

# Ignition, Combustion, Toxicity, and Fire Retardancy of Polyurethane Foams: A Comprehensive Review

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**ABSTRACT:** This review provides insight into the ignition, combustion, smoke, toxicity, and fire-retardant performance of flexible and rigid polyurethane foams. This review also covers various additive and reactive fire-retardant approaches adopted to render polyurethane foams fire-retardant. Literature sources are mostly technical publications, patents, and books published since 1961. It has been found by different workers that polyurethane foams are easily ignitable and highly flammable, support combustion, and burn quite rapidly. They are therefore required to be fire-retardant for different applications. Polyurethane foams during combustion produce a large quantity of vision-obscuring smoke. The toxicity of the combustion products is much higher than that of many other manmade polymers because of the high concentrations of hydrogen cyanide and carbon monoxide. Polyurethane foams have been rendered fire-retardant by the

incorporation of phosphorus-containing compounds, halogen-containing compounds, nitrogen-containing additives, silicone-containing products, and miscellaneous organic and inorganic additives. Some heat-resistant groups such as carbodiimide-, isocyanurate-, and nitrogen-containing heterocycles formed with polyurethane foams also render urethane foams fire-retardant. Fire-retardant additives reduce the flammability, smoke level, and toxicity of polyurethane foams with some degradation in other characteristics. It can be concluded that despite many significant attempts, no commercial solution to the fire retardancy of polyurethane foams without some loss of physical and mechanical properties is available. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 1115–1143, 2009

**Key words:** additives; halogenated; thermogravimetric analysis (TGA)

## INTRODUCTION

The commercial development of polyurethane foams was first studied in 1937 when Otto Bayer found that the reaction product of diisocyanate and polyol has properties that make it a polymer of interest.<sup>1</sup> Polyurethanes are extremely large and complex polymers produced by the reaction of isocyanate ( $R-N=C=O$ ) with compounds containing at least two active hydrogen atoms ( $R-OH$ ). A typical polyurethane foam structure may contain, in addition to the urethane linkages, aliphatic and aromatic hydrocarbon, ester, amide, disubstituted urea, biuret, allophanate, isocyanurate, uretidione, and carbodiimide groups. Polyurethane foams are the most important thermoset polymers and are manufactured in large quantities in the form of flexible and rigid foams. The worldwide demand for polyurethane foams has been estimated to be about 5% of the total world consumption of plastics. Flexible polyurethane foam is produced in a large volume (48%) and finds

greater usage in mattresses and furniture cushioning. On the other hand, rigid polyurethane foam is produced in a lower volume (28%) and finds applications in transportation, carpet underlay, refrigeration technology and appliances, building and construction industries, the automotive industry, packaging, and sporting goods.<sup>2</sup>

Polyurethane foams, being highly cellular polymers, are easily ignitable and highly flammable. The flammability of polyurethane foams has long been a factor that limits their greater uses. The fire retardancy of polyurethane foams is mostly required in mattresses, furniture cushioning, packaging, and building and construction industries with typical applications in insulation boards, light-weight concrete blocks, wall blocks with integrated insulation, curtain wall construction, preformed rigid panels, spray-applied wall construction, and many other industrial applications.<sup>3</sup>

There are a few approaches for enhancing the fire retardancy of polyurethane foams: (1) the incorporation of fire-retardant additives into the foam components by simple mechanical mixing at the compounding stage; (2) the addition of fire-retardant compounds containing functional groups, particularly hydroxyls, which become chemically bound in

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the polymer chain; and (3) coatings on the top surface of the flammable foam by means of fire-retardant materials. In the first approach, the additives usually adversely affect the physical properties of the foam. A decrease in the closed-cell content and strength properties and an increase in water absorption often occur. A significant reduction in strength properties and dimensional stability generally occurs under humid conditions, particularly if the additives are used in excess of 15 wt %. The second approach seems to be superior to the first because fire-retardant additives take part in the foaming reaction and become part of the polymer. The third approach is useful only for spray-applied foams for outdoor applications, for which low water vapor permeability and good weather protection are desired.<sup>2</sup>

Most known fire-retardant additives, particularly aliphatic phosphates, cause scorching (discoloration) of polyurethane foams because of the sensitivity of the foam components to even low concentrations of acids released on decomposition. Aliphatic phosphates are more hydrolyzable than aromatic phosphates. Thus, aliphatic phosphates tend to be more prone to aggravating scorch than aromatic phosphates.<sup>4</sup> Another problem encountered with some fire-retardant additives in polyurethane foams is the migration of the additives during processing or long-term use of the polymer, which might lead to a loss of fire retardancy.<sup>5</sup> Because of the migration and relatively high absorption of moisture, some fire-retardant additives can undergo hydrolysis, which leads to a decrease in the mechanical and physical characteristics of polyurethane foams. Thus, the stability, compatibility, migration of additives, effect on the physical and mechanical properties, smoke and toxicity, cost effectiveness, and color stability are some of the key factors in the selection of fire-retardant additives for polyurethane foams.<sup>6</sup> Therefore, the choice and selection of suitable fire-retardant additives for polyurethane foams are rather limited.

The fire retardancy of polyurethane foams has been previously studied and surveyed by many workers.<sup>7,8</sup> A review of the fire retardancy of polyurethanes, with an emphasis on commercial flame retardants in use, was published by Weil and Levchik.<sup>9</sup> Another review of the thermal decomposition, combustion, and fire retardancy of polyurethanes was presented; however, it was limited to publications of 1995 and later.<sup>10</sup> Recently, a brief review of fire retardants for polymeric foams, covering only physical and chemical aspects of intumescent fire retardants, was published.<sup>11</sup> This review is different from the earlier published reviews because it covers the ignition, combustion, smoke, toxicity, and fire-retardant additive/reactive approaches of polyurethane foams on the basis of patents and publications since 1961.

**TABLE I**  
Dissociation of Polyurethane Foam Linkages  
at Different Temperatures

Linkage	Dissociation temperature (°C)
Allophanate	100–120
Biuret	115–125
Urea	160–200
Urethane	180–200
Disubstituted urea	235–250
Carbodiimide	250–280
Isocyanurate	270–300

### IGNITION OF POLYURETHANE FOAMS

The ignition of polyurethane foams includes all gas-phase processes that occur between the fuel production step and the occurrence of a visible hot flame. The ignition of polyurethane foams occurs by the interdiffusion of the flammable gases with air.<sup>12</sup> The basic physical and chemical aspects of gas-phase ignition reactions have been studied by several researchers.<sup>13</sup> The ignition of polyurethane foams has been extensively studied with heat irradiation sources, thermogravimetric analysis (TGA), small pilot flames, and heat apparatus.<sup>14,15</sup> By using a series of selected oven temperatures and measuring times to ignition, one can establish the minimum heating rate required for ignition and the initial decomposition temperature at that rate. To obtain such relationships, the analytical tools of TGA, differential thermal analysis (DTA), and differential scanning calorimetry (DSC) have been used. These provide excellent insight into the reactions when conventional and fire-retardant polyurethane foam samples are heated at a standard rate in air and nitrogen atmospheres by qualitatively and quantitatively measuring the heat absorbed or liberated by the sample because of a phase change or a chemical change and by indicating the rate and extent of weight loss.<sup>16–18</sup> The thermal degradation process and its relation to foam ignition have been studied with a variety of analytical and existing fire-test methods.<sup>19–22</sup> The thermal stability and ignition of a conventional polyurethane foam mainly depend on the composition.<sup>23</sup> When a polyurethane foam is subjected to heat, various polyurethane linkages are broken at different temperatures. The dissociation of polyurethane foam linkages at different temperatures is shown in Table I. The ignition temperature of a polyurethane foam at a heating rate of 5°C/min is 150°C, whereas at a heating rate of 10°C/min, it is 260°C. The minimum heating rate required to ignite the polyurethane foam at the initial weight loss is 500°C/min, and the minimum decomposition temperature at this heating rate is 400°C.<sup>24</sup> Using similar

data for different cellular polymers, Miller et al.<sup>25</sup> suggested a relative ignition hazard scale. According to the ignition hazard, polyurethane foams fall between polyoxymethylene and cotton but are less hazardous than polyacetal and polyoxymethylene.<sup>12</sup> Measurements of the ignition and extinction limits were carried out, and it was found that polyurethane foams ignite at a 20% weight loss and are extinguished at an 80% weight loss. The ignition of cellular polymers in the glow wire test was characterized with thermography.<sup>26</sup> It was found that polyurethane foams ignite faster than cotton and cellulose acetate but more slowly than polyoxymethylene. Suzuki et al.<sup>27</sup> studied polyurethane foam smoldering with a siliconite heater as a heat source. It was found that smoldering spreads faster in the upward direction than the downward direction under natural draft conditions. Upward smoldering of foams in natural convection can be controlled by the initial smolder process being changed to an endothermic pyrolysis reaction that precedes the smolder reaction. A polyurethane foam ignited in a special apparatus consisting of a nichrome wire sandwiched between porous ceramic honeycomb plates shows that downward smoldering is controlled primarily by the supply of the oxidizer to the reaction zone. The oxygen supply and heat loss are the main factors that influence the foam ignition and smoldering.<sup>28</sup> The forced forward smoldering propagation velocity increases with air flow and then decreases with the air flow rate in a foam material placed horizontally.<sup>29</sup> A polyurethane foam covered with cellulose-based fabric poses a serious smoldering hazard if exposed to a burning cigarette because of the low temperature (400°C), which produces a substantial amount of carbon monoxide.<sup>28,30</sup>

In other experiments, the ignitability, heat release rate, effective heat of combustion, and mass loss were obtained by the exposure of polyurethane foams under cone calorimetry test conditions. It has been found by different workers that the uniform heat flux and peak rate of heat release depend to a large extent on the melting behavior and thickness of the foam, which should be limited to 25 mm. Density was found to be the key variable in controlling ignition resistance.<sup>31</sup> The ignition behavior of polyurethane foam and fabric mock-up combinations has also been studied under cone calorimetry test conditions. Covering a foam with a fabric results in a delay in the ignition and peak rate of heat release.<sup>32,33</sup> Checchin et al.<sup>34</sup> studied the postignition behavior of polyurethane foams with a cone calorimeter. The cone calorimetry apparatus allows us to measure the evolution of carbon monoxide and hydrogen cyanide, which are considered the major causes of fatal causalities during fire. The presence of bromine and phosphorous compounds in a burn-

ing foam increases the evolution of smoke and toxic gases, particularly carbon monoxide and hydrogen cyanide.

## COMBUSTION OF POLYURETHANE FOAMS

The combustion of polyurethane foams occurs only in the presence of a sufficient amount of oxygen. On combustion, polyurethane foams produce four types of products: combustible gases, noncombustible gases, entrained solid particles, and carbonaceous char. These combustion products vary with the foam composition, temperature level, rate of temperature rise, endotherms, exotherms, and rate of volatile evolution. The heat of combustion raises the temperature of combustible and noncombustible gases, resulting in increasing heat transfer by radiation. The heat transferred from the combustion zone to the adjacent material produces further decomposition and ignition resulting in flame propagation. Polyurethane foams exhibit a highly viscous melt on combustion. Thermal analysis has shown that the glass-transition temperature increases with the decrease in foam density, but the thermal stability decreases with the decrease in foam density.<sup>35</sup> Morphological changes that occur during combustion have been extensively studied with scanning electron microscopy.<sup>36</sup> In other publications, the combustion of polyurethane foams has been reported: experimentation was conducted with a ventilated tunnel and confirmed that polyurethane foams are highly combustible materials.<sup>37</sup> The combustibility of polyurethane foams has also been measured with some standard test methods.<sup>38</sup> TGA, differential thermogravimetry, and DTA studies have indicated that rigid polyurethane foams decompose in nitrogen and degrade in air through two and three weight-loss stages, respectively. Foam pyrolysis in nitrogen and combustion in air lead to 15 and 0% char residue, respectively. The results indicate that the thermal stability of rigid polyurethane foam is better in nitrogen than in an air atmosphere.<sup>39</sup> When urethane foams decompose in different atmospheres, the decomposition rates are almost identical *in vacuo*, in nitrogen, and in air at 250°C; however, at higher temperatures, the rate of decomposition is highest *in vacuo* and lowest in air. Complete weight loss takes place at about 750°C in air but at 950°C in nitrogen. The evolution of hydrogen cyanide starts at 550°C, and its quantity is almost equal to the nitrogen content of the foam.<sup>12</sup>

## SMOKE AND TOXICITY

Requirements regarding smoke density and toxicity are becoming increasingly stringent because of the increasing interest in fire and consumer safety.

