitation times, LT_{50} values, and the toxicity indexes, from both sets of experiments suggest that under these conditions the treated and untreated foams generate products of about equal toxicity (Table 17). When the results of the two series were compared to those from wood and flexible polyurethane foam decomposed under similar experimental conditions, both the untreated and the fire retarded rigid polyurethane foams were found to be less toxic than plywood but about as toxic as flexible polyurethane foams. Saito suggested that the HCN generated from polyurethane foams is consumed in a secondary combustion stage and the major toxic gas in actual fires is CO.

Kishitani used a tube furnace to determine the toxicity of combustion products from a rigid polyurethane foam as well as from other building materials [59]. The furnace was heated gradually from room temperature to 740°C in 15 minutes. Air flow through the furnace and exposure chamber was maintained at 2 ℓ/min. One mouse at a time was exposed in a whole-body mode to the combustion products from 3 g of the foam. The biological endpoints examined were changes in the electrocardiograms, blood COHb concentrations, and time of death.

In two experiments, flaming occurred at about 8 minutes. In three other experiments, the time of initial flaming was not measurable. Four out of five mice died within 15 minutes, with an average time to death of 14.44 minutes. One mouse died 1.5 min after the exposure. The presence of harmful fire gases was evident from electrocardiograms which showed abnormalities at 7 to 8 minutes. The average COHb concentration in the blood was 24.3%. Since in baseline studies with pure CO, Kishitani found that the lethal concentration of COHb in mice was 35 to 40% [59], the COHb levels found in these experiments are below the lethal concentration and are indicative that other toxic gases besides CO existed in the combustion atmosphere [59].

In a second investigation, Kishitani and Nakamura studied the toxicity of combustion products from building materials decomposed at 350, 500, and 750°C, the temperatures to which materials are normally exposed in the early stages of fires [60,61]. Materials were heated in a quartz tube furnace. One mouse at a time in a whole-body mode was exposed to the combustion products in an adjacent chamber. A vibration detection device was used to monitor movement of the test animal. Time of death, as indicated by cessation of respiration or loss of movement, was noted as the end point. The average maximum concentrations of CO and HCN in the exposure chamber produced by the decomposition of 5 g samples were 3700 ppm and 45 ppm at 350°C, 6100 ppm and 126 ppm at 500°C, and 3200 ppm and 52 ppm at 750°C, respectively. From the combustion studies presented in section 2.2.1.1, one would expect CO and HCN to increase with higher temperatures. Kishitani and Nakamura's results do not show this trend. The reason for this inconsistency is unclear. All lethalities occurred during the 500°C exposure (at 8.67, 12.67, and 14.25 min), during which the highest concentrations of CO and HCN were generated. A good correlation was found between the time of death of the mice, the concentration of HCN, and the temperature at which the highest HCN was produced. The authors concluded that the toxic effects of the combustion products from rigid polyurethane foam depended mostly on the presence of HCN and to lesser extent on CO [60,61].

Kishitani and Yusa examined the toxicity of combustion products from a rigid polyurethane foam at 850°C [62,63]. In these experiments, a vertical tubular furnace was used and the whole bodies of five mice were exposed simultaneously in revolving cages. In addition to visual observation of the mice, the revolution of the cages was monitored by electrical pulses. The time that the mice collapsed, as indicated by stoppage of the revolving cage, was considered the endpoint. The exposure lasted until all five mice collapsed but did not exceed 15 minutes. The results in Table 18 indicate that the maximum CO concentration varied from 600 to 800 ppm, regardless of sample size. The maximum HCN concentration varied from 52-124 ppm and was increased with sample size. The toxicity of combustion products from rigid polyurethane foam decomposed at 850°C was found to be about six times greater than those from Japanese cedar and lauan studied under the same conditions.

3.6 University of San Francisco (USF) Toxicity Test Method

Hilado et al. have evaluated the relative combustion product toxicity of many commercial products, including rigid polyurethane foams, using the University of San Francisco test method. This test method involves exposing four freely moving mice in the whole-body mode until death or for a maximum of 30 minutes to the thermal degradation products from 1 g samples decomposed in a tube furnace heated at either increasing or constant temperatures. Biological endpoints are time to incapacitation as indicated by staggering, prostration, convulsions, and collapse, and time to death as indicated by cessation of movement and lack of respiration.

The effect of flame retardants on combustion product toxicity was considered of special interest. Three rigid polyurethane foams, based on a propoxylated aromatic amino polyol formulation, were thermally degraded in a tube furnace at a rising temperature rate of 40°C/min from 200 to 800°C [64]. The first foam (R1) was untreated, the second foam (R2) contained 10% of a chlorinated butylene oxide-based polyol fire retardant, and the third foam (R3) contained 7% of FYROL 6[4] fire retardant. As seen from Table 19, times to incapacitation and death were not affected significantly by the presence of these fire retardants.

Preliminary toxicological screening tests also were conducted with a fourth rigid polyurethane foam based on a polymeric isocyanate and propoxylated trimethylolpropane formulation containing 16% of FYROL 6[4] [65]. This type of formulation had been reported to be unusually toxic when thermally degraded [32,66]. Under the same experimental conditions as previously described, except that the starting temperature was ambient and, in some tests, the maximum temperature was 500°C, no deaths were observed during the 30 min exposures when the upper temperature limit was 500°C (incapacitation, however, occurred at 9.5 min). Increasing the upper temperature limit to 800°C increased the toxicity of the degradation products, as indicated by the death of all mice within 20 minutes. The average incapacitation time (T_i) was 12.91 ± 1.92 min and the average time to death (T_d) was 15.73 ± 0.90 min. This mean and standard deviation was calculated for the mean times of three repeated experiments. Standardization of the furnace temperature profile (heating at 40°C/min from 200 to 800°C) did not change the mortality appreciably. All mice still died within 20 minutes and the average T_i and T_d times were only slightly less, at 11.23 ± 0.50 and 14.05 ± 0.60 min, respectively [65]. With this test method, this material does not appear to be any more toxic than the other FYROL 6 rigid polyurethane foam that was tested by Hilado and Saxton, the data for which are given in Table 19.

In a subsequent study, the same four rigid foams were reevaluated to compare the toxicity of decomposition products generated by the rising temperature program (40°C/min from 200 to 800°C) to those generated by a fixed temperature program at 800°C [67] (Table 20). In this study, concentrations of CO and methane (CH_4) were also measured by GC.

Hilado and Machado found that the constant temperature program (800°C) markedly reduced the time of incapacitation and time to death of the animals (Table 20). This is attributed to the more rapid rate of generation of the toxic degradation products at 800°C. However, even though the CO may be generated more rapidly at 800°C, the mean CO concentrations for R1, R2, and R3 are lower when the foams were decomposed at 800°C than when they were heated gradually at 40°C/min. The mean CH_4 concentrations are not significantly different between the two temperature modes. These results indicate that CO and CH_4 are not the only gases responsible for the observed biological effects for those three foams.

In an earlier study by Hilado and Cummings [68], mice were exposed to CO gas in air and 6000 ppm CO produced deaths in about 8 minutes and 10,000 ppm CO caused deaths in 5 minutes. When the rigid foams R1, R2, and R3 were decomposed at 800°C, the mean CO concentration was about 2500 ppm and deaths occurred at 8 to 9 minutes, which is earlier than expected by the CO concentrations alone. On the other hand, foam R4 produced a mean CO concentration of 6000 ppm and the animals died in one case at 24 min and in the other, at 12 min. These times are 16 and 4 minutes later than expected from the CO experiments alone. These data indicate that the deaths from samples R1, R2 and R3 are not due to CO alone. R4 produced enough CO to cause the deaths, but the time delay may be indicative of the unpredictability and variability in the test method.

Included in Table 20 also are T_i and T_d measurements for two other flame retarded rigid polyurethane foams, samples S1 and S2, which were decomposed with the rising temperature program [69]. The T_i times were somewhat longer and T_d times shorter than those for the foams R1 to R4. Because of the range in times to incapacitation and death from the decomposition products of these six rigid polyurethanes, Hilado et al. suggest that there is no "typical" or "representative" level of performance for rigid polyurethanes foams.

In his studies with rigid polyurethane foams, Hilado noted that the rigid polyurethane foams exhibit decreased toxicity upon aging. Longer times to death than those obtained in the earlier studies under the same experimental conditions were observed at later dates (Table 21). For example, time to death for rigid polyurethane foam R4 increased in seven months from 14.05 min [65] to 23.52 min [70] and then changed further after 15 months to 24.93 min [67]. Times to death for three foams R1, R2, and R3 also increased about 10 minutes over a two year period. Hilado attributed the decrease in toxicity to changes that occurred in the foams upon storage - such as continuation of the crosslinking process, oxidation, and loss of volatiles. Although the effect of material aging on toxicity is an important issue to investigate, it is not clear whether the time differences reported here are toxicologically significant. There certainly is no difference between 23.5 and 24.9 min.

Hilado and Machado also attempted to determine whether a correlation existed between the concentration of CO generated, the amount of char produced, and the times of death [71]. They made the following assumptions: (1) fraction of carbon oxidized to CO_2 is negligible under pyrolytic static conditions because of insufficient O_2, (2) the fraction of carbon converted to smoke particles is negligible because of little visible smoke formation, and (3) the residual char and CO produced theoretically represent the total carbon content of the material. Therefore, CO would be the primary toxicant and an increasing char yield would correspond to lower CO concentrations and lower toxicity as indicated by increased times of death. The char yields, times to death, and the highest CO concentrations measured when the rigid polyurethane foams R1, R2, R3, and R4 were decomposed under the fixed and rising temperature programs are shown in Table 22. With the rising temperature program, the maximum CO concentrations decreased somewhat with increasing char yield, but the times to death were about the same. However, with the fixed temperature program at 800°C there was no correlation between the amount of char and the amount of CO or between the amount of CO and the time to death. Again, it is not clear from Hilado's data whether these differences in time are toxicologically significant or even statistically significant since he never gives the within experiment variability, only the between experiment variability.

