Polyurethane Products in Fires: Acute Toxicity of Smoke and Fire Gases

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ABSTRACT

Toxic effluents occurring in fires of natural and synthetic materials are governed by likelihood of ignition, rate of flame spread, heat release and rate of build-up of smoke and combustion gases, including oxygen depletion. These aspects are also applicable to polyurethane products. These synthetic materials have widespread applications, and as with many common household items, may be subject to combustion. In building construction applications, their uses are regulated by building codes, so that the performance must meet specified criteria. For some consumer products, relevant authorities may regulate flammability properties. Combustible materials normally produce toxic effluents when burned. Ventilation and temperature can influence both the kind and amount of combustion products. Carbon monoxide (CO) is the most abundant toxicant in fires involving polyurethanes and natural materials under most combustion conditions. In this context, the acute toxicity of most synthetic and natural materials appears to be more similar than different. The relative toxic potencies of materials have been characterized by laboratory scale evaluations, but toxic potency is only one component of the hazards of fire situations. Acute toxicity has been a relevant focus because it can be related to escape from a fire. In recent years, performance-based fire codes have been developed, with the objective of building design that allows escape or refuge. Performance-based fire codes utilize factors including toxicity in fire models. Performance-based models can be very sensitive to the (semi-)empirical input assumptions, so that careful application of these models, including their constraints and limitations, is important to allow estimates of acute hazard likely to occur under specified conditions. The potential for toxic effects to occur may or may not be reflected as a hazard depending on many factors related to end-configuration and end-use of the product, as well as fire protection measures in the building or environment that contains the material.

EVALUATION FOR COMBUSTION PRODUCT TOXICITY: POTENCY OF MATERIALS AND ACUTE TOXIC HAZARD OF FIRE SITUATIONS

Toxic effluents occurring in fires of natural and synthetic materials are governed by likelihood of ignition, rate of flame spread, heat release and rate of build-up of smoke and combustion gases, including oxygen depletion. Especially in small scale tests, the last is contingent upon the fuel : air flow ratio utilized during testing. For the adverse effects of exposure to combustion products in a fire situation, the potency of such components can be considered. Toxic potency is an indication of the potential of a given material to produce a harmful effect, and allows for a comparison of different combustible materials. The concentration of a fire gas estimated to cause lethality in 50% of exposed animals (LC50) is an example of a potency metric. Small-scale tests are often performed to measure the potency of toxic smoke and fire gases, not to measure overall fire risk. Comparisons of acute smoke toxicity, as determined by several laboratory small-scale methods are presented in Table 1 [1]. LC50 values are provided for wood and polyurethanes (flexible, rigid, and polyester-covered foam).

Table 1.

Average LC50 values with 95% confidence limits (g/m^3) and sample size in small-scale combustion tests.

MATERIAL	Well-ventilated Combustion		Ventilation-limited Combustion		Oxidative Pyrolysis	
	LC50 (g/m^3)	Sample Size	LC50 (g/m^3)	Sample Size	LC50 (g/m^3)	Sample Size
Polyurethane, flexible	35.4 (31.8-38.9)	18	20.4 (16.0-24.9)	4	29.9 (26.5-33.0)	15
Polyurethane, rigid	13.0 (11.6-14.5)	12	25.9 (15.8-35.2)	1	29.5 (25.2-33.9)	10
Polyester fabric, Polyurethane foam	41.9 (30.5-55.9)	1	(no data reported)		29.9 (25.2-42.2)	1
Wood	40.2 (34.8-45.1)	14	(no data reported)		36.1 (30.8-41.0)	14

From Gann et al., 2001 [1]. *Confidence limits are listed in parentheses. Units (g/m^3) relate to amount of material subject to thermal degradation divided by the air volume or total airflow. Combustion conditions in the original reports were not always well defined, categorizations were based on criteria such as CO_2/CO ratio.*