TABLE II  
Decomposition Products of Polyurethane Foams by Mass Spectrometry

Peak nomenclature	Decomposition product	Peak nomenclature	Decomposition product
a	Nitrogen	r	Pyridine
b	Carbon dioxide	s	Toluene
c	Ethylene	t	Methyl pyridine
d	Ethane	u	Methyl pyridine
e	Water	v	Cyclooctatetrene
f	Propane	w	Vinyl pyridine
g	Hydrogen cyanide	x	Benzonitrile
h	Not identified	y	Not identified
i	Butyne or butadiene	z	Indene
j	Acetonitrile	A	Methyl cyanobenzene
k	Acrylonitrile	B	Methyl cyanobenzene
l	Propionitrile	C	Not identified
m	Methyl acrylonitrile	D	Not identified
n	Benzene	E	Naphthalene
o	Vinyl acetonitrile	F	Isoquinoline
p	Not identified	G	Not identified
q	Pyrrole		

Many techniques are being used to control smoke and toxicity problems. It is generally accepted that polyurethane foams produce large quantities of vision-obscuring smoke during combustion; however, smoke is mostly generated in the beginning of combustion. Herrington<sup>40</sup> observed a parallel trend for smoke production, mass loss, and heat release by putting polyurethane foams in a heat release rate apparatus at Ohio State University. The foam samples ( $100 \times 150 \times 25 \text{ mm}^3$ ) were placed in a horizontal position and exposed to a  $1.0 \text{ W/cm}^2$  background heat flux and a  $0.18\text{-kW}$ -intensity single-point gas flame ignition source. The ignition source was positioned to impinge perpendicularly at the center of the foam surface. The production of smoke from polyurethane foams was also estimated with the placement of the sample in the vertical position. The sample was ignited on a wire gauge with a flame from a propane burner placed beneath the gauge, and the smoke produced in flame and nonflaming modes was examined by a light/photocell arrangement for optical density.<sup>41</sup> The quantity of smoke production remains almost constant up to 10 min in the beginning. However, it depends on the density of the foam. High-density foams produce more smoke than low-density foams. The results also show that fire-retardant foams release roughly 5 times more smoke than untreated foam. In particular, phosphorous fire-retardant compounds reduce the thermal decomposition temperature of foams,

resulting in an increase in the smoke density. Polyurethane foams produce more smoke ( $1.0\text{--}7.4 \text{ mg}$  of deposited smoke) than rigid polystyrene ( $1.7$ ), wood, wood wool, and phenolic foam but less than poly(vinyl chloride) ( $28.9$ ), acrylics ( $40.6$ ), and nitrocellulose crystals.<sup>42</sup> Polyurethane foams produce smoke that is double in volume with respect to wood components. In the flaming mode, a flexible urethane foam produces less smoke than a rigid foam, whereas in the nonflaming mode, the smoke difference is quite low. Hurd<sup>43</sup> found that  $1 \text{ kg}$  of foam generates smoke that is equivalent to  $12 \text{ kg}$  of bitumen. The dependence of smoke formation on the temperature at which the polyurethane foam is exposed to pyrolysis and combustion was studied in a ceramic boat tube furnace at  $200\text{--}500^\circ\text{C}$  in nitrogen and air.<sup>44</sup> It was found that the maximum evolution of smoke occurs above  $650^\circ\text{C}$  and that it contains virtually all the nitrogen of the original foams. At lower temperatures, decomposition proceeds rather slowly to generate a significant amount of smoke. Woolley et al.<sup>45</sup> studied the combustion of polyurethane foams in a small ceramic boat inside a silica furnace tube for 15 min at  $200\text{--}800^\circ\text{C}$  in air. At  $200\text{--}300^\circ\text{C}$ , yellow smoke is generated, which appears to be a polymerized or condensed and somewhat free form of toluene diisocyanate (TDI). At  $500^\circ\text{C}$ , the nitrogen contents start evaporating at about 35% weight loss. The yellow smoke remains stable up to  $750^\circ\text{C}$ , decomposes at a temperature of  $800\text{--}900^\circ\text{C}$ ,



and produces cyano compounds together with other organic nitriles.<sup>46</sup> In another experiment, the foam samples were decomposed in a furnace system under conditions likely to be encountered in fire. The volatile products released from the thermal and thermal oxidative decomposition of polyurethane foams were collected in a refrigerated trap and were identified quantitatively and qualitatively by gas chromatography/mass spectrometry, ultramicroanalysis, and mass spectrometry.<sup>47</sup> Peaks of the decomposition products of yellow smoke obtained from the foam samples that decomposed at 850°C were interpreted with the data of Cornu and Massot<sup>48</sup> and are shown in Table II. The corrosivity of polyurethane foam smoke has not been studied in great detail, although the effects of some gases are well known.

The toxicity of the thermal decomposition and combustion products of polyurethane foams has been intensively documented. This topic was reviewed in detail by Woolley and Field,<sup>49</sup> who found that typical pyrolysis and combustion products from flexible and rigid polyurethane foams do not appear to differ greatly. Apart from relatively heavy polyurethane chain fragments, N<sub>2</sub>, CO, CO<sub>2</sub>, H<sub>2</sub>O, C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>, and HCN have been detected and reported by many authors.<sup>40,43–45,49,50</sup> Two approaches to the estimation of the toxicity of degradation, pyrolysis, and combustion products of polyurethane foams have been reported: (1) analysis of volatile products and calculation of their toxicity and (2) toxicity tests with various animals. The composition of gases that evolve during the thermal decomposition of polyurethane foams in air and nitrogen was studied by Woolley and coworkers.<sup>43–45</sup> The evolution rate of each gas initially increases slowly with temperature, but at a critical temperature, the rate begins to increase rapidly. At 300°C, there is a rapid and complete loss of the TDI unit of foams as volatile gases leaving a polyol residue. At 800°C, low-molecular-weight nitrogen-containing products are isolated. When the temperature reaches the range of 900–950°C, benzonitrile and hydrogen cyanide are virtually predominant. At 1000°C, approximately 70% of the available nitrogen of the polyurethane foams is converted into hydrogen cyanide. At 1000°C, polyurethane foams generate almost equal quantities of HCN (3.8%) in air and nitrogen, which are less than those produced by polyacrylonitrile and urea formaldehyde resin and more than those produced by nylons. The similarity of the activation energies for HCN evolution in air and nitrogen suggests that the mechanism of gas evolution is not affected by oxidation reactions.<sup>51</sup> In contrast, Jelinek and Dunkle<sup>52</sup> suggested that urethane groups (–NHCOO–) oxidize by atmospheric oxygen during the decomposition of polyurethane foam, resulting in

HCN formation. At low temperatures at which the oxidation of HCN is still negligible, the rate of HCN generation increases linearly with an increasing percentage of oxygen in the gas mixture. At higher temperatures, the oxidation of HCN becomes appreciable, and its formation rate rises to the maximum with increasing oxygen content of the gas mixtures. According to Morikawa and Woolley,<sup>45</sup> any nitrogen-containing material, except nitro compounds, gives off HCN when heated above 700°C, and the evolution of HCN is almost equal to the nitrogen content of the materials. The evolution of HCN from polyurethane foams has been determined qualitatively and quantitatively at different temperatures (700–1000°C), and its value has been compared with those of other polymeric materials. Woolley et al.<sup>43,45</sup> studied the combustion of polyurethane foams in a silica tube heated inside a furnace with the maximum temperature up to 1000°C in air. They detected benzonitrile, benzene, pyridine, acrylonitrile, acetonitrile, toluene, CO, HCN, methyl pyridine, butadiene, propane, and water at relatively high concentrations, and CO<sub>2</sub>, ethylene, ethane, propionitrile, methyl acrylonitrile, pyrrole, vinyl pyridine, indene, methyl cyanobenzene, naphthalene, quinoline, and isoquinoline were found to be minor products. The toxicity coefficient calculated for all gases showed that combustion gases from polyurethane foam are more toxic than those from wool and nylons. A series of gas chromatography/mass spectrometry analyses was carried out with polyurethane foams in combustion chambers in the flaming combustion mode at 700, 800, 900, and 1000°C and in the nonflaming combustion mode at 600°C.<sup>45,49</sup> The combustion products were primarily nitrogen-containing compounds and not oxygen-containing oxidation products other than CO, CO<sub>2</sub>, and H<sub>2</sub>O. The condensation of high-boiling products was also observed on the inside walls of the furnace. In contrast to other nitrogen-containing polymers, polyurethane foams yield only one product, that is, HCN at 1000°C. Thermal degradation and evolving gaseous products from the pyrolysis of rigid polyurethane foams have also been studied with thermal analysis/mass spectrometry and thermal analysis/Fourier transform infrared spectroscopy.<sup>53</sup> The degradation of urethane foams, studied with a cone calorimeter, and evolved gaseous compounds, quantified by Fourier transform infrared, shows high concentrations of isocyanates, amino-isocyanates, and amines.<sup>54</sup>

Woolley et al.<sup>45</sup> detected mostly HCN by heating a polyurethane foam under air or nitrogen at 700–1000°C. A higher evolution rate was observed at higher temperatures, so the amount of HCN that was produced increased with increasing temperature. A higher concentration of HCN was generated when the polyurethane foam was decomposed in a cup furnace

via a two-phase procedure (nonflaming phase followed by ramped heating) than when the foam was decomposed under only nonflaming or flaming conditions.<sup>55</sup> When a copper compound such as cuprous oxide ( $\text{Cu}_2\text{O}$ ) was added to the polyurethane foam, the formation of HCN during thermal decomposition in a quartz beaker set in a cup furnace was reduced substantially. When a cuprous oxide containing polyurethane foam was decomposed in a small-scale test, it showed an 87% reduction in the concentration of HCN, whereas during a large-scale test, this reduction was 70%. A melamine-treated polyurethane foam generated 10 times more smoke than a conventional foam when both decomposed in the two-phase cup furnace smoke toxicity test. Under similar conditions, a melamine-containing foam generated 90% less HCN when it was treated with  $\text{Cu}_2\text{O}$ .<sup>56</sup> Cuprous oxide acts as an oxidative catalyst that decomposes gaseous HCN into  $\text{N}_2$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , and a small amount of nitrogen oxides, resulting in a reduction of the HCN concentration. At a higher temperature, the addition of inorganic compounds has little effect on the formation of HCN. During combustion processes in which HCN is formed, air pollution by cyanoarenes and aza-arenes (part per million concentrations) may occur. Dennis et al.<sup>33</sup> studied combustion products of a composite material based on a polyurethane foam and wool fabric. It was shown that the evolution of the main toxic gases CO and HCN depends on the air flow in the combustion area. The evolution of HCN takes place toward the end of combustion at a low rate of aeration, whereas CO releases in the first minute of combustion at a high rate of aeration. The total content of both toxic gases increases when a low concentration of oxygen is passed through the zone of combustion. The addition of ammonium polyphosphate (APP) in urethane foams sharply decreases the emission of CO and HCN, smoke density, and formation of soot. Expandable graphite, when added to polyurethane, enables a decrease in toxic gases in a lower proportion than APP.<sup>57</sup> The toxicological effect depends on the concentrations of both gases together with their ratio. The combustion gases with higher ratios of HCN to CO are more toxic. The combustion of polyurethane foams was studied in a National Bureau of Standards (NBS) chamber, and it was found that the gases which evolve from the nonflaming combustion of polyurethane foams are more toxic than those from flaming combustion.<sup>41</sup>

The acute toxicity by inhalation and lethality of thermal decomposition products of polyurethane foams were investigated with a cup furnace smoke toxicity apparatus, a poly(methyl methacrylate) rectangular box, and a quartz tube inside an electrically heated annular furnace according to DIN 53436.<sup>58</sup> The concentrations of pertinent fire gases individually and in various combinations and the amount of material needed to

cause 50% lethality (LC50) during a planned 30-min exposure and 10-min recovery period were determined along with the lethal blood HCN and carboxyhemoglobin (COHb) concentrations. LC50 means that the concentration produced under the stated conditions leads to the death of 50% of the exposed animals within 14 days following exposure. The concentrations of toxic fire gases determined for the LC50 data were related to the mass of the test specimens used. From a series of experiments with polyurethane foam, the LC50 was calculated to be 6.6 g, and the time needed to cause 50% lethality was 9.5 min.<sup>59</sup> The blood and ambient concentrations of gases from the combustion of the polyurethane foam indicated CO and HCN as the principal toxicants. During the LC50 determination of the polyurethane foam, it was found that the blood cyanide value was very high; this indicated that HCN was the primary toxicant because the COHb levels were very low. It appears that HCN was absorbed very quickly into the blood, resulting in a low oxygen concentration that caused a rapid toxic effect, probably preventing the normal process of tissue oxidation and paralyzing the respiratory center of the brain, thus resulting in death. Similarly, the toxicity of CO is mainly due to its affinity to hemoglobin (Hb; the main structural protein of blood). Hb has 200–300 times more affinity toward CO than  $\text{O}_2$ . CO, when breathed in along with air, is absorbed by the blood, reducing the  $\text{O}_2$ -carrying capacity of blood. Hence, CO readily reacts with Hb to form COHb, a stable compound resulting in  $\text{O}_2$  deficiency in the body tissues, which causes headache, mental dullness, and tightness in the chest, which leads to death.<sup>60</sup> The air and blood data gathered during polyurethane foam combustion suggest that death can be attributed to HCN and CO in the  $\text{O}_2$ -deficient environment. Sakai and Okukubo<sup>61</sup> derived similar conclusions from their toxicological experiments with animals.