Except for R4, the CO concentrations alone were too low to be the principal toxicant at the time of death in the fixed temperature program [68]. A slight increase in times to death, with the exception of sample R4, was noted as the char yield decreased. The data suggest that, at 800°C, the increased relative toxicity observed with increasing char yield for rigid polyurethane (contrary to the trend observed for other groups of polymers) indicates that other volatile compounds (e.g., HCN) may be contributing to the toxicity of the pyrolysis gases [71].

The effects of temperature on the toxicity of the combustion products was further investigated by Hilado's group to see whether the rising temperature method can produce the same toxicity as observed from the average of the successive fixed temperatures [72]. Samples of a urethane-type rigid foam were decomposed at fixed temperatures from 200 to 800°C at 100°C intervals and also with the rising temperature program at 40°C/min starting at 200°C and ending at 800°C. This series of experiments was conducted both with no forced air flow and with a one ℓ/min air flow. Toxic effects, as observed by time to staggering, time to convulsions, and time to death were estimated by summation of all the times to the effects at successive fixed temperatures. The arithmetic averages of all the mean times to toxic effects at six fixed temperatures (300 to 800°C) and the corresponding times obtained using the rising temperature program are given in Table 23. In all cases, the calculated average times to incapacitating toxic effects and to death (survival time) at the fixed temperatures were 10 to 20% greater than those found during the experiments with rising temperatures. Less CO was produced under the rising temperature conditions than the calculated average of fixed temperature experiments for both series of experiments, with and without forced air flow. Again the experiments with less CO seem to produce faster times to incapacitation and death if these times can be considered significantly different. Experiments performed with a 1 ℓ/min forced air flow produced shorter times to effects than those without forced air. It appears that toxicity of rigid polyurethane is about the same when estimated by the rising temperature program of the University of San Francisco test method or by combined successive fixed temperatures.

In the course of his studies, Hilado evaluated a variety of materials and determined the relative toxicity using the USF toxicity test method. When the toxicological results of rigid polyurethane foams are compared to those of cellulose materials, evaluated by the rising temperature program (200 to 800°C, no forced air flow), rigid polyurethanes (R1, R2, R3, and R4) appear to be less toxic than wood. Average times to death for the four rigid polyurethanes range between 23 and 26 minutes as compared to times to death of 13 to 16 minutes for seven wood species [73]. The difference in relative toxicity of rigid polyurethanes and wood is less when the materials were evaluated with the fixed temperature program (800°C, no forced air flow). The average times to death for the same polyurethanes varied from 7 to 13 minutes as compared to 6 to 7 minutes for five wood species [74]. To determine the significance of these numbers, it would be necessary to know the within experimental variation, which is not given.

3.7 Miscellaneous Studies

3.7.1 University of Michigan Tests

A small-scale test procedure to investigate the toxicity of combustion products from polymeric materials was devised by Hartung [75]. The experimental procedure involves exposing rats in a whole body mode to the thermal degradation products generated by a radiant heat source in a static exposure system and determining the time to incapacitation by observing when the rats were no longer capable of maintaining their balance on a rotating rod located above an electrified grid and remounting the rotarod within 2 minutes after a fall.

Three and one-half gram samples of three rigid polyurethane foams (A,C,D), based on a THERMOLIN RF-230 formulation with different additives, were thermally decomposed under nonflaming conditions at a radiant heat flux of 3.2 W/cm^2. Four rats were placed in separate chambers in an adjoining exposure box and were exposed to the combustion products. CO_2 and CH_4 were analyzed in the exposure box atmosphere by GC, CO was examined by GC and NDIR, HCN and HCℓ were detected by specific-ion electrodes, and the oxides of nitrogen and acrolein were measured by a colorimetric technique. Gas and toxicological results from two tests were averaged and are summarized in Table 24.

The mean times to incapacitation were very similar for samples C (spray type) and D (slabstock), 28.16 and 28.48 min, respectively. Sample A (pour-in-place) produced an incapacitation time of 39.5 min, which was shown to be statistically significantly longer compared to the times of samples C and D. The reduced toxicity of the combustion products from Sample A is attributed to the lower production of CO, HCN, and HCl as compared to the yields from Samples C and D.

Douglas fir, under the same conditions, produced a mean time-to-incapacitation of 27.06 ± 2.39 minutes. Differences between the more toxic rigid polyurethane samples C and D and Douglas fir were not statistically different.

3.7.2 Mechanistic Studies of HCN and CO Toxicity

The cardiotoxic effects of multiple acute exposures to the pyrolysis products of rigid polyurethane foams were studied in rats and the relative contributions of CO and HCN to the cardiotoxicity were evaluated. Rats were exposed to one of several experimental atmospheres: polyurethane smoke or hemlock smoke generated at 500°C, both with or without added CO at various concentrations, or CO at a concentration of 2350 ppm in air [76]. The exposures were conducted in head-only mode in a flow-through exposure chamber and lasted for 10 to 20 minutes. Cardiotoxicity was documented by creatine phosphokinase activity (CPK/MB), ectopic beat frequency following norepinephrine stress and the incidence of myocardial lesions. A positive correlation was found between the level of CPK/MB activity and the duration of exposure, as well as the concentration of atmospheric CO during prolonged exposures. Similarly, the number of ectopic beats produced by groups of four animals increased as the CO concentration and/or the duration of exposure in each experimental atmosphere increased. Microscopic examination of cardiac tissue revealed acute lesions, some of which were under repair. The rats exposed to polyurethane smoke had a higher CPK/MB activity than did those rats exposed to CO in air at comparable concentrations of CO. The same phenomenon was observed with the ectopic beat measurements. These data strongly suggest that CO cannot fully account for the observed degree of cardiotoxicity induced by polyurethane pyrolysis products. Apparently, a pyrolysis product other than CO or in addition to CO must be partly responsible for the excessive cardiotoxicity observed upon exposure to polyurethane pyrolysis products. This excessive cardiotoxicity was not observed upon exposure to the pyrolysis products of hemlock.

The implication of HCN as the other responsible pyrolysis product was tested [77]. Using a similar experimental protocol, rats were exposed to test atmospheres with or without supplemental CO and/or HCN. The addition of HCN to the various atmospheres resulted in an increase in both the CPK/MB activity as well as the number of ectopic beats induced by norepinephrine stress. The cardiotoxic effects of HCN were further substantiated by the protection afforded by the administration of the cyanide antagonists chlorpromazine and thiosulfate prior to exposure to the test atmospheres. It is apparent that

HCN contributes to the production of cardiotoxicity observed when animals are exposed to an atmosphere of combustion products from rigid polyurethane foam.

The molecular mechanism potentially responsible for the toxicity of polyurethane pyrolysis products was investigated by Thomas and O'Flaherty [78]. The *in vivo* inhibition of cytochrome *c* oxidase was measured following 5 min inhalation exposures of rats to rigid polyurethane combustion products (generated at 500°C). The HCN present in the atmosphere was responsible for the noncompetitive inhibition of heart and brain cytochrome *c* oxidase. The magnitude of the *in vivo* inhibition correlated with the measured blood cyanide level. The blood cyanide levels responsible for 50% inhibition of cytochrome *c* oxidase in the brain and heart were nearly equivalent, 0.26 μg/ml and 0.29 μg/mℓ, respectively. Inhibition of hepatic cytochrome *c* oxidase was variable. Since these values of the fatal blood cyanide levels measured in rats exposed to pyrolysis fumes from rigid polyurethane are similar to those recorded for some human fire victims [79], cytochrome *c* oxidase inhibition in critical tissues is likely to be one of the molecular mechanisms contributing to the ultimate responses of incapacitation and death following exposure to the combustion products of rigid polyurethane foam.

3.7.3 Production of Unusual Toxicity

In most of the studies examined for this review, there have been no significant differences noted between the toxicities of the thermal decomposition products from fire retarded and non-fire retarded rigid polyurethane foams. However, as noted earlier in section 2.2.1.4, an unusual toxic effect was observed when animals were exposed to the combustion products from a laboratory formulated rigid polyurethane foam based on a propoxylated trimethylolpropane (MW 340) and polymethylene polyphenyl isocyanate containing the reactive fire retardant 0,0-diethyl-N,N-bis (2-hydroxyethyl)-aminomethyl phosphonate (4 to 8 weight percent) [32,66,80]. When this fire retarded foam was irradiated by a radiant heat flux of 5 W/cm^2 in the NBS smoke chamber, the non-flaming thermal degradation products produced grand mal seizures and death in rats following a 20 minute exposure [32]. The grand mal seizures occurred in the rats during the first hour following the exposure to smoke from this particular fire-retarded polyurethane foam. Additional physiological changes included alterations in the respiratory response to smoke irritants, high amplitude spike discharges in the EEG, and blood COHb levels of approximately 6%. However, cardiac arrhythmia was not observed. Control animals were exposed to 1500 ppm of CO, wood combustion products or the corresponding non-fire retarded foam, but these abnormal neurological effects occurred only following exposure to the fire retarded foam (Table 25). None of the foams tested (fire retarded or non-fire retarded) produced debilitating COHb levels (levels ranged from 5 to 33% COHb).

As noted earlier, these toxicological effects were attributed to the presence of 4-ethyl-l-phospha-2,6,7-trioxabicyclo [2.2.2] octane-l-oxide (commonly referred to as a bicyclic phosphate ester) in the combustion atmoshperes. Bicyclic phosphate compounds have been shown to cause seizures at very low concentrations [81].