Most studies in Table 1 were conducted with rats, using a 30-minute exposure duration, and a 10 minute to 14 day post-exposure observation period. A variety of bench-scale devices (e.g. cup and tube furnaces) were used to generate these values. There have been limited large scale tests for these purposes. The conditions of burning relate to whether the product flames (combustion) and how much air / oxygen is available (ventilation) in relation to the load of combustible material (equivalence ratio). Pyrolysis is a non-flaming rapid thermal degradation. The average acute toxicity of the products of polyurethanes are not remarkably different than those of wood, nor of sheep wool. The LC50 value for thermally degraded wool was 15 g/m^3 utilizing a DIN type furnace [2]. On this simple mass basis of a bench-scale test (grams of product per cubic meter of air), the respective values for polyurethane bracket that of wood and sheep wool-- differences are small relative to the many factors that can influence the precision and the significance. A range of airborne decomposition products for combustible materials has been determined in conjunction with animal exposure evaluation. These components can have properties as “asphyxiants”, or as respiratory tract irritants. Carbon monoxide (CO) and hydrogen cyanide (HCN) are ubiquitous asphyxiants produced in fires, whilst ammonia, acids (e.g., derived from halogens and sulfur), aldehydes and oxides of nitrogen are irritants. Asphyxiants prevent normal utilization of oxygen. Although hydrogen cyanide has a higher acute lethal potency than carbon monoxide, under most combustion conditions, CO has been identified as the prominent toxicant [3]. The LC50 values shown in Table 1 are similar because the principle toxicity is related to CO. Morikawa and Yanai (1986) [4] evaluated a room model with a mixture of combustible materials; concluding that the toxicity of fire effluent gases will probably not be much affected by the composition or layout of combustibles.

Very low oxygen concentrations can promote the formation of HCN, especially under small-scale laboratory test conditions. Evolution of hydrogen cyanide would be additive to the toxic effect of carbon monoxide (Prager et al., 1994) [5]. In Einbrodt [6], 4000 different experiments with various materials as well as different fire conditions are described. In 92% of the cases, lethality was causally related to CO. Two per cent of the lethality cases were caused by hydrochloric acid and two per cent were caused by unknown effects. Only in four per cent of all cases was a combined effect of HCN and CO recognized as the main contribution to animal toxicity. This did not correspond to the large amount of nitrogen containing materials tested. Therefore, the acute toxicity of fire emissions caused by polyurethane foams was typically in the same range of toxicity caused by non-nitrogen containing combustible materials under comparable test conditions. The contributions of soot and partially decomposed material are not considered to be major modulators of acute toxicity.

Fires progressing to flashover generate toxic quantities of smoke and harmful elevated temperatures. In the room of fire origin (i.e. smoke not travelling from a remote location), all life threatening components, including toxicity, heat, visibility impairment, and oxygen depletion, usually happen in a very similar time frame (at flashover).

At that point, the contribution of any of these individual components would not be likely to have a critical influence on the overall life threat. Though polyurethanes have typically not yielded unusual effects, the use of specific additives, such as flame retardants, is beyond the scope of this review.

A recent review by Alarie looked at the "Toxicity of Fire Smoke" in a more general way [7]. Alarie indicated that the major immediate threats in fire situations were carbon monoxide, irritant organic chemicals in the smoke, oxygen depletion and heat. Carbon monoxide was considered to likely be the major toxicant in modern fires, though Alarie reviewed some of the complexities of determining the contribution of cyanide. Alarie concluded that blood cyanide in fire victims seems to have increased over the years, though the role of cyanide in acute toxicity has been difficult to establish. Analysis of cyanide in blood of fire victims is more complex than blood carboxyhemoglobin. Blood cyanide concentration may either diminish or even be generated (increase) in samples that are not prepared and stored properly [8].

Although acute toxicity is normally the critical toxicity endpoint in a fire emergency (when survival is the primary concern), other issues include sublethal effects of fire effluents and of thermal degradation products in less extreme thermolytic conditions. A significant effort by the National Institute of Standards and Technology (NIST) has been the International Study on the Sublethal Effects of Fire and Smoke on Survivability and Health, or SEFS project [1]. Gann noted that 310,000 to 670,000 people in the U.S. are exposed to fire smoke per year. This compares to an average of 3,318 home civilian fire deaths and 11,505 civilian fire injuries per year involving smoke inhalation in part or in whole. Gann concludes that most of the injuries are burns from small cooking fires, and most of the exposures are brief and to dilute smoke—not resulting in any noticeable consequences. Many of the savable victims were asleep when injured and could have escaped if alerted by an operational fire alarm. The authors concluded that sublethal effects of fire smoke can play a substantive role in preventing safe escape from a fire, but lead to noticeable consequences in only a small fraction of the people exposed.