Levin et al.<sup>56</sup> exposed 344 male Fischer rats to thermal decomposition products of a polyurethane foam and a polyurethane–polyester combination. The decomposition products of the polyurethane foam and the foam in combination with polyester produced no animal deaths during exposure and caused postexposure deaths only in the nonflaming modes. Babrauskas et al.<sup>62</sup> exposed rats to thermal decomposition products of a fire-retardant polyurethane foam using a poly(methyl methacrylate) rectangular apparatus. Only the head of each animal was exposed for 30 min to avoid heating of the whole body. The toxicity of the combustion products from the fire-retardant foam was attributed to the formation of a bicyclic phosphate ester in the smoke, which resulted in the immediate death of the animals. An analysis of the combustion products revealed that HCN, CO, and vinyl pyridine are probably responsible for the toxic action. Various

polymeric materials including polyurethane foams have been evaluated at different temperatures, heating rates, and air flow rates for thermophysical and toxicological responses.<sup>63</sup> The weight of the pyrolyzed material, which corresponds to the lethal effect, is the weight of the material, which effectively causes death. Because the toxicity of the gases increases with increasing char yield for polymers containing nitrogen, it is believed to be indicative of the presence of toxicants other than CO and HCN. Many workers have come to similar conclusions in their toxicological experiments with various cellular plastics and polymers.<sup>64,65</sup> Small-scale and large-scale experiments on the toxicity of polyurethane foams were conducted by Levin et al.<sup>56</sup> In the small-scale experiments, mortality depended on the amount of material burned; thus, the amount of material required to produce 50% mortality (LC50) was measured. LC50 for the polyurethane foam was 6.6 g, lower than that for nylon (7 g), acrylic (8 g), cotton (10 g), or wood (11 g).

#### FIRE RETARDANCY OF POLYURETHANE FOAMS

Fire retardancy requires the disruption of the burning process at one or more stages so that the process is terminated within an acceptable period of time. In general, three methods have been employed to render polyurethane foams fire-retardant. The reactive fire retardants participate in the foaming reactions and build chemically into the polymer molecule together with the other starting foam components. This prevents them from bleeding out of the polymer, and their fire retardancy is thus retained. They have no plasticizing effect and do not affect the thermal stability of the foam structure. Basically, these compounds are based on phosphorus and halogen. Phosphorus is present in the form of phosphate, phosphite, phosphinate, phosphonate, phosphonitride, and organophosphorous polyols. Halogens are effective in brominated or chlorinated forms or in a combination of both derivatives. The nonreactive fire retardants are not believed to participate in the foaming reaction, and they provide a degree of fire retardancy on a weight basis. If they are compatible with the polymer, they act as plasticizers; otherwise, they are considered fillers. They are often volatile or tend to bleed, so their fire retardancy may be gradually lost during the aging process. A wide variety of nonreactive additives based on phosphorus, halogens, nitrogen, sulfur, boron, aluminum, antimony, carbon, and silicones are being used. A combination of reactive and additive fire retardants produces a synergistic effect. Synergists have achieved great importance because they are less expensive than actual fire retardants, and

the addition of reactive fire retardant can be greatly reduced in the presence of a synergist, without any reduction of the fire-retardant effect.<sup>66</sup> A flammable foam can also be rendered fire-retardant by the protection of its surface with fire-retardant coating compositions.

#### Phosphorus-containing additives

##### Phosphorus

Inorganic phosphorous compounds are used for fire retardants either by blending with polyurethane components or by reacting into the main polymer chain. Piechota<sup>67</sup> was the first to investigate polyurethane foams and found red phosphorus to be very effective as a fire retardant. Although red phosphorus is used in polyurethane foam formulations, phosphorous compounds in the form of phosphates, phosphites, phosphonates, phosphonitrides, phosphoric acid, phosphonic acid, and halogen-containing phosphorous compounds are more effective. As reported in the literature,<sup>68,69</sup> the general mechanism of the fire-retardant action of phosphorus in polyurethane foams is similar to that in other polymers. Phosphorus-containing fire retardants mainly influence the reactions taking place in the condensed phase. Thus, phosphorus appears to retard the combustion mechanism occurring primarily in the condensed phase in three steps.<sup>70</sup> First, phosphorus may form anhydrides of phosphoric and related acids by thermal decomposition, and they may act as dehydrating agents, extract water from the pyrolyzing polymer, and promote char formation. The presence of char will result in lower heat transfer from the flame to the condensed phase, and this will interfere with the heating and decomposition process. Second, phosphoric and related acids may act as a heat sink because they retard the oxidation of carbon and oxygen to carbon dioxide; this will decrease the heating process. Third, the acids may form a thin glassy or liquid protective coating on the condensed phase, thus lowering oxygen diffusion and heat and mass transfer between the gas and the condensed phases. This barrier disturbs the oxidation process of carbon at the carbon monoxide stage, thus decreasing the exothermic heat of combustion. According to Granzow,<sup>71</sup> the phosphorus-containing fire retardants can also be effective in the gas phase. Phosphorous compounds break down into small fragments that can be detected in the gas phase. These fragments catalyze the recombination of hydrogen atoms into hydrogen molecules and thus reduce the energy of the flame. Weil<sup>72</sup> reviewed the fire-retardant mechanism of phosphorus-containing compounds. A recent review of the phosphorus-

based fire retardants was written and published by Levchik and Weil.<sup>73</sup>

The addition of 1.5 wt % phosphorus increases the char formation of a polyurethane foam from weak to strong. Weight loss also is reduced from 100 to 26% because of more char formation. The incorporation of phosphorus is effective when its concentration is in the range of 1.0–1.5 wt % in the total formulation, and a further increase seems to produce no further benefit.<sup>74</sup> However, scorch generation is the main problem in phosphorus-modified fire-retardant urethane foams.<sup>75–77</sup> Ravey and Pearce<sup>50</sup> incorporated phosphorus into a polyurethane foam formulation using H<sub>3</sub>PO<sub>4</sub> (85%) in acetone, with the concentration ranging from 0.2 to 5.6%. TGA showed that the presence of phosphorus reduces the thermal stability of the polyurethane foam. A vertical flame test confirmed that the burning length is also reduced from 100 to 18 mm after 60 s of exposure. The phosphorous compounds hinder the flow of the molten polymer and thereby prevent flaming drips; this improves performance according to ASTM D 1692 59T, BS 4735, and DIN 4102-B3 fire tests. The main characteristic of a red-phosphorus-containing polyurethane foam is that the foam does not melt during fire exposure but forms a protective crust. The addition of red phosphorus does not change the mechanical properties of such foams. The main disadvantages of red phosphorus as a fire retardant for polyurethane foams are its color and generation of highly toxic phosphine through a reaction with water.<sup>68</sup> A stabilizer such as a metal oxide can be used successfully to minimize trace amounts of phosphine. It has been found that copper oxide, cadmium oxide, or zinc oxide can efficiently transform phosphine into phosphoric acid.<sup>68</sup> The efficiency of red phosphorus can be increased if it is dispersed in  $\delta$ -caprolactam before polymerization.<sup>78</sup> The presence of red phosphorus reduces the polymer molecular weight, enhancing the fire-retardant efficiency of phosphorus to the maximum. The limited oxygen index (LOI) values of polyurethane foams containing 0.3, 0.5 and 0.7 wt % phosphorus were 20.5, 21.8, and 22.8, respectively, whereas without phosphorus the value was 16.5.<sup>79</sup> Similarly, LOI and TGA values were also determined for a polymethylene polyphenyl isocyanate (PAPI) based phosphorus-containing polyurethane foam, which showed better fire performance than foams based on 4,4'-diphenylmethane diisocyanate (MDI) and TDI. A polyurethane foam containing 1.54–2.0 wt % phosphorus was self-extinguishing in air.

Phosphorus shows synergistic action with halogen-containing compounds and thus increases the fire retardancy of polyurethane foams. It has been suggested that a phosphorus/halogen molar ratio of 1 : 1 is optimal. It has been speculated that P<sub>4</sub> spe-

cies are derived from the thermal decomposition of red phosphorus, which reacts in the presence of O<sub>2</sub> with HCl to yield PCl<sub>3</sub>, a well-known flame inhibitor. The synergistic effect has also been observed with some metal oxides such as MgO.<sup>115</sup> MgO catalyzes the reaction of red phosphorus with O<sub>2</sub> in the presence of moisture to yield phosphoric acid and its derivatives. Thus, MgO induces a higher rate of phosphoric acid formation, which increases the charring rate on the burning polymer surface. Vanadium oxide<sup>80</sup> has been found to be an efficient synergist with red phosphorus. Vanadium oxide facilitates the oxidation of phosphorus, leading to the formation of vanadium phosphate, which in turn catalyzes charring of the polymer. Levchik et al.<sup>81</sup> found that apart from vanadium pentoxide, molybdenum trioxide and tungsten trioxide are mildly beneficial coadditives to phosphorus. Depending on the concentration, these additives improve the LOI rating. The general assumption is that phosphorus mostly shows fire-retardant properties only in the presence of an oxygen-containing polymeric substrate.<sup>78</sup> However, the researchers, noting the limited efficiency of phosphorus in nonoxygenated polymers, suggested another mode of action. On heating, phosphorus is depolymerized almost quantitatively into volatile white phosphorus, which diffuses from the polymer to the burning surface, at which it is oxidized into H<sub>3</sub>PO<sub>4</sub> derivatives. At the burning polymer surface, the formed H<sub>3</sub>PO<sub>4</sub> acts as a char-forming agent, thus physically limiting oxygen access and fuel volatilization. Although the mechanism of interaction of red phosphorus and polyurethane foam is not very clear, by finding parallel trends for the LOI and combustion index measured in a milder oxidizer (N<sub>2</sub>O), they experimentally showed that red phosphorus provides a condensed- and gas-phase fire-retardant action.<sup>79</sup> Furthermore, the amount of char produced from the polyurethane foam increases with an increasing content of phosphorus.

#### Phosphorus-containing organic products

A high-level effort is shown in the patent literature (Table III) with respect to organophosphorous fire retardants for polyurethane foams. Structurally bonded organophosphorous-based polyols are more effective than the nonreactive additives.<sup>7</sup> Foams formed from such polyols are more effective in retaining their fire retardancy after aging. Trivalent phosphorus (phosphines, phosphinites, phosphonites or phosphites, and phosphonates) usually exhibits low thermooxidative stability; therefore, it is a perfectly suitable fire-retardant additive for polyurethane foams. Curtat et al.<sup>110</sup> studied the fire-retardant effect of phosphine oxides and phosphonates in rigid polyurethane foams. The experimental



results have shown less weight loss than for other fire retardants by the formation of polyphosphate layers in char, which offer greater resistance to the diffusion of fuel volatiles and raise the mechanical stability of char. Phosphate polyols such as chlorinated aliphatic phosphites [tris(2-chloroethyl phosphate)s] have been used successfully.<sup>111</sup> The main disadvantage of phosphate polyols is that the presence of even a small amount of water causes hydrolysis. Hydroxyethyl phosphate and dimethylphosphite can be made to react with pentaerythritol or trimethylol propane to obtain phosphate polyols with as much as 20% phosphorus.<sup>112</sup> Phosphine oxides, in contrast to phosphites, are among the most thermally and oxidatively resistant organophosphorous products. However, their relatively high cost probably prevents their use as fire retardants for polyurethane foams.