The acute inhalation toxicity of this bicyclic phosphate ester generated as an aerosol was measured in rats by Kimmerle [82], who also noted seizures of varying severity. In addition, the unusual toxicity of the thermal decomposition products from this same fire retarded rigid polyurethane foam was confirmed by Potts and Lederer using the screening method developed by the Dow Chemical Company for evaluating potential smoke toxicity [80]. In this test method, rats were exposed in the whole body mode to products generated under non-flaming conditions in a quartz cup furnace and deaths were noted at significantly lower levels than when other cellulosic materials were decomposed under the same conditions. For example, a two gram sample of the bicyclic phosphate ester fire retarded rigid polyurethane foam affected 7/7 rats, whereas 0/7 rats were affected in the case of fir plywood. Rats also were noted to experience violent seizures just before death. However, when this formulation of rigid polyurethane foam was decomposed in the flaming mode, no unusual toxicity was noted and the lethalities occurred in the same concentration range that was found for fir plywood.

Keller et al. also studied this foam along with six other fire retarded polyurethane foams (Table 26) [66]. Rats were exposed to the combustion products from these fire retarded foams which were pyrolyzed at a heat flux of 5 W/cm^2 in the NBS smoke chamber. Sample 1 was similar to the bicyclic phosphate ester producing foam used by Petajan et al. [32] except it contained 16% of the fire retardant. Sample 2 was based on the same polyurethane formulation, but contained 18% of the commercial phosphate flame retardant known as VIRCOL 82. Samples 3, 4, 5, and 6 were based on an amine polyol formulation and contained 0 to 30% of the fire retardant, ANTIBLAZE 19. Sample 7 was based on trimethylolpropane polyol (similar to foam investigated by Petajan, et al. [32]) and contained 10% ANTIBLAZE 19. ANTIBLAZE 19 is a phosphorus-containing derivative of trimethylolpropane and the possibility existed of its conversion to the toxic bicyclic phosphate ester when thermally decomposed. Keller's results showed that the nonflaming decomposition products from both rigid polyurethane foams 1 and 2 caused convulsive seizures and deaths of the exposed rats either within the 20 minute exposure period or soon thereafter.

Rats exposed to products involving Antiblaze 19, with the exception of foam sample 6, did not exhibit any seizure type effects but showed normal behavior through the 14 days post-exposure period. The pyrolysis products from sample 6 caused the post-exposure deaths of 5/8 of the tested rats, but no signs similar to those caused by bicylic phosphate ester were observed. Thus, the addition of the fire retardants 0,0-diethyl-N,N-bis (2-hydroxyethyl)-aminomethyl phosphonate and VIRCOL 82 produced the neurological toxic effects but the fire retardant ANTIBLAZE 19 did not produce these unusual toxic effects.

The relative toxicity of combustion products of a trimethylolpropane-based rigid polyurethane foam containing various other types of phosphorus additives was investigated by Wright and Adams under flaming and non-flaming conditions [83]. The exposure and sample decomposition system was similar to that of Petajan et al. [32]. Foams were formulated to contain 16% of the following phosphorus additives: 1) a brominated phosphate ester, 2) a reactive phosphonate, 3) a polymeric chlorinated phosphonate, 4) a chlorinated phosphate ester, and 5) an inorganic polyammonimum phosphate.

The toxicological results, summarized in Table 27, show that, with the exception of the brominated phosphate additive, mortalities occurred when all trimethylolpropane-based rigid foam formulations with phosphorus additives were thermally degraded under nonflaming conditions. When the trimethylolpropane-based rigid foams were decomposed in the flaming mode, a marked reduction in the toxicity of the combustion products was observed. Mortalities were observed only when the foams with the chlorinated phosphonate and polyammonium phosphate additives underwent flaming combustion. When the same phosphorus additives were used in sucrose based - instead of trimethylolpropane-based rigid polyurethane foams, no mortalities occurred from exposure to the nonflaming combustion products (not shown in Table 27).

Relative toxicity studies of the type of rigid polyurethane foam reported to be unusually toxic [32] were also conducted by Hilado and Schneider using the University of San Francisco toxicity test method [70]. The formulation of their foam was based on polymeric isocyanate and trimethylolpropane with a hydroxy number of 550 and contained the fire retardant FYROL 6[4]. No unusual toxicity was observed when the tests were performed in absence of a forced air flow regardless of whether the material was decomposed under an increasing temperature program or at a fixed temperature of 800°C. Convulsions and seizures were observed when the fire retarded rigid polyurethane was pyrolyzed at 800°C in the presence of a forced air flow of 1 to 3 ℓ/min. Most times to death, however, for this foam were in general agreement with the times of death observed for other rigid polyurethane foam formulations, as shown in Table 20. In some experiments the seizures continued for extended periods, with as much as 50 minutes between onset and death. The authors did not propose, however, that these convulsive seizures indicated the presence of any unusual toxicants.

4. SUMMARY

In this report a review has been made of the chemical nature and toxicity of volatile products generated during the pyrolysis and combustion of rigid polyurethane foams. A great number of gaseous products have been identified; however, CO and HCN appear to be the predominant toxicants. The generation of both CO and HCN was found to increase with increasing temperature. At 1000°C, the highest yields observed were 26.5 mg/g for CO [6] and 73.3 mg/g for HCN [13].

The toxicities of the combustion products of rigid polyurethane foams were evaluated by various test methods using lethality and incapacitation as the biological endpoints. These results are summarized in Tables 28 and 29. The LC_{50} values for 30 minute exposures for most of the foams studied by the NBS and the University of Utah test methods (static systems) were greater than 34 mg/ℓ in the non-flaming mode and ranged from 10 to 17 mg/ℓ in the flaming mode. The LC_{50} values measured using the University of Pittsburgh and DIN test methods (dynamic systems) also fell within this range of values.

By comparison, the relative toxicity of different cellulosic and polymeric materials, including rigid and flexible polyurethane foams, evaluated by Levin et al. using the NBS toxicity test method ranged from about 10 to 50 mg/ℓ [37,38]. The data examined in this report indicate that the combustion products from rigid polyurethane fall within the toxicological range of a wide variety of other products. Comparison of the LC_{50} values for rigid polyurethane with the corresponding values for Douglas fir and flexible polyurethane foam suggests that rigid polyurethane is two to three times more toxic in the flaming mode than in the non-flaming mode. This difference, however, is less than an order of magnitude and is not considered toxicologically significant.

Toxicity studies on nitrogen-containing materials have shown that in many cases HCN is one of the primary toxicants along with CO and CO_2. Experimental studies on a rigid polyurethane (in the flaming mode) using the NBS test method have shown that the concentrations of CO, HCN, and CO_2 generated during the 30 min LC_{50} mass loading contribute to the toxicity. These concentrations were 1800 ppm, 140 ppm, and 12,900 ppm for CO, HCN and CO_2, respectively [37,38]. From individual pure gas experiments, 4600 ppm was the calculated LC_{50} (30 min) for CO and 160 ppm was the LC_{50} (30 min) for HCN [41]. In presence of 12,900 ppm CO_2, the LC_{50} (30 min) for CO is estimated to be reduced to 3700 ppm [41]. The experimental studies with CO and HCN gas mixtures have shown that the gases act in an additive manner such that if the relationship:

$$\frac{[CO]}{LC_{50}^{CO}(30\ \text{min})} + \frac{[HCN]}{LC_{50}^{HCN}(30\ \text{min})} \geq 1$$

the animals die, and if it is < 1, the animals live.

By combining the CO and HCN concentrations generated at the LC_{50} of rigid polyurethane with the LC_{50} (30 min) values for the mixture of HCN and CO one finds the following result:

$$\frac{1800\ \text{ppm CO}}{4600\ \text{ppm CO}} + \frac{140\ \text{ppm HCN}}{160\ \text{ppm HCN}} > 1$$

Since the sum is greater than 1, one can conclude that enough CO and HCN was generated in the combustion atmosphere of flaming rigid polyurethane to account for the deaths that occurred.

The EC_{50} values as determined with hind-leg flexion behavioral avoidance model for 30 minute exposures range mostly from 4 to 9 minutes in the flaming mode and 4 to 30 minutes in the non-flaming mode (Table 29). Toxicity results based on this model agree with the general conclusion based on the lethality data that rigid polyurethane is about two times more toxic in the flaming mode than in the non-flaming mode. The RD_{50} values for 10 minute exposures as determined by the University of Pittsburgh test method are similar for all rigid polyurethane foams tested, indicating that there is no difference of practical importance between the foams (Table 29).

The toxicity data based on time response (T_i and T_d) are very scattered and do not allow comparison as different experimental conditions (temperature, concentrations) were used by various workers. Times to incapacitation (as observed by collapse with the University of San Francisco's method) occur in about half the time needed for death.

The studies on the rigid polyurethane foams reviewed here indicate that the degree of toxicity observed was not a function of the specific foam tested. Furthermore, except in the case when a reactive type phosphorus containing fire retardant was added to a formulation containing propoxylated trimethylol propane, the addition of the fire retardants does not appear to change the toxicity of the combustion products. In the one exception, the very toxic bicyclic phosphate was formed during nonflaming combustion [32,66,80].

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6. REFERENCES

1. Materials '84. A Modern Plastics Special Report. Modern Plastics 61:45-67 (1984).

1a. Pigott, K.A., Urethane polymers. In "Encyclopedia of Chemical Technology", A. Standen, ed., Volume 21, John Wiley & Sons, Inc., New York, 1970, pp. 56-106.

2. Saunders, J.H., The reactions of isocyanates and isocyanate derivatives at elevated temperatures. Rubber Chem. Tech. 32:337-345 (1959).

3. Saunders, J.H., and Backus, J.K., Thermal degradation and flammability of urethane polymers. Rubber Chem. Tech. 39:461-480 (1966).

4. Backus, J.K., Darr, W.C., Gemeinhardt, P.G., and Saunders, J.H., Thermal decomposition of rigid urethane foams. J. Cell. Plastics 1:178-186 (1965).

5. Woolley, W.D., and Fardell, P.J., The prediction of combustion products. Fire Res. 1:11-21 (1977).

6. Voorhees, K.J., Hileman, F.D., Einhorn, I.N., and Futrell, J.H., An investigation of the thermolysis mechanism of model urethanes. J. Pol. Sci., Pol. Chem. Ed. 16:213-228 (1978).

