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THE TOXICITY OF SMOKE FROM POLYMERIC MATERIALS DURING THERMAL DECOMPOSITION

Yves Alarie

Department of Industrial Environmental Health, University of Pittsburgh School of Public Health, Pittsburgh, Pennsylvania 15261

INTRODUCTION

Synthetic polymers, because of their chemical composition, release smoke that is qualitatively different from the smoke of commonly used natural polymers such as cotton and wood (1, 2). In addition, the rate of release of smoke from synthetic polymers can be much faster than that for cotton or wood and the yield of principal toxicants may be higher (1, 2). For these reasons, we need to develop methods to evaluate the acute toxicity of smoke from both synthetic and natural materials.

Ideally, we should be able to make a complete qualitative and quantitative analysis of the smoke from each polymer, but such data cannot be obtained easily. As a result, researchers in this area have relied on animal exposures to rapidly evaluate possible differences in the potency of smoke from various materials. Most have measured key toxic gases such as carbon monoxide, hydrogen cyanide, formaldehyde, and hydrogen chloride while exposing animals to these substances. In addition, a large number of studies have been made on over 300 other polymeric materials by investigators in many countries. Several summaries of these investigations have recently appeared (1–4). In May of 1984, the Secretary of State of New York recommended that toxicity data on smoke from polymeric materials be filed at the Department of State as determined by the Uniform Fire Prevention and Building Code Council (5). The implementation of this recommendation is now under way.

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MEASURING THE ACUTE TOXICITY OF SMOKE

Researchers have used two different approaches to evaluate acute lethality during exposure to smoke.

Type I or Time to an Effect Approach

The time to an effect approach consists of thermally decomposing a given amount of material and exposing animals until a particular effect is observed. Many investigations have been conducted using this method. Among others, Hilado (6) has investigated more than 200 polymers and the Federal Aviation Administration has investigated 75 aircraft cabin materials with this approach (7). Its major drawback is that all the exposed animals die and taking the average time to death as a measure of toxicity is invalid. Furthermore, ranking acute lethality with this method is impossible for the following reasons:

1. By definition, toxicity is based on the amount of chemical or physical agent necessary to produce a given level of effect (8, 9). Therefore, if smoke from material A is to be declared more toxic than smoke from material B, it is necessary to demonstrate that less material A is needed to cause death.

2. The time element in these experiments is related to the rapidity of action of the toxicants released and their concentration in the exposure chamber in addition to the time it takes for the samples to decompose. In general, it has been demonstrated that as the concentration of toxicants increases the time for a given level of effect to occur is shorter. In addition, the proportion of animals exhibiting the effect increases (10–12).

The Type I approach yields only descriptive data on the time it takes to kill all the animals, i.e. onset of the effect, when the same amount (one gram) of each material is used. This is illustrated by the data in Table 1. Three materials produced 100% mortality within a planned 30-minute exposure period when one gram of each material was thermally decomposed. Because mortality in every case was 100%, we have no idea of how toxic the smoke from each material really was. Perhaps only 0.1 gram would have been sufficient to cause death.

The results in another test using the same approach with other polymers are presented in Table 2. When one gram of polymer was decomposed, a factor of 3.5 existed between the fastest and slowest times required for 100% mortality, being six minutes for wool and 21 minutes for Nylon 6. Also presented in Table 2 are the smallest amounts of each polymer that when thermally decomposed still induced 100% mortality, as well as the time it took for this to occur. It can be seen that reducing one gram by a factor of ten still killed all the animals, but the time for this effect to occur approximately only doubled. The most rapid effect occurred with red oak, 15 minutes, and the slowest with wool, 23

Table 1 Toxicity of thermal decomposition products from various polymers decomposed at 600°C

Polymers	Weight charged in furnace	% mortality	Time to death	References
Polytetrafluoroethylene	1 gram	100	22.9 minutes	13
Polypropylene	1 gram	100	21.7 minutes	14
Polyether sulfone	1 gram	100	6.05 minutes	15

minutes. From the data observed in this experiment (16), it was also possible to calculate the amount of material needed to kill 50% of the animals (LC_{50}) and the time needed to kill 50% of the animals (LT_{50}) when this amount was used. These data are also given in Table 2. They permit a valid comparison of toxicity and show that red oak is almost eight times less toxic than Nylon 6. They also show that the differences between LT_{50} values are small. If the LT_{50} is taken as a measure of toxicity, red oak seems more toxic than Nylon 6. This is obviously wrong, since it takes eight times less Nylon 6 than red oak to produce 50% mortality. Thus, the time required for a given level of effect to occur is secondary; it is an important measurement, but it cannot replace quantity as a measure for ranking toxicity.

Type II or Amount for an Effect for a Given Duration of Exposure Approach

The Type II approach consists of determining the amount of material necessary to produce sufficient smoke to kill 50% of the animals (LC_{50}) following exposure of all groups and all animals in each group to the exact same duration of exposure. The only laboratory adhering strictly to this protocol is the National Bureau of Standards (17).