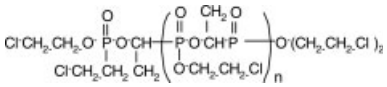
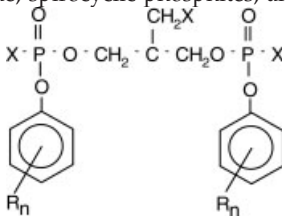
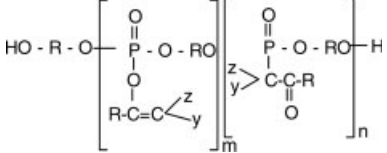
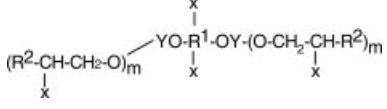
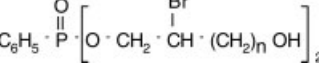
Most phosphites used in the polyurethane foams are ultimately converted into phosphonates. Amino-methyl phosphonate and dimethylmethyl phosphonate (DMMP) have been used as reactive fire-retardant additives to polyurethane foams and have been found to be very effective.<sup>113</sup> DMMP contains 25% phosphorus, and only about 8 wt % is required in rigid foam formulations. Diethylethyl phosphonates or triethyl phosphates are also used for the same purpose. Bayer recently introduced dimethylpropyl phosphonate and diethylpropane phosphonate as halogen-free fire retardants for urethane foams.<sup>114</sup> Triphenyl phosphate, isopropylphenyldiphenyl phosphate, tricresyl phosphate, and trixylene phosphate have found some use in rigid foam formulations.<sup>115</sup> Approximately 15% phosphonate fire retardant was required to introduce 1.5–2.0% phosphorus into the finished foam. The burning length of the foam decreased to 8 mm, and the self-extinguishing time was less than 15 s according to ASTM D 1692-59T. Another phosphonate that contains phosphorus connected to hydroxyl groups has been claimed to produce urethane foams with good fire retardancy. Phosphorus-sulfur additives such as  $P_4S_{10}$ ,  $P_4S_7$ , and  $P_4S_3$  have also been suggested for polyurethane foams.<sup>116</sup> It has been reported that 2% phosphorus, 6% antimony, 10% bromine, and 13% chlorine alone are necessary for the nonburning of urethane foams. Diisocyanates and triisocyanates such as phosphoryl triisocyanate have also been used to introduce phosphorus into the polyurethane foam structure.<sup>117</sup> Bakhitov et al.<sup>118</sup> described the preparation of phosphorus-containing urethanes from equimolar amounts of tris(hydroxymethyl) phosphine, tris(hydroxymethyl) phosphine oxide, tetrakis(hydroxymethyl) phosphonium chloride, hydroxymethyl phosphonic acid, and diisocyanates. Flexible urethane foams have also been prepared with phosphorus contents of 0.3–1.0% with a phosphate-containing polyol

(11.1%), diethyl-*N,N*-bis(2-hydroxyethyl)-aminomethyl phosphonate (12.2%), and tris(dipropylene glycol) phosphite (7.1–7.3% P). With a 3% phosphorus content in the urethane foam, the LOI values of phosphate-, phosphite-, and phosphonate-containing urethane foams are 20.9, 21.0, and 21.2, respectively; however, at a level of more than 4% phosphorus, there is a considerable increase in the LOI value of a phosphate-containing urethane foam (23.1), whereas LOI values of phosphite- and phosphonate-containing urethane foams remain unchanged. A TGA study of phosphate-, phosphite-, and phosphonate-containing foams showed that they decompose at 180, 140, and 200°C, respectively, and at 450°C, a phosphite-based foam shows maximum weight loss (82%), whereas a phosphate-based foam shows minimum weight loss (63%).<sup>119</sup> TGA and oxygen index studies of polyurethane foams containing poly[bis(carboxylatophenoxy) phosphazene], diethanolaminomethyl phosphate, and trisodium pyrophosphate have shown higher char yields and increased values of the oxygen index.<sup>120,121</sup> The phosphorus contents of fire-retardant urethane foams can be reduced greatly in the presence of halogens, which exhibit synergistic action with phosphorus. Usually, a 1.5% concentration of phosphorus is required to produce fire-retardant polyurethane foams in the absence of halogens. The content of phosphorus can be reduced to 1.0% with the addition of 10–15% chlorine, and 4–7% bromine may lower the need for phosphorus to about 0.5%. Thus, phosphorus-bromine synergistic systems are more efficient than phosphorus-chlorine systems, although the quantities of chlorine and bromine are reduced considerably when they are used in combination with  $Sb_2O_3$ .<sup>122</sup> LOI values of polyurethane foams containing 5% phosphorus in the form of phosphate, phosphonate, and phosphite in combination with 2% bromine increase from 19.5 to 23.2, 22.7, and 21.4, respectively. These LOI values indicate that bromine is more effective in combination with phosphates and phosphonates than with phosphites. Maximum char yields have been reached with 5% phosphorus from both phosphate and phosphonate with 2% bromine, at which maximum fire retardancy has also been observed. Foams containing phosphite produce about 30% char and are insensitive to the addition of bromine.<sup>119</sup> These foams exhibit fire retardancy just sufficient to pass the ASTM D 1692-67T flame test. A flexible polyurethane foam containing Phosgard 2XC20 (Monsanto Chemical Co.) with 10.6% phosphorus and 35.2% chlorine passes the flammability test (DOC FF-2-70 tablet test), and the diameter of the hole burned out has been reported to be 3.4 in.<sup>123</sup> Larsen and Ecker<sup>124</sup> studied the thermal stability and decomposition temperatures of polyurethane foams containing haloalkyl phosphates such as tris(2,3-dibromopropyl) phosphate, tris(tribromoneopentyl) phosphate, and pentabromodiphenyl oxide.

**TABLE III**  
**Phosphorus Reactive Products and Their Synergistic Combinations Disclosed in the Patent Literature**

Number	Fire retardant	Best example	Reference
1	Phosphorus-containing polyol and oxide-modified sucrose	No example has been reported. Flame-resistant polyurethane foam with 90% closed cells, good dimensional stability, and a K factor less than 0.13	82
2	Reaction product of methyl 3-(dimethylphosphono) propionate and polyoxypropylene sucrose containing 5.2% phosphorus $\begin{array}{c} \text{CH}_3\text{O} \\ \text{CH}_3\text{O} \end{array} \text{P} \begin{array}{l} \text{O} \\ \parallel \\ \text{CH}_2-\text{CH}_2-\text{C} \\ \parallel \\ \text{O} \end{array} \text{OCH}_3$	Foam containing 2.6 wt % phosphorus and classified as nonburning according to ASTM D 1692-59T	83
3	Hydroxyl phosphonate, a mixture of trimethylolpropane(trimethylol-propane butane phosphonate) $\begin{array}{c} \text{CH}_2\text{OH} \\   \\ \text{CH}_3-\text{CH}_2-\text{C}-\text{CH}_2-\text{P} \begin{array}{l} \text{O} \\ \parallel \\ \text{O}-\text{CH}_2 \\ \text{O}-\text{CH}_2 \end{array} \text{C} \begin{array}{l} \text{CH}_2\text{OH} \\   \\ \text{CH}_2\text{OH} \end{array} \\   \\ \text{CH}_2\text{OH} \end{array}$ $\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3-\text{P} \begin{array}{l} \text{O}-\text{CH}_2 \\ \text{O}-\text{CH}_2 \end{array} \text{C} \begin{array}{l} \text{CH}_2\text{OH} \\   \\ \text{CH}_2-\text{CH}_3 \end{array} \end{array}$	Flame-resistant polyurethane rigid foam having a burn length of 33 mm according to UL test	84
4	2-Chloro-1-hydroxyl ethane-1,1-diphosphonic acid or diphenyl 1,2-dihydroxyethane-1,1-diphosphonate $\begin{array}{c} \text{O} \\ \parallel \\ \text{R}_1 \text{R}_2 \text{C}-\text{C} \begin{array}{l} \text{P} \begin{array}{l} \text{O} \\ \parallel \\ \text{OR}_3 \end{array} \\ \text{P} \begin{array}{l} \text{O} \\ \parallel \\ \text{OR}_3 \end{array} \end{array} \end{array}$	Rigid polyurethane foam which exhibits a reduced burning rate and can be classified as nonburning	85
5	Terephthalic acid-polyoxypropylene alkoxy diphosphates	Self-extinguishing rigid polyurethane foam (phosphorus 0.36 wt %) with a burning extent of 38 mm according to ASTM D 1692-59T	86
6	Phosphorus (15%) and chlorine (12%) containing polyol obtained by the reaction between Union Carbide Niax polyol, propylene oxide-ethylene oxide adduct, bis(β-chloroethyl) vinyl phosphonate, and vinyl chloride	Resultant polyol can be used to form polyurethane foams having reduced flammability	87
7	Phosphated starch polyether containing 4.2% phosphorus with a hydroxyl number of 303	Resultant foam is nonburning according to ASTM D 1692-59T and has a 22-mm extent of burning	88

**TABLE III**  
Continued

Number	Fire retardant	Best example	Reference
8	Polyglycol hydrogen polyphosphonate such as tris(dichloropropyl) phosphate and chlorinated polyphosphonates 	Self-extinguishing foam classified by ASTM D 1692 with a burning rate of 2.3 mm/s	89
9	Vinyl chloride/bis(β-chloroethyl) vinyl phosphonate copolymer	Resultant urethane foam confers flame retardancy and lessens discoloration	90
10	Polymeric halogenated organophosphorous diol, a reaction product of chlorine or bromine, spirocyclic phosphites, and diol 	Flexible urethane foams so made are characterized by improved flame-retardant properties	91
11	Polyalkylene glycol vinyl phosphate 	Foam self-extinguishing in 52 s after a 70-mm burn with a burning rate of 1.42 mm/s when tested according to ASTM D 1692	92
12	Mixture of propylene oxide, tetrabromophthalic anhydride based polyol, and bis(2-hydroxyethyl) aminomethyl phosphonate with hydrated alumina	Flame-retardant rigid urethane foam that meets the 25-flame spread test of the ASTM E 84 tunnel evaluation	93
13	An adduct of polyepoxide (reaction product of epichlorohydrin and bisphenol A) and phosphorus- and halogen-based compounds 	Flame-retardant urethane foams containing 0.5–25.0% flame-retardant compounds	94
14	Trisdibromopropyl phosphate	Flame-resistant foam with a rise time of 90 s and a tack-free time of 15 min	95
15	Blend of bis(hydroxyl and halo alkyl) aryl phosphonates and tris(dibromopropyl) phosphate 	Resultant flame-retardant urethane foam having 0.9–1.0% phosphorus, 2.7% chloride, and 1.9% bromine	96

**TABLE III**  
Continued

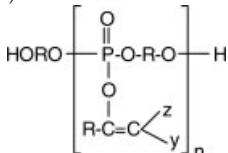
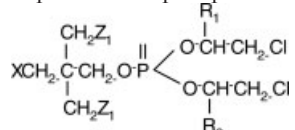
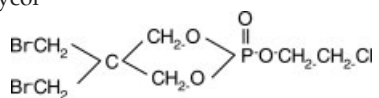
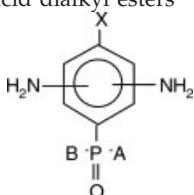
Number	Fire retardant	Best example	Reference
16	Reaction mixture of aromatic polyisocyanates having halogen-containing side chains such as 2,4-diisocyanatobenzotrichloride and 2,6-diisocyanatobenzotrichloride mixture	Fire-retardant urethane foams with good physical and mechanical properties	97
17	Poly(dipropylene glycol- $\beta,\beta$ -dichlorovinyl phosphate)	Fire-resistant urethane foams	98
			
18	13.5% phosphate oxide glass powder, 4.6% dicyandiamide, and melamine	Self-extinguishing, low-smoke urethane foam with an LOI value of 24.0 and maximum obscuration of 78% rated according to ASTM D 1692, ASTM D 2863, and ASTM D 2843	99
19	Bis(hydroxymethyl) methyl phosphine oxide	Urethane foam exhibits excellent flame-retardant properties	100
20	Polyalkylene glycol polyphosphorous compounds	Urethane foams with improved flame-retardant properties	101
21	Triesters of pentavalent phosphorus acid	Flame-retardant urethane foams with a 50-mm average char length in the California vertical burn test	102
			
22	Vinyl phosphate ester of dibromoneopentyl glycol	Urethane foam extinguished in 80–90 s with a burned length of 60–70 mm and a burning rate of 0.72 mm/s according to ASTM D 1692	103
			
23	2-Chloroethyl phosphate ester, a reaction product of 2-chloroethanol and phosphorochloridite	Flame-retardant rigid urethane foam with an LOI value of 24.9	104
24	Salts of benzene phosphonic acid and melamine	No flame initiation and no flame spread when tested in the flame of a Fisher-type burner	105
25	Phosphonic acid dialkyl esters	Self-extinguishing urethane foams having a burn length of 83 mm, an extinction time of 44 s, and a residue of 7.9% according to ASTM D 1692	106
			



TABLE III  
Continued

Number	Fire retardant	Best example	Reference
26	Microcapsules containing tris (2'3 dihalopropyl) phosphate	The resulting urethane foams are self-extinguishing	107
27	Diethyl- <i>N,N'</i> -bis(hydroxyethyl) amino-methyl phosphonate in combination with a mixture of substituted amines	Flame-retardant urethane foams having a burn distance of 0–4 mm according to the ASTM D 1692–68T test	108
28	Phosphorus–halogen-based or phosphorus- and nitrogen-based discrete chemical compounds	Flame-retardant flexible polyester foams	109