7. Chambers, J., Jiricny, J., and Reese, C.B., The thermal decomposition of polyurethanes and polyisocyanurates. Fire and Matls. 5:133-141 (1981).

8. Bott, B., Firth, J.G., and Jones, T.A., Evolution of toxic gases from heated plastics. Brit. Polym. J. 1:203-204 (1969).

9. Standard Guide for Measurement of Gases Present or Generated During Fires, ASTM E 800-81, American Society for Testing Materials, Philadelphia, PA (1984).

10. Napier, D.H., and Wong, T.W., Toxic products from the combustion and pyrolysis of polyurethane foams. Br. Polym. J. 4:45-52 (1972).

11. Woolley, W.D., and Field, P., A preliminary study of the thermal decomposition of polyurethane foams by elemental ultramicroanalysis. Fire Research Station, Borehamwood, Hertfordshire, England, Fire Research Note No. 880 (July 1971).

12. Woolley, W.D., Nitrogen-containing products from the thermal decomposition of flexible polyurethane foams. Br. Polym. J. 4:27-43 (1972).

13. Woolley, W.D., Fardell, P.J., and Buckland, I.G., The thermal decomposition products of rigid polyurethane foams under laboratory conditions. Fire Research Station, Borehamwood, Hertfordshire, England, Fire Research Note No. 1039 (Aug. 1975).

14. Hileman, F.D., Voorhees, K.J., Einhorn, I.N., and Futrell, J.H., Pyrolysis of a rigid-urethane foam. U. of Utah, College of Engineering. Flammability of Materials. Polymer Conference Series, July 7-11, 1975.

15. Mumford, N.A., Chatfield, D.A., and Einhorn, I.N., Component analysis of rigid polyurethane foams. Fire Res. 1:107-117 (1977/78).

16. Chambers, J., and Reese, C.G., The thermal decomposition of some polyurethane foams. Brit. Polym. J. 7:48-53 (1976).

17. Michal, J., Determination of hydrogen cyanide in thermal degradation products of polymeric materials. Fire and Matls. 6:1-4 (1982).

18. Michal, J., Determination of carbon monoxide in thermal degradation products of polymeric materials. Fire and Matls. 5:149-152 (1981).

19. Ashida, K., Yamauchi, F., Katoh, M., and Harada, T., HCN generation from urethane and isocyanurate foams. J. Cell. Plastics 10:181-185 (1974).

20. Gaskill, J.R., Smoke development in polymers during pyrolysis or combustion. J. Fire and Flamm. 1:183-216 (1970).

21. Sumi, K., and Tsuchiya, Y., Combustion products of polymeric materials containing nitrogen in their chemical structure. J. Fire and Flamm. 4:15-22 (1973).

22. Tsuchiya, Y., and Sumi, K., Evaluation of the toxicity of combustion products. J. Fire and Flamm. 3:46-50 (1972).

23. Woolley, W.D., and Fardell, P.J., Studies of the combustion products of cyanides in a hydrogen diffusion flame. Fire Research Station, Borehamwood, Hertfordshire, England, Fire Research Note No. 1000 (Feb. 1974).

24. Herrington, R.M., The rate of heat, smoke and toxic gases release from polyurethane foams. J. Fire and Flamm. 10:308-325 (1979).

25. Ball, G.W., Ball, L.S., Walker, M.G., and Wilson, W.J., Fire performance data for urethane cellular plastics. J. Cell. Plastics 7:241-264 (1971).

26. Ball, G.W., Ball, L.S., Walker, M.G., and Wilson, W.J., Fire test data for urethane-based and isocyanurate-based rigid cellular plastics. Plastics and Polymers 40:290-293 (1972).

27. Sax, N.I., Dangerous properties of industrial materials, 3rd Edn., Reinhold Publishing Corp., New York (1968).

28. Paciorek, K.L., Kratzer, R.H., Kaufman, J., and Hartstein, A.M., Oxidative thermal degradation of selected polymeric compositions. Am. Ind. Hyg. Assoc. J., 35:175-180 (1974).

29. Hartstein, A.M., and Forshey, D.R., Coal mine combustion products: identification and analysis. U.S. Dept. of Interior, Bur. of Mines, Report of Investigation No. 7872 (1974).

30. Hartstein, A.M., and Forshey, D.R., Coal mine combustion products: neoprenes, polyvinyl chloride compositions, urethane foam, and wood. U.S. Dept of Interior, Bureau of Mines, Report of Investigation No. 7977 (1974).

31. Lee, T.G., Parker, W.J., and Tryon, M., Evaluation of the fire performance of a dibromotetrafluoroethane - blown rigid polyurethane foam. National Bureau of Standards, Gaithersburg, MD NBSIR 74-456 (April 1974).

32. Petajan, J.H., Voorhees, K.J., Packham, S.C., Baldwin, R.G., Einhorn, I.N., Grunnet, M.L., Dinger, B.G., and Birky, M.M., Extreme toxicity from combustion products of a fire-retarded polyurethane foam. Science 187:742-744 (1975).

33. Voorhees, K.J., Einhorn, I.N., Hileman, F.D. and Wojcik, L.H., The identification of a highly toxic bicyclophosphate in the combustion products of a fire-retarded urethane foam. Poly. Lett. 19:293-297 (1975).

34. Woolley, W.D., and Fardell, P.J., Formation of a highly toxic organophosphorus product (TMPP) during the decomposition of certain polyurethane foams under laboratory conditions. Dept. of the Environment of Fire Offices' Committee. Fire Research Station, Borehamwood, Hertfordshire, England, Fire Research Note No. 1060 (Nov. 1976).

35. Joseph, K.T., and Browner, R.F., Analysis of particulate combustion products of polyurethane foam by high performance liquid chromatography and gas chromatography-mass spectrometry. Anal. Chem. 52:1083-1085 (1980).

36. Kaplan, H.L., Grand, A.F., and Hartzell, G.E., A critical review of the state-of-the-art of combustion toxicology. Final Report 01-6862, Southwest Research Institute, San Antonio, TX (June 1982).

37. Levin, B.C., Fowell, A.J., Birky, M.M., Paabo, M., Stolte, A., and Malek, D., Further development of a test method for the assessment of the acute inhalation toxicity of combustion products. National Bureau of Standards, Gaithersburg, MD NBSIR 82-2532 (June 1982).

38. Levin, B.C., Paabo, M., and Birky, M.M., An interlaboratory evaluation of the 1980 version of the National Bureau of Standards test method for assessing the acute inhalation toxicity of combustion products. National Bureau of Standards, Gaithersburg, MD NBSIR 83-2678 (April 1983).

39. Products Research Committee. Materials bank compendium of fire property data. Nat. Bur. Stand. (U.S.), [Washington, D.C.] February 1980.

40. Packham, S.C., Jeppsen, R.B., McCandless, J.B., Blank, T.L., and Petajan, J.H., The toxicological contribution of carbon monoxide as a component of wood smoke. J. Comb. Tox. 5:11-24 (1978).

41. Levin, B.C., Paabo, M., Bailey, C., Harris, S.E., and Gurman, J.L., Toxicological effects of the interactions of fire gases and their use in a toxic hazard assessment computer model. The Toxicologist 5:127 (1985).

42. Huggett, C., Letter to Mr. D.M. Hurley, Harrison County Sheriff's Office, Gulfport, MS, May 16, 1983. National Bureau of Standards, Gaithersburg, MD.

43. Farrar, D.G., Hartzell, G.E., Blank, T.L., and Galster, W.A., Development of a protocol for the assessment of the toxicity of combustion products resulting from the burning of cellular plastics. Final Report to the Products Research Committee, Vol. 1, Flammability Research Center, University of Utah, (September 1979).

44. Hartzell, G.E., Packham, S.C., Hileman, F.D., Israel, S.C., Dickman, M.L. Mickelson, R.W., and Baldwin, R.C., Physiological and behavioral responses to fire combustion products. The 4th International Cellular Plastics Conference of the Cellular Plastics Division, Society of the Plastics Industry. Montreal (November 1976).

45. Alarie, Y.C., and Anderson, R.C., Toxicologic and acute lethal hazard evaluation of thermal decomposition products of synthetic and natural polymers. Tox. Appl. Pharm. 51:341-362 (1979).

46. Barrow, C.S., Lucia, H., Stock. M.F., and Alarie, Y., Development of methodologies to assess the relative hazards from thermal decomposition products of polymeric materials. Am. Ind. Hyg. Assoc. J. 40:408-423 (1979).

47. Alarie, Y.C., Wilson, E., Civic, T., Magill, J.H., Funt, J.M., Barrow, C., and Frohliger, J., Sensory irritation evoked by polyurethane decomposition products. JFF/Comb. Tox. 2:139-150 (1975).

48. Anderson, R.C., and Alarie, Y.C., Screening procedure to recognize "Supertoxic" decomposition products from polymeric materials under thermal stress. J. Comb. Tox. 5:54-63 (1978).

49. Anderson, R.C., Stock, M.F., and Alarie, Y.C., Toxicologic evaluation of thermal decomposition products of synthetic cellular materials. Part I. J. Comb. Tox. 5:111-129 (1978).

50. Alarie, Y., and Anderson, R.C., Toxicologic classification of thermal decomposition products of synthetic and natural polymers. Tox. Appl. Pharm. 57:181-188 (1981).

51. Kimmerle, G., Aspects and methodology for the evaluation of toxicological parameters during fire exposure. JFF/Comb. Tox. 1:4-51 (1974).

52. Kimmerle, G., and Prager, F.K., The relative toxicity of pyrolysis products. Part II. Polyisocyanate based foam materials. J. Comb. Tox. 7:54-68 (1980).

53. Herpol, C., Biological evaluation of toxicity caused by combustion of building materials. Fire and Matls. 4:127-143 (1980).