With this protocol, each material was thermally decomposed and all animals were exposed to the smoke for 30 minutes. Lethality was then observed over a period of 14 days. A concentration-response relationship was obtained from a series of experiments that varied the amount of material being decomposed to yield between 0 and 100% mortality. The LC_{50} was calculated by using an appropriate statistical method. While it sometimes occurred that a few animals died close to the end of the exposure period rather than following exposure, such a small deviation is of minor consequence. Results obtained with this method using a variety of polymers are presented in Table 3. Valid conclusions about the toxicity of smoke from these materials in comparison with Douglas fir were possible, since the protocol followed basic toxicological principles with proper statistical analysis.

Table 2 Lethality data obtained for thermal decomposition products of various polymers decomposed under the same conditions[a]

Samples	Amount of material used (grams)	% mortality	Exposure time for 100% mortality (minutes)	Amount to kill 50% of the animals (grams)[b]	Time to kill 50% of the animals at the LC_{50} (minutes)[c]
Polyphenylene sulfide	1	100	11	0.135	27
	0.2	100	20		
Polyaryl sulfone	1.0	100	11	0.092	29
	0.15	100	26		
Nylon 6	1	100	21	0.04	30
	0.047	100	30		
Douglas fir	1	100	13	0.09	23
	0.11	100	22		
Wool	1.0	100	6	0.10	29
	0.12	100	23		
Red oak	1.0	100	12	0.31	23
	0.4	100	15		

[a] Taken from (16)
[b] This would be described as the LC_{50}.
[c] Not reported by these authors but approximated from their tables. This is described as the LT_{50}.

Table 3 Comparison of toxicity of thermal decomposition products (non-flaming mode) obtained at the National Bureau of Standards for 30 minutes of exposure and 14 days observation period[a]

Material	LC_{50} material / LC_{50} Douglas fir
Red oak flooring boards	1.45
Flexible polyurethane foam	1.31
Acrylonitrile-butadiene-styrene pellets	1.27
Wool: unbleached, unwoven fibers	1.07
Douglas fir	1.00
Poly (vinylchloride) pellets	0.74
Polyphenylsulfone pellets	0.71
Poly (vinylchloride) with zinc Ferrocyanide	0.48
Modacrylic knit fabric	0.26
Polytetrafluoroethylene	0.006

[a] Taken from (17)

Type III or Amount for an Effect Within a Planned Duration of Exposure Approach

The Type III approach combines the methodology of both Type I and Type II. In a strict sense, the 50% mortality calculation (LC_{50}) should be based on a similar exposure period for all animals at all concentrations of smoke, as in the Type II approach. A variation on this method is to allow deaths to occur within a given, or planned, duration of exposure rather than merely observing deaths following a given exposure period. One advantage of this variation is that it is less costly, but delayed toxicity cannot be as accurately measured as with the Type II approach unless a larger number of animals are exposed. The second advantage is that deaths are observed with a time frame more appropriate to fire situations than during a 14-day observation period following exposure.

Several investigators have used this approach and have sometimes made post-exposure observations on the surviving animals (16, 18–22). Data from these investigators are presented in Tables 4–7 and the last two columns of Table 2. These tables make it very easy to see the toxicity of the thermal decomposition of polymeric materials. However, the thermal decomposition methods used and durations of exposure varies widely. Therefore, it is impossible to compare the results obtained from these methods.

With the Type III approach, the amount of toxicant necessary to kill 50% (LC_{50}) of the animals can be combined with the time necessary to kill 50% (LT_{50}) of the animals in order to make a comparison among materials for both potency (LC_{50}) and rapidity of action (LT_{50}). This can be done by plotting both variables, as shown in Figure 1, for a wide variety of materials (see also Table

Table 4 Amount of material decomposed at 800°C necessary to kill 50% of the animals (mice) in 10 minutes[a]

Materials	Amount of material (grams)
Polyacrylonitrile	0.16
Polyamide 6	0.023
Polypropylene	0.030
Acrylonitrile-butadiene-styrene	0.034
Polyurethane A	0.038
Polyethylene	0.052
Macrolon	0.095
Polystyrene	0.12
Polyvinylchloride	0.14

[a] Taken from (18)

Table 5 Amount of materials decomposed up to 1000° necessary to kill 50% of the animals within an exposure period of two hours but also including death within a two-week post-exposure observation period[a]

Materials	Amount of materials (grams)
Y-2000: Aromatic polyamide	0.15
Y-1797: Aromatic-type nylon with flame retardant	0.205
Y-1796: Aromatic type nylon without flame retardant	0.36
Y-4959: Polyarelene rigit material	2.20
Y-4397: Polyimide resin on fiberglass	4.71

[a] Taken from (19)

Table 6 Amount of material decomposed to kill 50% of the animals (LC_{50}) within a planned 30-minute exposure period. Heating rate at 20°C/minute[a]