These foams decompose thermally in the temperature range of 160–234°C, and no significant differences have been found between compounds that contain only chlorine and those that contain both chlorine and bromine. Weil et al.<sup>125</sup> recently reviewed phosphorus-, chlorine-, and bromine-based fire retardants and their mode of action in flexible and rigid polyurethane foams such as tris(1,3-dichloro-2-propyl) phosphate, bromoneopentylchloro(bromo)ethyl phosphate, tris(2-chloroethyl) phosphate, tris(1-chloro-2-propyl) phosphate, and diethyl bis(2-hydroxyethyl)aminomethyl phosphonate. Ravey et al.<sup>126</sup> studied fire retardation by tris(1,3-dichloro-2-propyl) phosphate in flexible polyurethane foams in both condensed and gas phases using candle-like and top-down burning. Many phosphorus–halogen compositions are additives rather than reactive fire retardants. Tris(monochloro-propyl) phosphate, tris(2-chloroethyl) phosphate, tris(1-chloro-2-propyl) phosphate, tris(chloroisopropyl) phosphate, and especially tris(dibromopropyl) phosphate are among the most widely used fire-retardant additives. Tris(2-chloroethyl) phosphate and tris(1-chloro-2-propyl) phosphate are fairly low viscosity liquids. Tris(1-chloro-2-propyl) phosphate is a much more suitable fire-retardant additive for polyurethane foams than tris(2-chloroethyl) phosphate because of its hydrolytic stability and lack of reactivity toward the amine catalyst.<sup>127</sup> The addition of lithium salts has been found to improve heat and humidity resistance. It has also been found that fire resistance does not increase proportionally with increased phosphorus content, and maximum fire retardancy may be reached with a phosphorus content of 1–2%.<sup>119</sup>

#### Phosphonitrides

A highly crosslinked iminophosphazene can be prepared by a severe thermal treatment of aminophosphazene with the elimination of ammonia. This type of product has a chemical structure that approxi-

mates  $(PN_2H)_m$  and is called phosphasm. It is a lightly colored and very thermally stable product, so it can be incorporated into polyurethane foams to render them fire-retardant. The fire-retardant efficiency of phosphasm is similar to that of red phosphorus in urethane foams if it is compared on the basis of the phosphorus content in the fire-retardant formulation. Both red phosphorus and phosphasm provide an increase of LOI from 16.5 to about 23.0 with a 1.0% phosphorus content. However, compared to red phosphorus, phosphasm has the advantages of a light color and freedom from phosphine release. The fire-retardant performance of phosphasm has been improved by its use in combination with a novolac-type phenol–formaldehyde resin and zinc borate. Urethane foams can be rendered fire-retardant by the replacement of ordinary polyols with a reactive phosphonitride-substituted polyol such as tetrakis(hydroxymethyl) phosphonium chloride, which has been evaluated as a prereactor with a polyol and used in place of ordinary polyols.<sup>128</sup> Phosphorous oxynitride is another phosphorus–nitrogen-containing product that is effective for fire retardancy in urethane foams. It can be easily prepared via the heating of phosphoric acid with urea or melamine at 750°C or via the heating of ammonium phosphate at about 600°C.<sup>129</sup> The mode of the fire-retardant action of phosphorous oxynitride is believed to be its tendency to create a low-melting glass on the polymer surface.<sup>130</sup>

#### Inorganic phosphates

Monoammonium phosphate, diammonium phosphate, and triammonium phosphate are water-soluble and do not dissolve in the urethane components, but urethane foams containing these phosphates survive humid aging with good fire retardancy.<sup>7</sup> However, on total immersion in running water, the monoammonium, diammonium, and triammonium phosphates can be extracted from the foam, and the

resulting flame spread values are similar to those of conventional foams. The water solubility of these phosphates is largely overcome by the use of high-molecular-weight APP.<sup>131</sup> Foams containing APP are self-extinguishing even after 2 weeks of immersion in running water. APP works through a solid-phase mechanism and provides lower smoke compared to halogen-based fire retardants. APP formulated with melamine cyanurate demonstrates a rapid decrease of the heat release rate and rate of weight loss in flexible and rigid polyurethane foams under a cone calorimeter.<sup>132</sup> Miles and Lyons<sup>7</sup> compared some nonreactive inorganic phosphorus-containing fire retardants (APP) with some organophosphorous fire retardants in sucrose polyether polyol based rigid urethane foams. Urethane foams treated with liquid organophosphorous fire retardants and solid inorganic (APP) fire retardants (both containing 1.8% phosphorus) lose about 15 and 10% of their weight, respectively, when tested according to the vertical-bar flammability test. However, after 7 days of immersion in water, the flame spread of organophosphorous-fire-retardant-containing foams increases greatly, whereas inorganic-fire-retardant (APP)-containing foams experience very little increase in flame spread. APP is widely used in fire-retardant coatings because of its ability to catalyze the charring of organic materials and to produce intumescent protective char.<sup>133</sup> The thermal insulation properties of intumescent char have been measured with a modified cone calorimeter cell, which allows monitoring of the temperature on the bottom side of a specimen.<sup>134</sup> These experiments have shown that APP can efficiently decrease heat transfer to the polymer surface, and this makes a urethane foam containing APP decompose more slowly than a conventional polyurethane foam. Urethane foams containing 5% APP in combination with 25% pyromellitic anhydride on burning produce 28% char with a moderate quantity of smoke.<sup>135</sup> Some inorganic coadditives such as alumina trihydrate (ATH), manganese dioxide, zinc carbonate, calcium carbonate, manganese carbonate, ammonium carbonate, antimony trioxide, arsenic oxide, and calcium sulfate have also been evaluated. If APP added to urethane foams at a concentration of 20–30 wt % of the foams is partially substituted by one of the coadditives at a concentration of 1.5–3.0%, this leads to an increase in fire performance. These coadditives decompose endothermically under the influence of heat, giving off nonflammable gases such as CO<sub>2</sub>, SO<sub>2</sub>, and HCl. These gases act by diluting the mixture of flammable gases and shield the surface of the polymer against oxygen attack. Mechanistic studies have shown that these coadditives react with poly(phosphoric acid) produced from APP, probably crosslinking them and increasing the viscosity. This

leads to the favorable morphology of the intumescent char, which becomes less voluminous but more heat-protective and mass-transfer-restrictive for combustible gases. At higher concentrations of the coadditives, the intumescent char becomes rigid and cracks upon solidification and loses protective properties because of the formation of crystalline phosphate, which leads to a decrease in the char flexibility.<sup>136</sup> Applications of phosphorus as fire-retardant additives for polyurethane foams reported in the patent literature are shown in Table IV.

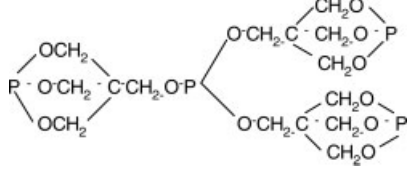
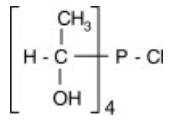
### Halogen-containing additives

A wide variety of halogen-containing products have been reported in the technical literature as fire retardants for polyurethane foams.<sup>74,144</sup> The effectiveness of halogen-containing fire retardants increases in the order of F < Cl < Br < I. Fluorine- and iodine-based fire retardants are not used in practice because fluorine has strong bonds to carbon and iodine is attached to carbon quite loosely. Out of the two remaining halogens, bromine is more effective than chlorine because of its weaker bonding to carbon, which enables it to interfere at a more favorable point in the combustion process.<sup>145</sup> Chlorine and bromine can be used alone or in combination with synergistic metal oxides, metal salts, phosphorus-containing compounds, and high-charring agents. Petrella<sup>146</sup> and Dixon-Lewis<sup>147</sup> suggested three basic mechanisms of fire-retardant action of halogen-containing compounds in polyurethane foams:

1. Generation of lower energy free-radical chain-terminating agents.
2. Promotion of char formation through dehydrogenation reactions.
3. Formation of a hydrogen halide noncombustible protective layer that acts as a barrier between the fuel gas and condensed phases.

Halogens containing fire-retardant additives are less effective than phosphorus fire-retardant additives in polyurethane foams.<sup>74</sup> The average quantities of fire-retardant elements required to render polyurethane foams self-extinguishing are shown in Table V. To achieve satisfactory fire retardancy in polyurethane foams, a relatively high level of halogen additives is needed together with the metal oxide synergists, which can lead to inferior mechanical properties. High concentrations of fire-retardant halogen additives are at least partly responsible for reducing the stability of the polymer. A main disadvantage of some halogenated fire retardants in polyurethane foams is that they are extremely susceptible to hydrolysis, so the foam must be

**TABLE IV**  
**Phosphorus Flame-Retardant Additive Products Disclosed in the Patent Literature**

Number	Fire retardant	Best example	Reference
1	Bis(2-chloroethyl) benzyl phosphonate	Resultant foam with a cream time of 15 s, a rise time of 120 s, and a tack-free time of 140 s that is self-extinguishing and nonburning according to ASTM D 1692-59T	137
2	Tri-β-chloroethyl phosphate	Flame-retardant polyurethane foam	138
3	Pentaerythritol phosphite prepared from pentaerythritol and triphenyl phosphite	Flame-proof foam confirmed with the ASTM D 757-48 flame-proofing test	139
			
4	Tetrakis(hydroxymethyl) phosphonium chloride	Fire-retardant polyurethane foam	140
			
5	APP (water-insoluble)	Fire-resistant polyurethane foam containing 0.1–5% phosphorus	141
6	Red phosphorus	Fire-retardant rigid polyurethane isocyanurate foams tested according to DIN 4102	142
7	Phenyl bis(pentachlorophenyl iminoethyl) phosphite, a reaction product of triphenyl phosphite and <i>N</i> -pentachlorophenyl ethanol amine	Self-extinguishing polyurethane foam tested according to ASTM D 1692-59T	143

manufactured by methods that exclude water completely. Another disadvantage is their ability to produce corrosive combustion products. Halogen-containing fire retardants do not change the composition of the main degradation products but cause the appearance of toxic volatile products at lower temperatures.

### Chlorinated products

The principal chlorine-containing fire-retardant compounds in commercial use are chlorinated hydrocarbons and chlorinated cycloaliphatics. The main disadvantage of chlorinated fire retardants is that they have to be used in quantities that adversely affect the foam properties to provide a sufficient level of fire retardancy. Cycloaliphatic chlorine compounds are stable up to 260°C and have found widespread applications as reactive fire retardants. Technical publications and patent literature on reactive chlorinated fire retardants (Table VI) report that

hexachloroendomethylene tetrahydrophthalic acid is the most widely used chlorinated fire retardant for polyurethane foams.

It is a reaction adduct of maleic anhydride and hexachlorocyclopentadiene or tetrachlorophthalic acid containing about 35% chlorine formed by the Diels–Alder reaction. Tetrachlorophthalic acid and derivatives of chlorinated bisphenol A are also used

**TABLE V**  
**Average Fire-Retardant Element Requirement for Polyurethane Foam**

Elements	Percentage required
Phosphorus	1.5
Phosphorus and nitrogen	0.9–1.4 and 4–5
Chlorine	18–20
Bromine	12–14
Phosphorus and chlorine	1 and 10–15
Phosphorus and bromine	0.5–4–7
Chlorine and antimony chloride	4 and 4
Bromine and antimony chloride	2.5 and 2.5

TABLE VI  
Reactive Chlorinated Fire Retardants and Their Synergistic Combinations Disclosed in the Patent Literature

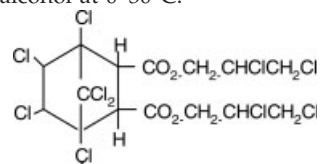
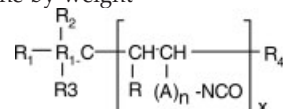
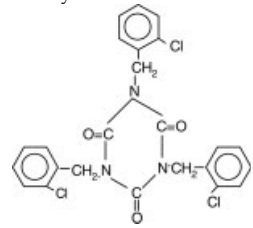
Number	Fire retardant	Best example	Reference
1	Crude 4,4,4-trichloro-1,2-epoxybutane containing 75% 4,4,4-trichloro-1,2-epoxybutane, 3% tetrachlorobutanol, 2% dichloroepoxybutane, and tetrachlorobutanol	Nonburning polyurethane foam with an 18-s cream time, a 121-s rise time, and an 111-s tack-free time tested according to the SPI torch test and ASTM D 1692 with a 25-mm burn extent	148
2	Chlorinated quasiprepolymer PAPI, AFPI, Mondur MR, and Carwinat 390P are the reaction products of organic polyisocyanates and monofunctional-chlorine-containing alcohols	Polyurethane foam with a 15-mm burn length in a flammability test with a cream time of 45 s, a rise time of 350 s, a tack-free time of 330 s, and a closed cell content of 93%	149
3	Chlorine-containing prepolymer prepared from 1,2-dichloroneopentyl glycol and an excess of polyisocyanate containing 13.9% chlorine and 31.2% NCO	Resultant foam containing 7.96% chlorine and rated nonburning by ASTM D 1692-67T	150
4	Halogenated TDI is a reaction mixture of undistilled halogenated TDI and toluene diisocyanate containing at least 20% chlorine by weight	Resultant foams exhibiting outstanding flame resistance because they contain 32% chlorine	151
5	Chlorine-containing diallyl chlorendate is obtained by the chlorination of diallyl chlorendate in the presence of butyl alcohol at 0–30°C.	Resultant foam with a cream time of 17 s, a rise time of 55 s, a tack-free time of 42 s, and a charred length of 25 mm when ignited to a blue flame according to ASTM D 1692-59T	152
			