54. Herpol, C., Minne, R., and Van Outryve, E., Biological evaluation of the toxicity of gases produced under fire conditions by synthetic materials. Part 1: Methods and preliminary experiments concerning the reaction of animals to simple mixtures of air and carbon dioxide and carbon monoxide. Comb. Sci. and Technol. 12:217-228 (1976).

55. Herpol. C., Comparative study of the toxicity of combustion products from flame retardant and untreated materials. Fire and Matls. 7:193-201 (1983).

56. Purser, D.A., and Woolley, W.D., Biological studies of combustion atmospheres. J. Fire Sci. 1:118-144 (1983).

57. Purser, D.A., and Grimshaw, P., The incapacitative effects of exposure to the thermal decomposition products of polyurethane foams. Fire and Matls. 8:10-16 (1984).

58. Saito, F., Combustion gas toxicity of urethane and related foams. International Progress in Urethanes 3:149-171 (1981).

59. Kishitani, K., Study on injurious properties of combustion products of building materials at initial stage of fire. J. Faculty of Engineering, University of Tokyo, Ser. (B) 31:1-35 (1971).

60. Kishitani, K., and Nakamura, K., Toxicities of combustion products. JFF/Comb. Tox. 1:104-123 (1974).

61. Kishitani, K., and Nakamura, K., Study on toxicities of combustion products of building materials at initial stage of fire. 2nd Joint Meeting, U.S.-Japan Panel of Fire Research and Safety, UJNR, Tokyo, (Oct. 1976).

62. Kishitani, K., and Yusa, S., Research on evaluation of relative toxicities of combustion products of various materials. 3rd Joint Meeting, U.S.-Japan Panel on Fire Research and Safety, UJNR, Washington, D.C., (March 1978).

63. Kishitani, K., and Yusa, S., Study on evaluation of relative toxicities of combustion products of various materials. J. of the Faculty of Engineering, The University of Tokyo 35:1-17 (1979).

64. Hilado, C.J., and Saxton, G.L., Relative toxicity of pyrolysis products of some cellular polymers. J. Comb. Tox. 3:259-269 (1976).

65. Hilado, C.J., and Miller, C.M., The effect of changes in the USF/NASA toxicity screening test method on data from some cellular polymers. J. Comb. Tox. 3:237-257 (1976).

66. Keller, J.G., Herrera, W.R., and Johnston, B.E., An investigation of potential inhalation toxicity of smoke from rigid polyurethane foams and polyester fabrics containing Antiblaze 19 flame retardant additive. J. Comb. Tox. 3:296-303 (1976).

67. Hilado, C.J., and Machado, A.M., Toxicity of pyrolysis gases from some cellular polymers. J. Comb. Tox. 5:162-181 (1978).

68. Hilado, C.J., and Cumming, H.J., Effect of carbon monoxide on Swiss albino mice. J. Comb. Tox. 4:216-233 (1977).

69. Hilado, C.J., Cumming, H.J., and Solis, A.N., Relative toxicity and flash fire propensity of the pyrolysis gases from polyurethane foams. J. Cell. Plast. 13:408-415 (1977).

70. Hilado, C.J., and Schneider, J.E., Toxicity studies of a polyurethane rigid foam. J. Comb. Tox. 4:79-86 (1977).

71. Hilado, C.J., and Machado, A.M., Effect of char yield and specific toxicants on toxicity of pyrolysis gases from synthetic polymers. Western States Section, The Combustion Institute, Laguna Beach, Calif., (October 1978).

72. Hilado, C.J., and Huttlinger, P.A., Comparison of rising and fixed temperature conditions in testing cellular plastics and other materials. J. Cell. Plast. 17:104-112 (1981).

73. Hilado, C.J., Carbon monoxide as the principal toxicant. J. Comb. Tox. 6:177-184 (1979).

74. Hilado, C.J. and Brauer, D.P., Concentration-time data in toxicity tests and resulting relationships. J. Comb. Tox. 6:136-149 (1979).

75. Hartung, R., Ball, G.L., Boettner, E.A., Rosenbaum, R. and Hollingsworth, Z.R., The performance of rats on a rotarod during exposure to combustion products of rigid polyurethane foams and wood. J. Comb. Tox. 4:506-521 (1977).

76. Thomas, W.C. and O'Flaherty, E.J., The cardiotoxicity of carbon monoxide as a component of polymer pyrolysis smokes. Tox. and Appl. Pharm. 63: 363-372 (1982).

77. O'Flaherty, E.J. and Thomas, W.C., The cardiotoxicity of hydrogen cyanide as a component of polymer pyrolysis smokes. Tox. and App. Pharm. 63: 373-381 (1982).

78. Thomas, W.C. and O'Flaherty, E.J., Cytochrome c oxidax activity in tissues of rats exposed to polyurethane pyrolysis fumes. Tox. and Appl. Pharm. 49:463-472 (1979).

79. Wetherell, H.R., The occurrence of cyanide in the blood of fire victims. J. Forensic Sci. 11:167-174 (1966).

80. Potts, W.J. and Lederer, T.S., A method for comparative testing of smoke toxicity. J. Comb. Tox. 4:114-162 (1977).

81. Bellet, E.M. and Casida, J.E., Bcyclic phosphorus esters: high toxicity without cholinesterase inhibition. Science 182:1135-1136 (1973).

82. Kimmerle, G., Toxicity of combustion products with particular reference to polyurethane. Ann. Occup. Hyg. 19:269-273 (1976).

83. Wright, P.L. and Adams, C.H., Toxicity of combustion products from burning polymers: development and evaluation of methods. Env. Health Persp. 17:75-83 (1976).

Table 1

Thermal Degradation Products Produced from Rigid Polyurethane Foam

Compound	Atmosphere	Reference
Acetaldehyde	I,0	6,14,47
Acetamide	0	26
Acetic acid	0	30
Acetone	I,0	6,14,26,30,42
Acetonitrile	I	13,16
Acetylene	I,0	6,14,28
Acrolein	0	30
Acrylonitrile	I	13,16
Alkene	I,0	10,25
Allene	I	6,14
Ammonia	0	26,30
Aniline	I,0	6,14,30,35
Aniline hydrochloride	0	26
Benzene	I,0	6,13,14,15,26,30
Benzonitrile	I	6,13,14,16
Benzoquinoline	0	35
Butadiene	I	6,14,15
1-Butene	I	6,14
1-Butene-3-yne	I	6,14
Butyraldehyde	0	47
Carbazole	0	35
Carbon dioxide	I,0	4,6,10,21,28,29,30,35
Carbon monoxide	I,0	4,6,8,14,18,20,21,24,25,26,28,29,31,37,38,42,43,45,51,53,55,56,57,58,59,60,61,62,63,67,73,74,75,76,80
Carbon tetrachloride	0	26
Chlorine	I,0	10
Chlorobenzene	0	30
Chloroethane	I,0	15,30
Chloroethanol	0	30
Chloroethylene	0	30
Chloroisopropanol	0	30
Chloromethane	I,0	15,30
Chloropropylene	I,0	15,30
4,4'-Diamino dimethyl diphenylmethane	0	35
4,4'-Diamino diphenylmethane	0	15,30
4,4'-Diamino methyl diphenylmethane	0	35
4,4'-Diamino trimethyl diphenylmethane	0	35
Dichlorobenzene	0	26
Dichloroethane	I,0	15,28,30

Table 1 (Continued)

Compound	Atmosphere	Reference
Dichlorofluoromethane	0	30
Dihydropyran	I	6,14
Dimethyl benzoquinoline	0	35
2,6-Dimethyl quinoline	0	35
Dimethyl toluidine	0	35
1,4-Dioxane	0	30
Diphenylamine	0	35
Dipropoxydiene-trimethylolpropane	I	6,14
Dipropoxyene-trimethylolpropane	I	6,14
Dipropoxy-one-trimethylolpropane	I	6,14
Dipropoxy-trimethylolpropane	I	6,14
Dipropropylene glycol methyl ether	0	35
Ethane	I,0	6,14,15,47
Ethanol	I,0	15,26,30
Ethylbenzene	I	15
Ethylene	I,0	6,14,15,28
Ethylene oxide	0	44
4-Ethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2] octane-1-oxide [bicyclic phosphate ester]	I,0	32,33,34
4-Ethylquinoline	0	35
Formaldehyde	0	80
Formamide	0	47
FREON	I	6,14
Hydrocarbons (C_4)	I	13
Hydrocarbons (C_xH_y)	0	29,30
Hydrogen bromide	0	31
Hydrogen chloride	0	20,26,28,29,30,75
Hydrogen cyanide	I,0	8,13,16,17,19,20,21, 25,26,29,30,31,37,38, 42,43,45,47,51,56,57, 58,60,61,62,63,75, 77,80
Hydrogen fluoride	0	31
Indazole	0	35
Indole	0	35
Isobutene	I	15
Isopropropanol	0	30
Isoxazole	0	35
Methane	I,0	6,14,26,30,67,72, 73,74,75
Methanol	I,0	6,14,30
Methylacetylene	I	6,14
3-Methyl benzoquinoline	0	35
2-Methyl-1-butene	I	6,14
Methyl ethyl ketone	0	30
2-Methyl propenal	I	6,14

Table 1 (Continued)