CHARACTERIZATION OF COMBUSTION PRODUCTS: SMALL-SCALE TESTS FOR SMOKE AND FIRE GAS

For small-scale smoke toxicity tests, identification of the fire conditions may be used to put the results into the larger fire framework. The German DIN method [9] is designed to control mass/volume combusted per unit of time, ventilation and temperature. This utilizes a quartz tube and annular furnace. Over the test period a steady-state concentration of combustion products is attained, in practice though, the smoke composition will be time-varying to some degree, especially when the selected temperature is close to the ignition point of the test specimen. Other decomposition apparatus may rely on a specific furnace condition, but do not specifically control ventilation or mass burned per unit of time. The NIST device [10] is used to thermally decompose samples under non-flaming and flaming conditions. Pieces of configured product systems have been evaluated in the NIST device-this is likely to offer some advantage, though there is still a question of scale-up. These small scale devices are not designed to include important fire hazard parameters such as likelihood of ignition, extent of fire, fire suppression, overall combustible configuration, and potential for egress / escape. Small scale tests are designed for "hazard identification" by assessing relative toxic potency under highly standardized/reproducible conditions, not for determining the probability that the harmful effect will occur.

Today, the use of animal tests to evaluate toxic potency values, has decreased to a minimum. The information from many experiments allows test results to be combined with mathematical calculation systems, calibrated in an animal test, so that toxic potency of products can be reasonably assessed. The mathematical prediction is based on analytical elucidation of the main toxic smoke components: CO, CO_2, SO_2, HCN, NO_x, NH_3 and depleted O_2 content of the fire atmosphere. A "Fractional Effective Dose" (FED) model has been used to cumulate the toxicity [11]. This FED concept may be adjusted for use with irritants (rather than asphyxiants) by using a "Fraction Effective Concentration" [3]. By integrating the dose of asphyxiants or concentrations of irritants as "Fractional Effective Concentration (FEC)", it is possible to estimate both the toxic potency of the combustion products and to verify the analytical approach chosen.

Gann et al. have been continuing their "SEFS" project with large scale test burns of well characterized materials. These tests are intended to provide a full-scale reference for evaluation or selection of small-scale tests for evaluations of thermal degradation. One anticipated application of these small-scale tests is to measure degradation and use these data in a performance-based fire model.

BUILDING CODES: PRESCRIPTIVE VS. PERFORMANCE-BASED

"Prescriptive fire codes" have been used for many decades. These indicate how fire doors, some alarms, sprinkler systems, fire exits etc. are to be used in a building. New "performance-based" fire standards have the objective of providing a building design that allows escape or refuge from a fire. An ISO technical specification has been developed that provides tools for the fire safety engineer to apply toxicity information for estimation of time available for escape [12]. Performance-based standards use computer models to estimate what protection measures are needed for a building. These standards can include many variables such as small-scale combustion product potency, ignition, ventilation, availability of sprinkler systems, and fuel load. Though these performance-based fire standards have a worthwhile objective, they have a weakness in that the model's predictions are highly dependent on the many specific assumptions used. Differing predictions are possible, with difficulty in determining which model prediction is correct.

CONCLUSION

Combustible materials (synthetic or man-made) generally produce toxic products when burned. Carbon monoxide is the most prevalent and abundant toxicant in fires involving natural products and synthetic materials under most combustion conditions. Although the smoke from some synthetic materials may produce unusual potency utilizing specific, sometimes ill-validated small-scale test-procedures, the acute toxicity of natural and synthetic materials, including polyurethanes, is generally more similar than different. The potential for toxicity to occur in humans may or may not be reflected as a hazard depending on many factors, including the end-use configuration of the product, as well as fire protection measures in the building or environment that contains the material. Burning rate can be an important determining factor. Predicting long-term effects as a sequel to a near lethal exposure is beyond the scope of this review. There are a substantial number of fire injuries (mostly burns) in the United States and most of the fire smoke exposures are to dilute smoke with no immediate apparent consequence.

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This report is a revised review written for the International Isocyanate Institute. It is based on (and supercedes) the report of the same name, dated 2002, prepared for the Alliance for the Polyurethane Industry.