6	4,4,4-Trichloro-2-bromobutyl isocyanate containing 37.85% chlorine by weight	Resulting foam containing 3–15% chlorine and 5–10% bromine by weight and showing nonburning characteristics when tested for flammability according to ASTM D 1692-59T	153
			
7	Polyhalogenide with antimony is the reaction product of chlorinated propylene trimer and tris(2-chloro ethyl) antimonite containing 15.23% chlorine and 2.47% antimony by weight	A uniform fine, closed-cell polyurethane foam having a density of 1.66 pounds per cubic foot that is nonburning according to the flame resistance test of ASTM D 1692-59T	154
8	Chlorine-containing organic isocyanate, a reaction product of <i>ortho</i> -chlorobenzyl chloride and sodium cyanate		155
			



TABLE VII  
Chlorine Flame-Retardant Additive Products Disclosed in the Patent Literature

Number	Fire retardant	Best example	Reference
1	Bis(2,4,4,4-tetrachlorobutyl) 3-chloropropionol	Self-extinguishing urethane foam with a burning rate of 1.1 mm/s according to ASTM D 1692	166
2	Bis(2-chloroethyl) nitrilo(trimethylene phosphonate) $\text{N}[\text{CH}_2 - \overset{\text{O}}{\parallel} \text{P} \cdot (\text{OC}_2\text{H}_5\text{Cl})_2]$	Rigid urethane foam with an LOI value of 27.0 exhibiting excellent flame-retardant properties	167
3	Reaction product of methylene chloride, glycidol, and chloromethyl phosphonic dichloride with tris(dibromopropyl) phosphate	Rigid urethane foam with a self-extinguishing time of 42 s and a burning rate of 1.2 mm/s	168

as reactive fire retardants. They are used to give about 18–20% chlorine, which is enough to render polyurethane foams fire-retardant. Other chlorinated products tried in urethane foams are hexachlorometaxylene, pentachlorophenol with epichlorohydrin, and chlorinated polyisobutylene.<sup>74</sup> The fire-retardant performance of chlorinated compounds can be enhanced further when they are used with an appropriate synergist. The choice of synergist generally is made from among antimony trioxide, ferric oxide, zinc oxide, and zinc borate. The antimony–halogen molar ratio of 1 : 3 was found to yield an optimal synergistic effect. Approximately 20% chlorine is required in urethane foams to produce nonburning foam, but when it is used in combination with  $\text{Sb}_4\text{O}_6$ , the chlorine level is reduced considerably. Dezzinger et al.<sup>156</sup> suggested that 4.4%  $\text{Sb}_4\text{O}_6$  and 3.8% chlorine are adequate to produce a fire-retardant foam. In another publication, 6.3%  $\text{Sb}_4\text{O}_6$  and 7% chlorine were reported to be enough to produce a nonflammable urethane foam.<sup>157</sup> The use of 5.9%  $\text{Sb}_4\text{O}_6$  reduces the chlorine requirement to 2.4% in chlorinated polyether polyol to produce a urethane foam with equal fire retardance.<sup>158</sup>

A polyurethane foam incorporated with 3,3'-dichloro-4,4'-diamino diphenylmethane shows good fire retardancy and passes the MVSS-302 test for motor vehicles. However, considering their nature from a health hazard point of view has led to the elimination of chlorinated diamine in automotive and other foam applications. Farrissey<sup>159</sup> prepared a fire-retardant rigid urethane foam using a blend of 4,4,4-trichloro-2-bromobutyl isocyanate (1 part) and PAPI (3 parts) with polyester polyol. Polyurethane foams containing trichlorophenol (11.7 or 10.8%) in combination with antimony trioxide (5 or 2.8%) have burning rates of 0.6 and 1.03 mm/s and are rated self-extinguishing by ASTM D 1692.<sup>160</sup> Urethane

foams based on polyether polyols modified with the 3,3,3-trichloropropylene oxide reactive fire retardant have been classified as nonburning by ASTM D 1692 and pass flame penetration and ASTM E 84 tests.<sup>161</sup> Urethane foams based on 4,4,4-trichloro-1,2-butylene oxide-modified polyol generate less smoke and are characterized by their ability to meet the requirements of flammability tests ASTM D 1692 and ASTM E 84 without affecting physical properties.<sup>162</sup> Pielichowski et al.<sup>163</sup> studied the thermal degradation and flammability of a 3-chloro-1,2-propanediol-based urethane foam using TGA, DSC, and LOI. A urethane foam containing 40% chlorinated diol showed enhancements of the initial decomposition temperature from 106 to 206°C, the char residue from 20 to 34%, and the LOI value from 20.5 to 25.8. The introduction of chlorinated diol into the urethane foam caused an increase in LOI values, which increased with an increase in the initial decomposition temperature and char residue. Flexible urethane foams incorporated with tetrakis (2-chloroethyl)ethylene diphosphate (30% chlorine and 13% phosphorus) showed increased thermal stabilities, as confirmed by TGA, and reduced burning rates according to ASTM D 1692 and MVSS-302 standard tests.<sup>164</sup> This fire-retardant additive remains initially inert during foam processing and interacts with the foam during the burning process. The incorporation of *trans*-1,2 dichloroethylene improves the fire performance of urethane foams.<sup>165</sup> Some chlorinated fire-retardant additives for polyurethane foams disclosed in the patent literature are shown in Table VII.

#### Brominated products

There are far fewer nonpatent literature references on brominated fire retardants in polyurethane

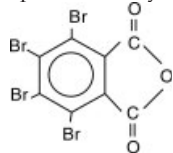
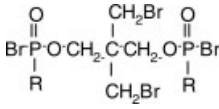
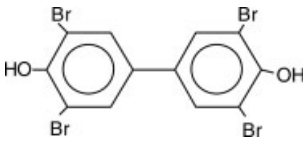
foams. Bromine compounds are better fire retardants than chlorine compounds because they are used in lower concentrations. Brominated fire retardants affect the physical and mechanical properties less than chlorinated fire-retardant compounds. Brominated compounds do not bleed and can be readily incorporated as both reactive and additive fire retardants. Aliphatics and cycloaliphatics are the main bromine-containing fire retardants. Cycloaliphatic bromine compounds are better fire retardants than aliphatic bromine compounds because they provide a high degree of fire retardancy to polyurethane foams. Rigid urethane foams based on tetrabromoendomethylene tetrahydrophthalic anhydride,<sup>169</sup> 2,3-dibromo-1-propanol,<sup>170</sup> and brominated allyl glucoside polyether<sup>171</sup> exhibit good fire resistance and humidity aging. Pape et al.<sup>172</sup> reported a series of results for a polyol from tetrabromophthalic anhydride polyester used to produce a nonburning urethane foam; however, it cannot be used in pre-packaged foam systems because of the insolubility of  $Sb_4O_6$ , which has a tendency to settle down. The addition of 2 or 5% dibromoneopentyl glycol to the urethane foams increases the LOI value from 19.5 to 20.4 or 20.8, respectively. These foams produce 58% char at 300°C and 25% char at 500°C and are rated self-extinguishing by ASTM D 1692-67T. A series of bromine-containing polyols such as 3,4-dibromocyclohexane-1,1-dimethanol, brominated propylene oxide adducts of 3-cyclohexene-1,1-dimethanol, tetrabromophthalic anhydride/diethanolamine propylene oxide amide-ester adducts,  $\beta,\gamma$ -dihydroxypropyl 2,3,7,8-tetrabromooctyl ether, and 1,2,5,6-tetrabromo-3,4-dihydroxyhexane have been studied for their fire-retarding efficiency when incorporated as part of the polymer in flexible and rigid urethane foams.<sup>173</sup> The LOI values of 2.0% and 2.5% bromine-containing urethane foams increase to 21.0 and 21.2, respectively, and they are rated self-extinguishing by ASTM D 1692. Urethane foams containing about 3.0% bromine from brominated polyols show slightly lower porosity, 91% compression sets, and somewhat greater load-bearing properties and tensile strength. Walch and Lesceux<sup>174</sup> studied the fire performance of a rigid urethane foam modified with the IXOL B251 halogenated polyether polyol (32% Br, 6.8% Cl, and 1.1% P) as a permanent active fire retardant, using the ASTM D 2863 oxygen index test, ASTM E 662 smoke density chamber test, ASTM 30145 Butler chimney test, DIN 4102 B2, and ASTM E 84 tunnel test. The resultant rigid urethane foam was rated class I in the Butler chimney test, had a low flame spread with a retained weight higher than 85%, and had LOI values ranging from 24 to 26. When urethane foams are incorporated with nonreactive brominated additives, 8–10% bromine produces self-extinguishing foams, whereas

12–14% bromine gives nonburning foams.<sup>74</sup> These bromine quantities can be reduced considerably when bromine is used in combination with antimony trioxide. More attention has been paid in the literature to the fire-retardant effectiveness of aliphatic and aromatic bromine compounds in urethane foams. A conventional rigid urethane foam has an LOI value of 20.5; however, this value increases to 22.7, 22.8, 22.6, 22.7, 22.8, 22.6, 22.7, 22.7, and 22.4 when it is incorporated with 2,3-dibromopropyl ether, 1,2,3,4-tetrabromobutane, 4-(1,2-dibromoethyl)-1,2-dibromocyclohexane, 1,2,5,6-tetrabromocyclooctane, 1,2,5,6,7,10-hexabromocyclododecane, 2,2-bis(bromoethyl)-3-bromopropanol, 2,2-bis(bromomethyl)-1,3-propanediol, dibromopropylether of tetrabromo bisphenol A, and hexabromobiphenyl, respectively. The prepared rigid foams contain 7.5% bromine; however, the differences in their oxygen index values show that aliphatic brominated compounds are more effective than aromatic brominated compounds.<sup>175</sup> Pentabrominated diphenyl ethers are also used predominantly in fire-retardant urethane foams.<sup>176</sup> Theodore et al.<sup>177</sup> found that decabromodiphenyl oxide (DBDPO) containing 83.3% bromine, when used as an inert fire-retardant additive, is quite effective in a thermoset polyester resin, an important ingredient of urethane foams. DBDPO has a high bromine content, excellent thermal stability, a minimal effect on physical properties, and less toxicity. A combination of DBDPO and antimony oxide exhibits a low heat release rate and smoke release rate in a flexible polyurethane foam under a cone calorimeter.<sup>178</sup> Brominated reactive and additive fire retardants disclosed in the patent literature are listed in Tables VIII and IX, respectively.