Compound	Atmosphere	Reference
Methylquinoline	0	35
Monoproproxy-trimethylolpropane	I	6,14
Naphthalene	I	13
Nitric oxide	0	75
Nitrogen dioxide	0	75
Nitrogen oxides	0	25,26,28,31
3,8-Phenathroline	0	35
Phenol	I	15
p-Phenylenediamine	0	30
N-phenyl P-toluidine	0	35
Polycyclic aromatics	0	35
Propane	I,0	13,28,47
n-Propanol	0	30
Propenitrile	I	6,14
Propionaldehyde	I	6,14
Propylene	I,0	6,14,15,28,47
Propylene oxide	0	47
Pyridine	I	13,16
Quinoline	0	35
Styrene	I	6,14
Tetrapropoxydiene-trimethylolpropane	I	6,14
Tetrapropoxyene-trimethylolpropane	I	6,14
Tetrapropoxy-trimethylolpropane	I	6,14
Toluene	I,0	6,13,14,15,26,30
2,4-Toluenediamine	0	30
Toluene monoisocyanate	0	47
Toluidine	0	30,35
Toluidine hydrochloride	0	26
N-tolyl butylurethane	0	35
Trichlorofluoromethane	I,0	4,6,14,15,26,28, 29,30
Trichloroethyl phosphate	I,0	10
Trimethyl benzoquinone	0	35
Trimethylindole	0	35
Trimethyltoluidine	0	35
Trimethylquinoline	0	35
Tripropoxydiene-trimethylolpropane	I	6,14
Tripropoxyene-trimethylolpropane	I	6,14
Tripropoxy-one-trimethylolpropane	I	6,14
Tripropoxy-trimethylolpropane	I	6,14
Tripropylene glycol methyl ether	0	35
Urea	I,0	10
Water	I,0	4,6,14,29
Xylene	I	6,14,15

I - inert atmosphere
0 - oxidative atmosphere

Table 2

Products from Pyrolysis of a Sample of a Rigid Urethane Foam [6]

	Product Concentration (μg)[a]		
Compound	500°C	750°C	1000°C
N_2			0.67 ± 0.10
CO	0.29 ± 0.11	2.77 ± 1.07	26.45 ± 10.0
CH_4	0.02 ± 0.02	0.66 ± 0.34	15.31 ± 6.4
CO_2	39.31 ± 10.80	70.77 ± 6.64	83.99 ± 25.0
Ethene	0.02 ± 0.01	0.49 ± 0.16	11.40 ± 5.31
Ethyne			1.40 ± 0.67
Ethane	0.02 ± 0.01	0.30 ± 0.18	2.02 ± 0.76
Propene	1.20 ± 0.31	5.43 ± 2.0	16.27 ± 3.95
H_2O	10.44 ± 0.90	9.59 ± 1.14	26.87 ± 1.23
Propyne		0.02	1.10 ± 0.46
Allene			2.25 ± 1.50
Ethanal	0.21 ± 0.08	1.85 ± 0.70	9.07 ± 1.63
1,3-Butadiene			1.11 ± 0.44
1-Buten-3-yne			0.13 ± 0.02
FREON	7.53 ± 1.23	9.41 ± 2.93	8.04 ± 1.37
2-Methyl-1-butene	0.08	1.27 ± 0.65	3.57 ± 0.38
Acetone (+propanal)	1.15 ± 0.96	3.78 ± 0.36	8.14 ± 0.97
Propenitrile		0.32 ± 0.22	2.78 ± 1.68
2-Methyl propenal			1.75 ± 0.19
Benzene	0.67 ± 0.51	3.40 ± 1.47	7.38 ± 2.92
Toluene	0.22 ± 0.03	1.28 ± 0.59	3.73 ± 2.06
Xylene		1.07	1.98 ± 0.61
Styrene			1.22 ± 1.05
Benzonitrile			7.73 ± 3.15
Propoxylated trimethylol propanes			

[a] One mg samples of foam were pyrolyzed.

Table 3

Major Combustion Products from Rigid Polyurethane Foams Decomposed in a Nitrogen Atmosphere [13]

	Maximum Gas Concentration (mg/g)							
Foam	HCN	Acetonitrile	Acrylonitrile	Benzene	Pyridine	Toluene	Benzonitrile	Naphthalene
A	50.9	3.3	3.3	47.8	1.1	10.1	11.4	15.1
B	73.2	4.8	2.5	43.8	1.5	29.8	12.6	10.4
C	38.1	3.8	4.5	33.9	0.7	4.7	14.9	14.1
D	50.8	3.0	3.6	37.8	0.4	2.9	9.3	6.5

A MDI/polyester commercial foam, fire retarded with tris(chloroethyl)phosphate
B MDI/polyether commercial foam
C MDI/polyether polyol commercial foam
D Same as C, fire retarded with tris(chloropropyl)phosphate

Table 4

Major Nitrogen-Containing Thermal Products from Flexible and Rigid Polyurethane Foams Decomposed in a Nitrogen Atmosphere [16]

	Gas Concentrations (mg/g)				
Polyurethane Foam	HCN	Acetonitrile	Acrylonitrile	Pyridine	Benzonitrile
Flexible	28.0	1.1	0.3	0.2	2.4
Rigid	36.0	1.1	0.4	0.2	3.9

Table 5

Temperature Dependent Yield of HCN from
Rigid Polyurethane Foams Decomposed in Inert Atmospheres

Foam	Temp (°C)	HCN Concentrations (mg/g)							Ref.
		500	600	700	800	900	1000	1200	
A				5.1	8.6	31.5	50.9		13
B				5.1	6.4	47.1	73.2		13
C				1.5	6.5	18.6	38.1		13
D				1.5	3.1	7.6	50.8		13
4					1.1	11.1	36.0		16
SYSPUR			0.5		8.0		48.8	60.7	17
PAPI No. 3		0.23							19
TDI No. 8		0.45							19

Table 6

HCN Generation from Rigid Polyurethane Foams Decomposed in Air at 500°C [19]

Foam	Fire Retardant	Blowing Agent	Nitrogen in Foam (%)	HCN (mg/g)
PAPI	Tris(2-chloroethyl) phosphate	$CFCl_3$	4.53	8.0
PAPI	-	$CFCl_3$	4.87	11.5
PAPI	-	$CFCl_3$	4.87	12.8
PAPI	-	$CFCl_3$	4.99	14.1
TDI	-	$CFCl_3$	5.09	0.5
TDI[a]	-	$CFCl_3$	5.53	9.0
PAPI	FYROL 6	$CFCl_3$	5.73	4.3
PAPI	-	CO_2	6.66	17.1
PAPI	-	CO_2	6.85	14.6
TDI	-	CO_2	7.05	0.5

[a] Crude TDI

Table 7

Combustion Products from Rigid Polyurethane Foam Under Flaming Conditions [20]

Foam	Blowing Agent	Fire Retarded	Maximum Gas Concentration CO (ppm)	Maximum Gas Concentration HCN (ppm)
PAPI-ether	CO_2	+	275	10
PAPI-ether	Fluorocarbon	+	700	32
PAPI-ester	CO_2	-	2000	100
MDI-sucrose	Fluorocarbon	+	950	100

Table 8

Release Rate Data for Rigid Boardstock Polyurethane [24]

Gas	Maximum Generation Rates (mg/min-m^2)	Time to Maximum (sec)
NO_x	5070	13
HCN	1750	12
CO	45800	36
CO_2	805000	17
Total organics	18900	10

m = Meter

Table 9

Rigid Polyurethane Foam (GM 30) Toxicity Measurements Using the NBS Toxicity Test Method [37, 38]

Mode	Laboratory	Furnace temp. (°C)	LC_{50} (95% Confidence Limits)		EC_{50} (95% Confidence Limits) (mg/ℓ)
			30 minutes (mg/ℓ)	30 min + 14 days (mg/ℓ)	
Flaming	NBS	570-575	14.3 (13.4-15.3)	13.3 (12.2-14.5)	-
	4	610-625	>38.4[a]	>38.4[a]	-
	8	640	14.4 (11.7-17.8)	11.3 (7.6-16.8)	8.9 (5.1-15.6)
Non-Flaming	NBS	525-550	>39.6[a]	>39.6[a]	-
	4	560-577	>33.9[a]	>34.0[a]	-
	8	590	>35.1[a]	>35.1[b]	∿29.3
440°C	4	440	>39.6[a]	>39.6[a]	-
	8	440	>35.2[a]	>35.2[a]	>35.2[a]

[a] 0% of the animals were affected.
[b] One animal was affected.

Table 10

Atmospheric Gas Concentrations and Percent Carboxyhemoglobin Calculated at the LC_{50} (30 min) Values for GM 30 Decomposed by the NBS Toxicity Test Method [37]

Combustion Mode	LC_{50} (mg/ℓ)	COHb (%)	CO (ppm)	HCN (ppm)
Flaming	14.3	64	1800	140
Non-Flaming	>40	>47	>1700	> 44

Table 11

Toxic Effects of the Combustion Products of Rigid Polyurethane Foam Using the University of Utah Test Method [43]

Combustion Mode	Material	FR[a]	EC_{50}[b] (mg/ℓ)	LC_{50}[c] (mg/ℓ)
Flaming	GM 29	-	5.2 ± 1.8	11.2 ± 1.9
	GM 31	+	6.7 ± 1.2	14.2
	GM 35	-	5.8 ± 1.3	12.1 ± 4.1
	GM 37	-	3.9 ± 1.0	10.9 ± 1.5
	GM 39	-	4.8 ± 2.1	16.6
Non-Flaming	GM 29	-	8.9 ± 3.8	>40
	GM 31	+	9.0 ± 2.2	>40
	GM 35	-	10.8	>36.7
	GM 37	-	6.8 ± 3.4	>36.7
	GM 39	-	4.0 ± 1.6	10.9 ± 1.6

[a] Fire-retardant.

[b] EC_{50} values ± standard error calculated for loss of the leg-flexion avoidance response during 30 minute exposure.

[c] LC_{50} values calculated on deaths occuring during the 30 minute exposure and 14 days post-exposure period.

Table 12

Calculated CO and HCN Mean Concentrations Generated at the Incapacitating and Lethal Smoke Concentrations Produced During the Flaming Decomposition of Rigid Polyurethane Foam in the University of Utah Studies [43]

Material	EC_{50} (30 min)		LC_{50} (30 min. + 14 days)	
	CO (ppm)	HCN (ppm)	CO (ppm)	HCN (ppm)
GM 29	790	60	1690	130
GM 31	910	70	1930	140
GM 35	880	70	1340	145
GM 37	610	40	1710	110
GM 39	710	45	2460	150

Table 13

RD_{50} Values Calculated for Different Rigid Polyurethane Foams Decomposed by the University of Pittsburgh Test Method [49]

Sample	Fire Retardant	RD_{50} Values[1] RD_{50} (mg/ℓ)	 95% Confidence Limits (mg/ℓ)
GM 29	-	0.28	0.23 - 0.36
GM 31	+	0.21	0.11 - 0.39
GM 35	-	0.20	0.07 - 0.58
GM 37	-	0.23	0.11 - 0.49

[1] RD_{50} values were based on a 10 minute exposure and 5 minute recovery period.