### Nitrogen-containing additives

The principal nitrogen-containing compounds of interest as fire retardants for polyurethane foams include melamine, urea, dicyandiamide, ammonium baborate, ammonium pentaborate, and APP.<sup>191</sup> The mechanism of the fire-retardant action of melamine in urethane foams has been claimed to take place in three stages.<sup>192</sup> Melamine sublimates at about 250°C.<sup>193</sup> Thus, the incorporation of melamine into a urethane foam formulation results in the liberation of vapors and gases. A 30 wt % concentration of melamine is sufficient to produce a self-extinguishing urethane foam. Urethane foams incorporated with 10, 20, or 30% melamine exhibit a burning rate of 2.1, 1.7, or 1.5 mm/s according to ISO 3582 and an oxygen index of 19.0, 22.0, or 24.0 according to ASTM D 2863, respectively. The use of melamine not only enhances the fire retardancy but also suppresses the smoke level.<sup>194</sup> Melamine exhibits good

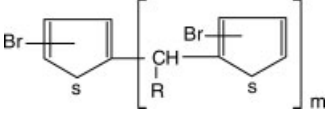
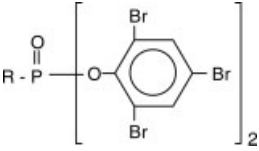
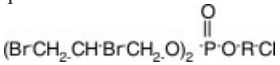
TABLE VIII  
Reactive Brominated Flame Retardants Disclosed in the Patent Literature

Number	Fire retardant	Best example	Reference
1	Prereaction product of polyaryl polyisocyanate and tetrabromophthalic anhydride product 	Fire-retardant polyurethane foam	179
2	Brominated spirocyclic phosphoramidite polyol 	Polyurethane foams characterized by improved flame retardancy properties versus the virgin polyurethane foam	180
3	2,3-Dibromo-2-butenediol-1,4 and tetrabromophthalic or dibromosuccinic acid	Nonburning polyurethane foam with a bromine content of 10.7%	181
4	Tetrabromobisphenol with a trimerization catalyst 	Fire-retardant urethane-modified polyisocyanurate foam	182
5	3,4-Dibromocyclohexane-1,1-dimethanol and 3-cyclohexene-1,1-dimethanol	Flame-retardant polyurethane foam containing 53.19% bromine	183
6	1–8% 1,2-dibromoneopentyl glycol of the weight of polyether polyol	Self-extinguishing flexible urethane foam rated by MVSS-302	184

fire retardancy when it is used with liquid fire retardants such as tris(2-chloropropyl) phosphate and tris(1,3-dichloroisopropyl) phosphate.<sup>195,196</sup> The fire-retardant efficiency of melamine in urethane foams also increases when it is used in combination with phosphorus-halogen additives. The addition of a phosphorus-halogen additive at a 3% concentration has the same effect on the fire performance of a foam as the addition of about 20% melamine. By the addition of 1, 3, or 5% thermolin in combination with 30% melamine in urethane foams, LOI values are increased to 23.5, 24.0, or 25.0, respectively. The fire performance of urethane foams modified with urea is better than that of foams modified with melamine. Urea and dicyandiamide have been evaluated both as single additives and in combination with melamine. Urea and dicyandiamide begin to decompose at 130 and 210°C, respectively, versus 250°C for melamine. The maximum weight loss of urea occurs in the temperature range of 150–250°C with the evolution of carbon dioxide, ammonia, and water vapors.<sup>197</sup> LOI of a foam containing 20% urea is 24.9, whereas that of a foam with the same quantity

of melamine is 22.1. A foam containing 20% dicyandiamide exhibits an oxygen index of 22.4, which is almost equal to the LOI value of a melamine-incorporated foam. Similarly, the burning rate in both the vertical and horizontal flammability tests of a urethane foam containing urea is 0.5 mm/s, whereas for foams incorporated with melamine and dicyandiamide, it is 1.2 and 1.0 mm/s, respectively. A recent study by Dick et al.<sup>198</sup> showed that a polyurethane foam modified with 10% melamine decomposes at a slightly lower temperature than a conventional foam in an inert atmosphere. There is little difference in the char yield with melamine-modified (20%) and conventional foams (19%). In addition to many flammability standards, high-performance liquid chromatography (HPLC) is also a very important tool for differentiating between combustion-modified and conventional polyurethane foams. Cody and Patterson<sup>199</sup> reported melamine-modified foam samples tested by HPLC. The results of an HPLC study on melamine-modified and non-modified urethane foams demonstrated that chemical tests can be used as a successful screen to

TABLE IX  
Brominated Fire-Retardant Additives Disclosed in the Patent Literature

Number	Fire retardant	Best example	Reference
1	Tetrabromoquinone	Resultant foam extinguished within 1–6 s after the flame has been removed	185
2	Brominated thiophene–ketone condensation product containing 67–68% bromine by weight 	Flame-retardant polyurethane foam tested according to ASTM D 2863-70 with an LOI value 24.0	186
3	Diglyceryl ester of tetrabromophthalic anhydride	Self-extinguishing urethane foam with an LOI value of 26.6 and 85.5% weight retention	187
4	Bis(2,4,6-tribromophenyl) phosphonates 	Self-extinguishing time of 44 s and burning rate of 1.2 mm/s according to ASTM D 1692	188
5	Bis(2,3-dibromopropyl) chloroalkyl phosphates 	Nonburning urethane foam with an LOI value of 27.5 and a burning rate of 0.0 when tested according to ASTM D 2863 and MVSS-302	189
6	A mixture of 15% 2,3-dibromopropanol and 85% tris(2,3-dibromopropyl) phosphate	Urethane foams with an LOI value of 23.5 and a burning rate of 0.0 according to MVSS-302	190

differentiate between combustion-modified and non-combustion-modified polyurethane foams. Melamine-modified urethane foams pass the BS 5852 test; however, they generate more smoke with some degradation in their physical and mechanical properties.<sup>200</sup> Nitrogen-containing fire-retardant products disclosed in the patents are listed in Table X.

### Silicon-containing products

Silicones are nonhalogen and noncorrosive and generate minimal smoke on fire exposure. Silicone compounds have a backbone that consists of alternating silicon and oxygen atoms. The silicone–oxygen linkage found in the backbone is the same as that found in high-temperature-resistant materials such as quartz, glass, and sand. The strong Si–O bond linkage enables these compounds to have thermal stability and to show properties that are fairly constant over a wide range of temperatures.<sup>204</sup> Clearly, it has been shown that the incorporation of a siloxane compound into the polyurethane foam backbone

provides enhanced thermal stability and fire-retardant characteristics.<sup>205</sup> Silicone compounds can contribute to fire retardancy in two ways: (1) as a silicone base for fire-retardant additives and (2) by incorporation as a part of the polymer backbone.<sup>206</sup> Recently, polyurethane/clay layered silicate nanocomposites have been prepared, and their thermal and combustion properties have been reported. A clay–silicate nanocomposite lowers the peak of the rate of heat release in cone calorimeter tests, and the fire-induced dripping of the nanocomposite sample is eliminated during the UL 94 test.<sup>207</sup> The most common and widely used silicones are based on polydimethylsiloxane. Oxygen index studies on polyurethane foams have shown that the oxygen index is highly dependent on the siloxane content in the finished product. A urethane foam with a 7.5% siloxane content has an LOI value of 20.8, which increases further up to 29.8 with the siloxane content at a level of 50%. A silicone–bromine combination exhibits better fire-retardant properties than a silicon–phosphorus combination in polyurethane foams. Silicones in



TABLE X  
Nitrogen-Containing Fire-Retardant Additives Disclosed in the Patent Literature

Number	Fire retardant	Best example	Reference
1	Diethyl- <i>N,N</i> -diethanolaminomethyl phosphonate and fumaric acid	Flame-retardant polyurethane foam with reduced smoke quantity	201
2	Alkylene oxide, urea, and tris(2-hydroxybutylene) amine	Self-extinguishing polyurethane foam in accordance with ASTM D 1692-59T	202
3	Diisocyanate mixtures modified with 1,3-dimethyl urea $\begin{array}{c} \text{CH}_3\text{NH}\overset{\text{O}}{\parallel}\text{C}\text{NHCH}_3 \\ \text{CH}_3\text{NH}\overset{\text{S}}{\parallel}\text{C}\text{NHCH}_3 \end{array}$	Self-extinguishing and smoke-resistant urethane foams tested according to ASTM D 1692 and JIS-A13	203

combination with platinum, fumed silica, quartz, magnesium carbonate, magnesium stearate, and zinc stearate are effective in improving the fire retardancy of polyurethanes. Urethane polymers with silicone and dibromoneophenyl diol show an LOI value of 25.7, which is reduced to 21.0 in a siloxane-phosphorated diol combination.<sup>208</sup> A survey of the patent literature on silicone-based fire retardants in polyurethane foams is shown in Table XI.

Silicone compounds act as fire retardants by forming a high quantity of char residue. Silicone compounds have an effect on the LOI values of polymers to some extent and cause a rise in pyrolytic char and improvement in char oxidation resistance. The enhanced char oxidation resistance arising from silicone is retained in the char and converted to a continuous protective silica layer during oxidation.<sup>208</sup> A TGA study of urethane foams incorporated with 30% polydimethylsiloxane silanol (OHPDMS) showed that these foams produce 26% char residue in an inert atmosphere and 33% char residue in air. A urethane foam incorporated with a brominated chain extender and OHPDMS under a cone test produces 61% char residue. A urethane foam incorporated with aminopropyldimethyl polydimethylsiloxane [ $\text{NH}_2(\text{CH}_2)_3\text{PDMS}$ ] shows a weight loss of 30% in the temperature range of 400–500°C and produces 36% sandlike residue at 650°C in an inert atmosphere.<sup>211</sup> The results obtained from TGA, DTA, DSC, and LOI show that the modification of polyurethane foams with OHPDMS and  $\text{NH}_2(\text{CH}_2)_3\text{PDMS}$  is a successful method for enhancing the fire-retardant properties of polyurethane

foams. The toxicity of siliconated materials has been studied, and it has been found that the silicone materials appear to be less toxic than phosphorus- and halogen-based fire-retardant compounds.

#### Miscellaneous additives

In the literature, some studies have been reported on ATH, which imparts fire-retardant and smoke-suppressant properties to polyurethane foams. ATH is nonhygroscopic, noncorrosive, nontoxic, and stable at room temperature; however, it undergoes endothermic decomposition at 200°C. Between 205 and 220°C, decomposition occurs slowly, and as the temperature exceeds 220°C, decomposition occurs rapidly; at this point, the hydroxyl groups of ATH begin to decompose endothermically through the liberation of 34.6% of chemically combined water and anhydrous alumina. ATH acts as a heat sink and retards polymer combustion and suppresses smoke by endothermic decomposition as follows:<sup>212</sup>

1. Water released during the endothermic decomposition of ATH dilutes the combustible gases and makes the combustion process more difficult.
2. Alumina obtained during the decomposition of ATH forms an insulating barrier on the surface of the burning polymer, which acts to insulate the polymer from fire.
3. The smoke-suppression characteristic of ATH is due to the dilution effect of water vapors on the combustible gases from the burning polymer.

TABLE XI  
Silicone-Containing Flame-Retardant Additive Products Disclosed in the Patent Literature

Number	Fire retardant	Best example	Reference
1	Cyano-substituted organosiloxane-polyoxyalkylene polymer	Flexible urethane foam with good stability and flame retardancy	209
2	Cyano-substituted organosiloxane-polyoxyalkylene polymer	Flame-retardant urethane foams	210

**TABLE XII**  
**Miscellaneous Flame-Retardant Products and Their Synergistic Combinations Disclosed in the Patent Literature**

Number	Fire retardant	Best example	Reference
1	15% ATH, 20% antimony trioxide, and 15% polyhalogenated aromatic compound	Flexible urethane foams with outstanding flame-retardant properties	230
2	Antimony trioxide, zinc oxide, and chlorinated paraffin	Flame-retardant, hot-molded urethane foam passing the flammability requirements of FMVSS-302	231
3	PAPI and trimellitic anhydride	Flame-retardant polyurethane foam showing a weight loss of 15%	232
4	Polyhydroxyl compounds and polyether polyols	Flame- and smoke-resistant flexible urethane foam with a burning distance of 38 mm and a smoke generation coefficient of 56.6 in accordance with JIS-A-1321-70	233
5	Polyhalogenated aliphatic diols, antimony trioxide, and ATH	Ignition-resistant flexible urethane foams	234

Polyurethane foam incorporated with ATH shows high ignition resistance according to BS 5852 Part 2 and PSA test standards.<sup>213</sup> ATH can be added to either a polyol or isocyanate to impart fire retardancy to urethane foams. Because of the higher density of ATH, the viscosity of a polyol or isocyanate to which it is added increases. It makes the mixing process of polyol, isocyanate, and other foam ingredients difficult. With the addition of 50% ATH to a foam formulation, the rise time and tack-free time are increased by 20%. ATH has a synergistic effect with DMMP, magnesium hydroxide, and antimony trioxide. The viscosity of an ATH-containing polyol decreases, whereas the fire-retardant properties are increased. However, the smoke level increases when ATH is used in combination with DMMP. The oxygen index of a rigid urethane foam containing ATH increases from 20.7 to 24.3, and the smoke level decreases from 49 to 13%. However, with the addition of 15% DMMP to the same formulation, the LOI and smoke level increase up to 25.8 and 48%, respectively. Bonignore et al.<sup>214</sup> reported that the addition of 50% ATH to a foam formulation increases LOI from 22.0 to 23.0, and a further 3% addition of DMMP increases LOI to 26.0 and the smoke obscuration number (the higher the smoke obscuration number, the higher the smoke generation) from 64.9 to 95.6. Calcium carbonate has a small effect on fire performance because the addition of CaCO<sub>3</sub> to a foam formulation increases LOI from 22.0 to 22.5; however, the smoke obscuration number is lowered from 122 to 57.2. The fire-retardant properties of urethane foams are greatly enhanced by the synergistic action of an ATH and magnesium hydroxide combination. Synergism is the result of the difference in the temperatures at which the two metal hydroxides give off their water. ATH loses water at 220–250°C, whereas magnesium hydroxide loses

water at 300–340°C when they are used in combination. It is believed<sup>215</sup> that apart from a significant amount of water that evolves into the flame, magnesium hydroxide also produces a substantial amount of char residue that prevents flame penetration. It has been found that a combination of magnesium hydroxide<sup>216</sup> and ATH<sup>217</sup> is very efficient in increasing the fire-retardant performance and decreasing smoke release from the combustion of urethane foams.

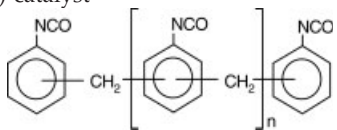
Rigid polyurethane foams impregnated with phosphorus–nitrogen additives and impregnated and surface-coated with carbon exhibit enhanced fire retardancy and reduced smoke density.<sup>218,219</sup> Decreases in the flammability and increases in the oxygen index of rigid polyurethane foams have been found with expandable graphite, exfoliated vermiculite, mica, organic borates, calcium sulfate, and arsenic oxide.<sup>2,220–229</sup> Miscellaneous fire-retardant products for polyurethane foams mentioned in the patent literature are shown in Table XII.

#### Carbodiimide- and isocyanurate-containing groups

Conventional methods used for improving the fire retardancy of urethane foams include the addition of phosphorus-, halogen-, and nitrogen-containing compounds. They have some obvious shortcomings such as relatively high smoke evolution and inferior physical and mechanical properties. Hence, many efforts in the technical and patent literature (Table XIII) have been made to modify polyurethane foams into low-flammability foams by the incorporation of more heat-resistant groups such as carbodiimide-, isocyanurate-, and nitrogen-containing heterocycles.

In the presence of certain catalysts, isocyanates react with themselves and undergo dimerization and trimerization reactions. Dimerization of isocyanates

**TABLE XIII**  
**Heat-Resistant Isocyanurate- and Carbodiimide-Group-Containing Polyurethane Foams Disclosed in the Patent Literature**

Number	Fire retardant	Best example	Reference
1	Polyisocyanurate obtained by the trimerization of polyisocyanate in the presence of a tertiary amine and quaternary ammonium salt of alkanolic acid catalysts	Isocyanurate-group-containing polyurethane rigid foam having resistance to flame and heat and excellent thermal insulating capacity	235
2	Trimerization of the isocyanate group in the presence of a potassium $\beta$ -tertiary amine propionate catalyst (the activity of the tertiary amine is affected by the isocyanate index)	Polyurethane foam containing thermally stable isocyanurate groups	236
3	Trimerization of PAPI in the presence of a potassium octoate (potassium-2-ethylhexoate) catalyst	Resultant isocyanurate foam exhibiting a cream time of 18 s, a firm time of 35–45 s, and good temperature stability	237
			
4	Trimerization of polymethylene polyisocyanate and an organosulfur compound	Resultant fire-retardant and low-smoke foam containing 0.5–25% organosulfur compound	238
5	Dimerization of polyisocyanate in the presence of oxazolidine and an amine	Carbodiimide-group-containing urethane foams exhibiting excellent flame retardancy	239
6	Polyisocyanurate containing 10% 2,3,4,5-tetrahydrofuran carboxylic acid	Flame-retardant rigid urethane foam with reduced smoke, that is, SV-12 according to ASTM D 2843-70 with the Rohm & Hass XP2 smoke chamber test	240
7	<i>N,N',N''</i> -Tris(dimethylaminopropyl) hexahydro- <i>sym</i> -triazine, a trimerization catalyst, and an organosilicate such as tetramethyl or ethyl silicate	Isocyanurate-group-containing rigid urethane foam with a very low level of smoke	241

is catalyzed by trialkyl phosphine and pyridine to form unstable uretidine dione, which immediately converts into carbodiimide. The trimerization reaction is strongly favored by 2,4,6-tris *N,N*-dimethylaminomethyl phenol (DMP) and 1,3,5-tris 3-dimethylamine-propyl hexahydrotriazine to form isocyanurate.<sup>242,243</sup> Peng et al.<sup>244</sup> studied the process kinetics of rigid isocyanurate foams with DSC. The DSC study showed that first a blowing reaction takes place, which is followed by the formation of urethane and trimerization of isocyanate into isocyanurate. Pure isocyanurate foams are very friable, but 20% urethane-modified isocyanurate foams have an acceptable balance of physical properties and flammability characteristics.<sup>2</sup> Burkus<sup>245</sup> described the preparation of the first isocyanurate-containing rigid foams by the trimerization of an isocyanate-terminated prepolymer. Nicholas and Gmitter<sup>243</sup> described the preparation of DMP-catalyzed, isocyanurate-modified, heat-resistant rigid urethane foams stable up to 232°C. MDI-based isocyanurate rigid

urethane foams catalyzed by DMP show low flame spread according to ASTM E 84 and low smoke density.<sup>246</sup> An increase in the MDI index has a positive effect on flame spread and smoke evolution. Isocyanurate urethane foams with MDI indices of 200, 250, and 300 exhibit flame heights of 81, 78, and 71 mm and smoke densities ( $D_{max}$ ) of 290, 288, and 222, respectively, in DIN 4102 and the NBS chamber test.<sup>172</sup> Isocyanurate rigid foams prepared from a high-equivalent-weight diol and triol have reduced inherent brittleness, but flame and degradation resistance is also reduced, as measured by the Butler chimney test and TGA, respectively. The preparation of rigid urethane-modified isocyanurate foams with acrylonitrile-grafted polyether polyol, which begin to cyclize at temperatures around 200°C to produce heterocyclic structures, was reported by Riccitiello et al.<sup>247</sup> Isocyanates in the presence of DMP and 2,4,6-tris(dialkanolamino)-*s*-triazine produce urethane foams that contain both isocyanurate and carbodiimide groups.<sup>248</sup> The reaction between polyisocyanate

and monomeric polyepoxide in the presence of a DMP catalyst produces an isocyanurate- and polyoxazolidone-group-containing foam. The resulting foam exhibits just about 19% weight loss and 14% smoke obscuration in the Butler chimney and NBS chamber tests, respectively.<sup>249</sup> An isocyanurate foam, when incorporated with tris(2-chloroethyl) phosphate or a mixture of DMMP and tetrabromophthalic ester diol, exhibits enhanced fire performance.<sup>250</sup> The fire retardancy of isocyanurate foams is also enhanced by the modification of these foams with the incorporation of phosphorus or chlorine or a combination of phosphorus with chlorine-containing polyols.<sup>251</sup> The synergistic effects of nitrogen, phosphorus, and chlorine on the flammability of polyisocyanurate-urethane foams have been investigated and compared to those of the corresponding polyurethane foams. The influence of isocyanurate groups on these foams is apparent from the shift in the oxygen index from 27.5 to 30.0 at the same chlorine level. Similarly, both polyurethane and polyisocyanurate foams containing 2 and 3% phosphorus demonstrate differences in their LOI values, which are increased from 24.0 and 25.0 to 25.5 and 28.0, respectively. The superior fire performance of polyisocyanurate foams compared with TDI- and MDI-based conventional rigid urethane foams on small-scale tests such as ASTM D 1692-68, ASTM 3014-73, and BS 476 Part 7 (surface spread of flame test) was reported by Ball et al.<sup>252</sup> A 12-mm asbestos board filled with a 2-mm-thick conventional urethane foam as the core material has a failure time of 46 min, but the failure time increases substantially to 59 min by the use of the same-thickness polyisocyanurate foam in the BS 476 Part 8 (ISO-R834) test.<sup>253</sup>

Carbodiimide-group-containing urethane foams were described by Mann.<sup>254</sup> Carbodiimide groups are formed in the presence of special catalysts such as aromatic or aliphatic phospholanoxides. The reaction to form carbodiimide is slightly exothermic, and the maximum temperature observed is 70°C. During the formation of carbodiimide bonds, an increase in branching and crosslinking takes place in the polymer structure, as it does in the trimerization to isocyanurate foams. The stiffness of the carbodiimide foam is due to the cumulative double bonds. Carbodiimide-group-containing urethane foams on exposure to fire char and generate less smoke than conventional urethane foams. Polyurethane foams containing carbodiimide and oxazolidinone groups are decomposed at 290°C and produce 30% residue at 600°C and 15% char at 800°C, whereas conventional urethane foams are decomposed at 275°C, and nothing is left at 600–800°C.<sup>255</sup> The fire performance superiority of carbodiimide- and isocyanurate-group-containing urethane foams has been confirmed by ASTM 3014-73, in which they have retained 90 wt % versus 30 wt % for conventional

urethane foams. Polyether polyols containing purine rings in their structure produce rigid polyurethane foams of improved thermal stability.<sup>256</sup>

## CONCLUSIONS

Polyurethane foams are highly flammable polymers but have great commercial importance. The ignition of polyurethane foams has been studied extensively and reported in the literature. Depending on the method used, the sample heating rate, air flow, and weight loss and the ignition and decomposition temperatures for polyurethane foams have been found in the ranges of 260–500 and 400–650°C, respectively. The rates of urethane foam decomposition are similar *in vacuo*, in oxygen, and in nitrogen at lower temperatures; however, at higher temperatures, the rate is highest *in vacuo* and lowest in air. The combustion of urethane foams in some ways is easier than that of other polymers because of their high insulation properties. Urethane foams ignite faster than cotton and acetate cellulose but more slowly than polyoxymethylene. Under natural draft conditions, the smoldering of urethane foams spreads faster in the upward direction than in the downward direction. Urethane foams produce large quantities of vision-obscuring corrosive smoke during combustion. The toxicity of the combustion products of urethane foams is extensively documented in the literature. Carbon monoxide and hydrogen cyanide are considered to be the main toxic combustion products from urethane foams, the evolution of which depends on the oxygen concentration in the combustion environment. The gases that evolve from the nonflaming combustion of urethane foams are more toxic than those from flaming combustion. Under similar conditions, the toxicity of combustion products of fire-retardant polyurethane foams is higher than that of conventional urethane foams because of the formation of bicyclic phosphate ester in the smoke. The toxicological and biological effects depend on the concentration of hydrogen cyanide and carbon monoxide gases together with their ratio. The LC50 values of combustion products of urethane foams have shown that the combustion gases of urethane foams are more toxic than those from nylon and less toxic than those from polyacrylonitrile.

Phosphorus-containing additives in the form of phosphates, phosphites, phosphonates, phosphonitrides, phosphoric acid, phosphonic acid, and halogen-containing phosphorous compounds are used to render polyurethane foams fire-retardant. The quantities of phosphorus additives are reduced considerably in the presence of chlorine and bromine because of the synergistic effect between them. Although phosphorus additives are excellent fire retardants for urethane foams, their main



disadvantage is that they increase the smoke level. Inorganic phosphates are promising fire-retardant additives for urethane foams, particularly high-molecular-weight phosphates such as APP, which remains with the foam even after 2 weeks of immersion in water.

Both chlorinated and brominated halogen additives together with some metal oxide synergists have been extensively studied and presented in many publications and in the patent literature. Halogenated fire retardants are not always feasible for use in urethane foams because rather high levels of addition are required, which often lead to a significant reduction of physical and mechanical properties. Halogen-containing fire-retardant additives are less effective than phosphorus fire-retardant additives in polyurethane foams. Phosphorus-based fire-retardant additives have a synergistic effect with nitrogen that increases the fire performance of phosphorous compounds. However, halogen-modified urethane foams generate less smoke of low toxicity than foams modified with phosphorus-based fire-retardant additives.

Nitrogen-containing compounds, particularly melamine, urea, and dicyandiamide, seem to be the principal fire retardants for urethane foams. Being nitrogen-rich structures, they have to be considered better fire retardants than phosphorus and halogens. Melamine appears to have multiple modes of fire-retardant action in both condensed and gas phases. On the basis of burning rates and oxygen index values, urea is a better fire-retardant additive for urethane foams than melamine and dicyandiamide additives.

Many studies have been reported in the literature on silicone- and boron-containing products as potential fire retardants for polyurethane foams. These products mainly work as synergistic compounds that may help to improve the performance of the principal fire-retardant additives. Silicone compounds containing urethane foam on fire exposure produce a large quantity of char, which is further converted to a continuous protective silica layer and stops the burning process. Silicone-based fire-retardant additives are less toxic than additives based on phosphorus and halogen when incorporated into urethane foams.

ATH is the other important inorganic fire-retardant additive for urethane foams. It acts endothermically and retards burning and smoke generation of urethane foams. Fire-retardant and smoke-suppressant properties of ATH are enhanced in the presence of DMMP, antimony trioxide, and magnesium hydroxide because of synergistic effects. However, a high loading is still required, and thus the cost and loss of the physical properties of urethane foams still impede its commercial use.

Dimerization and trimerization are the unique characteristics of urethane foams, by which they form heat-stable groups such as carbodiimide and isocyanurate groups, respectively, in the presence of some special catalysts. These groups are part of the urethane foam structures and provide them necessary fire retardancy. Urethane foams containing carbodiimide and isocyanurate groups char on exposure to fire and generate less smoke than conventional urethane foams. Fire-retardant properties of carbodiimide- and isocyanurate-group-containing urethane foams can be enhanced further in the presence of phosphorus- and halogen-based fire-retardant additives.

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