Table 14

Sensory Irritation (RD_{50}), Stress Index (SI 100), Acute Mortality (LC_{50}) Values, and Asphyxiation Concentrations from Rigid Polyurethane Foams Examined by the University of Pittsburgh Test Procedure [45]

Samples	RD_{50}[a]		SI 100[b]		LC_{50}[c]		Asphyxiation Conc.	
	(g)	(mg/ℓ*)	(g)	(mg/ℓ)	(g)	(mg/ℓ)	(g)	(mg/ℓ)
GM 29	0.124	0.62	0.7	1.17	10.4	17.3	2-8	3.3-13.3
GM 31 (FR)	0.093	0.47	0.7	1.17	8.2	13.7	2-8	3.3-13.3
GM 35	0.092	0.46	0.9	1.50	7.5	12.5	2-7	3.3-11.7
GM 37	0.085	0.42	0.5	0.83	8.0	13.3	2-6	3.3-10.0

[a] Concentration necessary to reduce respiration rate by 50% in a 10 minute exposure and 5 minute recovery period.

[b] Concentration which produces a 50% decrease in the stress index (maximum is SI 200).

[c] Concentration necessary to kill 50% of the test animals in a 30 minute exposure and 10 minute recovery period.

* recalculated value by using the following formula

$$\frac{\text{wt (g)}}{\text{chamber air flowrate } (\ell/\text{min}) \times \text{exposure time (min)}} \times 1000 \text{ mg/g}$$

Table 15

Toxicity of the Pyrolysis Products of Rigid Urethane Foams Decomposed on a Volume Basis^{v} or a Weight Basis^{w} [51]

Sample	Volume or weight	Fire retardant	Temp (°C)	Gas Conc. in Air CO (ppm)	Gas Conc. in Air HCN (ppm)	COHb (%)	Number of Deaths Out of 20
1	v	-	600	1,100	60	34.2	0
2	v	+	600	1,000	75	43.6	0
3	v	+	550	1,500	100	45.2	0
			600	1,800	150	55.0	2
1	w	-	300	450	25	22.9	0
			400	1,900	75	48.0	4
2	w	+	350	1,000	50	36.1	0
			400	2,200	100	59.8	11
3	w	+	400	2,000	60	55.2	0
			450	4,400	100	62.4	20

v: 300 x 10 x 5 mm

w: 1.2 g/100 mm

Table 16

Toxicological Effects on Rats Exposed to Combustion Products from Polyurethane Foams Evaluated According to the DIN Toxicity Test Method [53, 55]

Sample Designation	Fire Retardant[a]	Sample Weight (g)	Temp. (°C)	CO Index[b] (ppm)	CO_2 Index (%)	No. rats dead / No. rats tested	Mean COHb %		Mean[c] Respiration Frequency (%)
							A	D	
K14[d]	+	5.0	400	16,660	12.2	0/23	7	-	
		5.5	600	143,430	30.8	17/20	29	56	
		5.4	800	4,380	37.0	0/18	4	-	
K5[e]	-	5.0	500	114,900	57.0	18/18	-	59	20
		5.0	600	35,700	87.0	0/18	23	-	108
		5.1	700	39,000	93.0	15/18	1	42	21
K6[e]	+	10.0	500	124,800	129.0	18/18	-	64	28
		10.0	600	27,300	120.0	9/23	18	42	70
		10.0	700	61,800	162.0	12/18	26	47	57

A: animals alive
D: animals dead
a: self-extinguishing type
b: integrated concentrtion for 30 minutes
c: expressed as a percentage of the nominal mean value before exposure
d: reference 53
e: reference 55

Table 17

Toxicological Effects on Mice Exposed to Combustion Products from Rigid Polyurethane Foam [58]

Materials	Fire Retardant	Incapacitation Time Mean (min)	Incapacitation Time S.D.[a] (min)	LT_{50} (min)	T_s[b] (min)
Series 1[c]					
RFA	-	5.77	0.47	5.75	2.60
RFB	+	6.15	0.35	6.25	2.23
RFC	+	7.52	0.50	7.50	1.69
Series 2[d]					
RFA	-	16.9	8.47	13.2	2.99
RFB	+	19.7	6.06	17.0	2.16

[a] Standard deviation of mean incapacitation time

[b] T_s: Toxicity index = $\frac{V}{\Delta W \cdot t_i}$

where V is the volume of exposure chamber, t_i is the incapacitation time, and ΔW weight of material consumed.

[c] Surface area of specimen: 300 cm^2; exposure chamber volume 125 ℓ.

[d] Surface area of specimen: 450 cm^2; exposure chamber volume 600 ℓ.

Table 18

Mean Time to Collapse After Exposure of Mice to the Thermal Decomposition Products from a Rigid Polyurethane Heated at 850°C [62]

Sample Weight	Maximum Gas Concentrations		Time to Collapse	
	CO	HCN	Mean	S.D.
(g)	(ppm)	(ppm)	(min)	(min)
0.50	700	52	3.80	0.35
0.74	800	48	2.58	0.39
0.91	800	68	2.26	0.21
1.15	700	105	2.20	0.47
1.45	800	122	1.69	0.18
1.75	600	124	1.56	0.18

S.D. Standard deviation of the mean of 5 exposed animals.

Table 19

Comparison of Toxicity Results from Fire Retarded vs Non-Fire Retarded Rigid Polyurethane Foams Decomposed According to the University of San Fransisco Toxicity Test Method [64][a]

Material	Fire Retardant	T_i (min)	T_d (min)	M_{10} (%)	M_{20} (%)
R1	-	9.64 ± 2.31	14.10 ± 0.74	0	100
R2	CBO[b]	8.28 ± 1.39	10.62 ± 1.10	38	100
R3	FYROL 6	10.91 ± 1.51	13.69 ± 1.41	0	100

a = rising temperature mode (40°C/min from 200 to 800°C)

b = chlorinated butylene oxide-based polyol fire retardant

T_i = mean time to first sign of incapacitation ± standard deviation of the mean times from 2 tests

T_d = mean time to death ± standard deviation of the mean times from 2 tests

M_{10} = mean mortality after 10 minutes from 2 tests

M_{20} = mean mortality after 20 minutes from 2 tests

Table 20

Toxicity Results for Rigid Polyurethane Foams Decomposed According to the University of San Francisco Method Using Different Temperature Modes [67, 69]

Sample Designation	T_i (min)	T_d (min)	Mean CO (ppm)	Mean CH_4 (ppm)
Rising temperature program (40°C/min from 200 to 800°C)				
R1	10.64 ± 0.85	23.92 ± 2.14	4630	3735
R2	8.56 ± 1.57	23.74 ± 2.11	4125	2660
R3	8.14 ± 2.45	25.69 ± 0.80	4660	1765
R4	6.53 ± 2.52	24.93 ± 2.69	6215	2290
S1	12.62 ± 1.24	15.14 ± 0.62	-	-
S2	12.12 ± 0.16	17.29 ± 0.96	-	-
Fixed temperature program (800°C)				
R1	4.00 ± 1.44	8.70 ± 0.35	2290	2960
R2	3.10 ± 0.37	7.56 ± 0.53	2375	2320
R3	3.04 ± 0.46	9.43 ± 0.55	2740	1760
R4	4.80 ± 3.52	12.15 ± 0.47	5935	2605

T_i = Mean time to incapacitation as indicated by staggering ± standard deviation of the mean times for 4 tests for R2, 2 tests for all other foams.

T_d = Mean time to death ± standard deviation of the mean times for 4 tests for R2, 2 tests for all other foams.

Table 21

Effect of Aging on Toxicity of Rigid Polyurethane Foams as Determined According to the University of San Francisco Method[a]

Sample Designation	Time of Testing	Time to Death (min)			
		0 time	9 months	16 months	2 years
R_1		14.10[b]			23.92[e]
R_2		10.62[b]			23.74[e]
R_3		13.69[b]			25.69[e]
R_4			14.05[c]	23.52[d]	24.93[e]

a Rising temperature mode (40°C/min from 200 to 800°C)
b Reference 64
c Reference 65 (sample composition similar to R4)
d Reference 70
e Reference 67

Table 22

Char Yield and Toxicity of Pyrolysis Gases from Rigid Polyurethane Foams as Determined According to the University of San Francisco Toxicity Test Method [70]

Sample Designation	Char Yield[a] (%)	T_d (min)	Maximum CO (ppm)
Rising temperature program (40°C/min from 200 to 800°C)			
R4	12.6	24.93	7180
R3	15.9	25.69	6380
R1	19.6	23.92	5760
R2	28.6	23.74	5650
Fixed temperature program (800°C)			
R3	10.2	9.43	3220
R4	10.9	12.15	8250
R1	12.2	8.70	2770
R2	16.8	7.56	3280

[a] Char yield at time of death of the last surviving animal.

Table 23

Comparison of Toxic Effects from a Rigid Polyurethane Foam Decomposed at Either Fixed Temperatures (300 to 800°C) or With a Rising Temperature Program According to the University of San Francisco Toxicity Test Method [72]

Forced Air Flow	Temperature Mode	CO[a] (ppm)	Mean Time[b] To Staggering (min)	Mean Time[b] To Convulsions (min)	Mean Time[b] To Death (min)
None	Fixed	8040	19.15	22.85	25.12
	Rising	2760	18.1	19.5	22.5
1 ℓ/min	Fixed	5600	7.78	9.63	12.93
	Rising	720	5.7	8.0	10.1

[a] CO concentration at the time of death of the last surviving animal or at the end of 30-minute test.

[b] Average CO concentration and time to toxic effect was calculated by arithmetic averaging the results from all the fixed temperatures (300 to 800°C) or those values obtained experimentally using the rising temperature program (40°C/min from 200 to 800°C).

Table 24

Gas Generation and Time-to-Incapacitation Results Following Exposure of Rats to the Combustion Products from Rigid Polyurethane Foams Decomposed According to the University of Michigan Test Procedure [75]

			Maximum Gas Conc.[c]			Average Gas Conc.[d]				
Sample[a]	Mean Time to Incap. (min)	S.D.[b] (min)	CO (ppm)	CO_2 (ppm)	CH_4 (ppm)	HCN (ppm)	HCl (ppm)	Acrolein[e] (ppm)	NO_2[e] (ppm)	NO (ppm)
A	39.5	2.95	1300	11500	20	9	30	0.06	0.1	1.3
C	28.5	4.47	1850	8000	15	28	51	0.20	0.2	1.8
D	28.2	1.47	2238	6675	8	44	123	0.44	0.1	1.4

[a] 3.5 g sample.

[b] Standard deviation of all the times to incapacitation of four rats in two tests.

[c] Highest concentrations measured at 25 to 45 min.

[d] Average concentration over the length of run.

[e] Acrolein and NO_2 may not be accurate due to possible color interferences.

Table 25

Toxicological Effects Produced in Rats Following a 20-Minute Exposure to CO, Smoke from the Combustion of Douglas Fir, Rigid Polyurethane Foam, or a Fire-Retarded Rigid Polyurethane Foam [32]

Test Material	Conc.	FR	COHb (%)	Time to Move from 25-cm Circle (sec)	Response to Pain (pinprick)	Other Comments
CO	1500 ppm	-	38-53	12.4	Suppressed	
Wood	5 g	-	30-46	11.4	Normal	Respiratory distress
Wood	18 g	-	62	>60	None	Extreme respiratory distress All died within 24 hours
Foam	ING	0%	28-33	6	Suppressed	Normal behavior Slight staining of nares
Foam	ING	4%	23-26	ING		One dead at end of exposure Focal seizures at end of exposure Grand mal seizures in 43 to 70 minutes No parasympathetic signs Normal CO unloading
Foam	ING	8%	5-6	>60	None	All animals showed myoclonic jerks which progressed to status epilepticus and death No parasympathetic signs

FR = Fire retardant: 0,0-diethyl-N,N-bis(2-hydroxyethyl)-aminomethyl phosphonate.
ING = Information not given.

Table 26

Summary of Behavioral Assessments of Rats Following 20 Minute Exposures to Smoke From the Non-Flaming Combustion of Fire Retarded Rigid Polyurethane Foams [66]

Sample	FR	Time to Move From 25 cm Circle	Additional Observations
1	I[a,b] (16%)	-	Convulsions in chamber 8/8 dead at 18 minutes
2	VIRCOL (18%)	-	Convulsions in chamber 4/8 dead on removal 2 were immobile and 2 were still convulsing 7/8 dead at 6 minutes after removal 8/8 dead at 15 minutes after removal
3	none	1-4 sec.	8/8 active and normal behavior
4	ANTIBLAZE 19 (10%)	1-4 sec.	8/8 active and normal behavior
5	ANTIBLAZE 19 (15%)	1-4 sec.	8/8 active and normal behavior
6	ANTIBLAZE 19 (30%)	2-8 sec.	No convulsions or tremors observed 3/8 active and normal behavior 5/8 inactive-had difficulty breathing, Expired 18-24 hours after test
7	ANTIBLAZE 19 (10%)	2-4 sec.	8/8 active and normal behavior

FR: Fire retardant

a: foam known to produce the toxic bicyclic phosphate ester

b: FR = 0,0-diethyl-N,N-bis(2-hydroxyethyl)-aminomethyl phosphonate

Table 27

Acute Toxicity of Smoke from Trimethylol Propane-Based Rigid Polyurethane Foams[a] Containing Various Phosphorus Additives [79]

Additive[b]	Total Phosphorus Content (Wt. %)	Non-Flaming		Flaming	
		Specimen Consumed (g)	Rat[c] Mortality	Specimen Consumed (g)	Rat[c] Mortality
None	0	2.9-3.0	0/8	5.1	0/8
Brominated Phosphate	0.8	4.3	0/8	ND	ND
Reactive Phosphonate	2.1	3.0	7/8	4.8-5.0	0/8
Chlorinated Phosphonate	2.6	4.1	8/8	4.8-5.9	0/8-8/8
Chlorinated Phosphate	1.7	4.5	5/8	5.0	0/8
Polyammonium Phosphate	5.1	3.7	8/8	4.9-8.0	0/8-1/8

[a] Sample size was 8 x 8 x 2.5 cm weighing approximately 5g

[b] 16% by weight

[c] Number of rats that died/number of rats exposed for 20 minutes and observed during a 14 days post-exposure period

[ND] Not determined

Table 28

Toxicological Effects Based on 30 Minute Exposures to Rigid Polyurethane Foams Thermally Decomposed by Different Test Methods

				LC_{50} Values		
Combustion Mode	Test Method	Furnace Temp. (°C)	Material Designation	30 min (mg/ℓ)	30 min + Post Exposure (mg/ℓ)	Reference
F	NBS	570-575	GM 30	14.3	13.3[a]	37,38
		640	GM 30	14.4[e]	11.3[a,e]	37,38
		610-625	GM 30	>38.4[a]	>38.4[a,e]	37,38
		600	RPU[b]	_	11.0[a]	42
F	UTAH	570	GM 30	-	11.2[a]	43
		570	GM 31/FR	-	14.2[a]	43
		600	GM 35	-	12.1[a]	43
		580	GM 37	-	10.9[a]	43
		700	GM 39	-	16.6[a]	43
NF/F	PITT	ramped 20°C/min	GM 30	-	17.3[c]	44
			GM 31/FR	-	13.7[c]	44
			GM 35	-	12.5[c]	44
			GM 37	-	13.3[c]	44
NF	DIN	400	PUR 1	29.0[d]	-	52
		500	PUR 1	7.5[d]	-	52
		600	PUR 1	6.6[d]	-	52
NF	NBS	560-577	GM 30	>33.9[e]	34.0[a,e]	37,38
		525-550	GM 30	>39.6	>39.6[a]	37,38
		590	GM 30	>35.1[e]	>35.1[a,e]	37,38
		440	GM 30	-	>39.6[a,e]	37,38
		440	GM 30	-	>35.2[a,e]	37,38
NF	UTAH	540	GM 30	-	>40[a]	43
		560	GM 31/FR	-	>40[a]	43
		550	GM 35	-	>36.7[a]	43
		530	GM 37	-	>36.7[a]	43
		630	GM 39	-	10.9[a]	43

F : Flaming
NF: Non-flaming
FR: Fire retardant
a : Post-exposure period 14 days
b : Sample from real fire
c : Post-exposure period 10 min.
d : Post-exposure period not noted
e : Study performed with NBS Toxicity Test Method by non-NBS laboratory for ILE [38]

Table 29

Incapacitation Effects from Exposure to Rigid Polyurethane Foams Decomposed by Different Test Methods

Combustion Mode	Test Method	Incapacitation Model	Material	EC_{50} (30 min) (mg/ℓ)	RD_{50}[a] (10 min) (mg/ℓ)		Reference
F	NBS	HLF[b]	GM 30	8.9	-	-	37,38
				>38.4	-	-	38
	UTAH	HLF	GM 30	5.2	-	-	43
			GM 31/FR	6.7	-	-	43
			GM 35	5.8	-	-	43
			GM 37	3.9	-	-	43
			GM 39	4.8	-	-	43
NF/F	PITT		GM 30	-	0.62[c]	0.28[d]	44,49
			GM 31/FR	-	0.47[c]	0.21[d]	44,49
			GM 35	-	0.46[c]	0.20[d]	44,49
			GM 37	-	0.42[c]	0.23[d]	44,49
NF	NBS	HLF	GM 30	29.3	-	-	37,38
NF	UTAH	HLF	GM 30	8.9	-	-	43
			GM 31/FR	9.0	-	-	43
			GM 35	10.8	-	-	43
			GM 37	6.8	-	-	43
			GM 39	4.0	-	-	43

a : Amount of material causing 50% decrease in respiratory rate/volume
b : Hind-leg flexion behavioral avoidance response
c : 11 ℓ/min air flow through the furnace (ref. 44)
d : 7.5 ℓ/min air flow through the furnace (ref. 49)
F : Flaming
NF: Non-flaming
FR: Fire retardant

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11. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here)*

The literature on rigid polyurethane foam has been reviewed with an emphasis on the gaseous products generated under various thermal decomposition conditions and the toxicity of those products. This review is limited to publications in English through 1984. Carbon monoxide (CO) and hydrogen cyanide (HCN) were the predominant toxicants found among more than 100 other gaseous products. The generation of CO and HCN was found to increase with increasing combustion temperatures. Many test methods were used to assess the acute inhalation toxicity of combustion products from various rigid polyurethane foams. Lethality, incapacitation, physiological, and biochemical parameters were employed as biological end points. In general, the combustion products generated from rigid polyurethane foam in the flaming mode appear to be more toxic than those produced in the non-flaming mode. The LC_{50} values for 30 minute exposures ranged from 10 to 17 mg/ℓ in the flaming mode and were greater than 34 mg/ℓ in the non-flaming mode. With the exception of one case in which a reactive type phosphorus containing fire retardant was used, the addition of fire retardants to rigid polyurethane foams does not appear to generate unusual toxic combustion products.

12. KEY WORDS *(Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)*

Carbon monoxide; combustion products; fire retardants; hydrogen cyanide; literature reviews; polyurethane foams; rigid foams; thermal decomposition; toxicity

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