	Materials	LC_{50} (gram)	Time to kill 50% of the animals (minutes)
GM-21:	Flexible urethane foam	12.9	13
GM-47:	Expanded polystyrene	5.8	11
PTFE:	Polytetrafluoroethylene	0.64	8
PVC:	Polyvinylchloride (92% homopolymer)	7.0	10
MOD:	Modacrylic	4.9	18
UF:	Urea formaldehyde foam	2.5	22
D. fir:	Douglas fir	63.8	22
Wool:	Wool fiber, undyed	3.0	27

[a] Taken from (20)

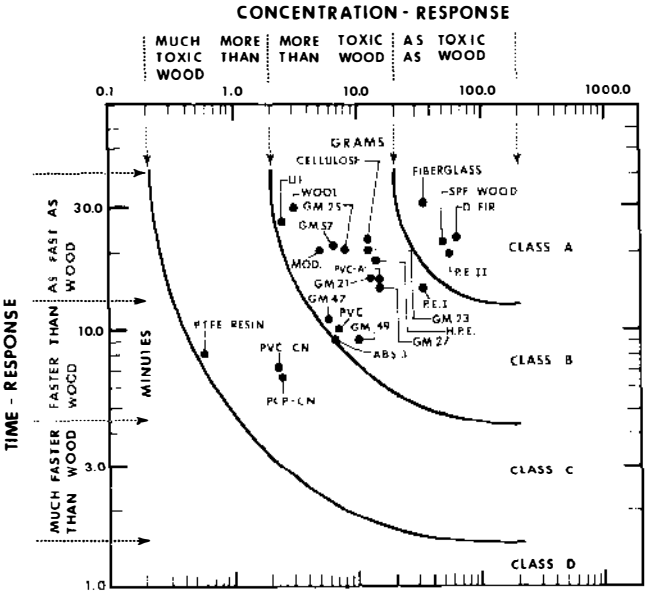

Figure 1 Each point represents the amount of material (gram on the X axis) needed to produced sufficient smoke to kill 50% of the animals tested (LC_{50}) and the time (minutes on the Y axis) necessary for this effect to occur (LT_{50}) using this amount of material. Vertically each material is classified in terms of potency, horizontally each material is classified in terms of onset of action, always in comparison to Douglas fir, the wood standard. To combine both potency and onset of action, parallel quadrants separate class A, B, C, and D materials. A description of the materials presented is given in Table 8. Taken from (21).

8) in order to compare them with Douglas fir, which is used as the standard (21).

It should be understood that with Type II and III approaches the investigators predetermined the exposure period or planned for an exposure period relevant to a fire survival situation. With the Type II protocol, the investigators were trying to find out the maximum amount of smoke tolerable for a particular period of time without producing a lethal effect afterward. With the Type III

Table 7 Amount of material decomposed to kill 50% of the animals within a period of two hours with decomposition of samples at 822°C[a]

Materials	Amount (grams)
FR-polycarbonate	8.6
High-impact polystyrene	8.9
Wool	9.4
Red oak	16.8
Phenolic general purpose	47.5

[a] Taken from (22)

Table 8 Samples tested and summary of the results presented in Figure 1

Abbreviation	Sample name and description	LC_{50} (grams)	LT_{50} (minutes)	Class[a]
PRC materials[b]				
GM 21	Flexible polyurethane foam	12.9	13	B
GM 23	Same as GM 21, with fire retardant	10.4	18	B
GM 25	High-resilience flexible polyurethane foam	8.3	19	B
GM 27	Same as GM 25, with fire retardant	14.4	15	B
GM 29	Rigid polyurethane foam	10.4	28	B
GM 31	Same as GM 29, with fire retardant	8.2	23	B
GM 35	Rigid polyurethane foam, fluorocarbon blown	7.5	17	B
GM 37	Same as GM 35, CO_2 blown	8.0	15	B
GM 41	Rigid isocyanurate foam	6.4	18	B
GM 43	Same as GM 41, contains some polyurethane	6.1	16	B
GM 47	Polystyrene expanded	5.8	11	B
GM 49	Same as GM 47, with fire retardant	10.0	9	B
GM 57	Phenol formaldehyde-phenol resin, expanded with blowing agent	6.3	20	B
Non-PRC materials				
PTFE	Polytetrafluoroethylene resin	0.64	8	C
PVC	Polyvinylchloride (92% homopolymer)	7.0	10	B
PVC-A	Polyvinylchloride (46% homopolymer)	15.2	15	B
PVC-CN	Polyvinylchloride (46% homopolymer + 5% zinc ferrocyanide)	2.3	7	C
PCP-CN	Polyvinylchloride (92% homopolymer + 5% zinc ferrocyanide)	2.5	6	C
ABS-3	Standard acrylonitrile/butadiene/styrene	6.3	9	B
Mod.	Modacrylic	4.9	18	B
Wool	Wool fibers — undyed	3.0	27	B
UF	Urea formaldehyde foam	2.5	22	B
Cellulose	Blowing type cellulose fiber insulation	11.9	21	B
D. fir	Douglas fir	63.8	22	A
Fiberglass	Fiberglass building insulation, 3.5 in. thick with paper and vapor barrier	35.7	25	A
PE I	Polyester resin — commercial acrylic modified unsaturated	34.8	14	B
PE II	Polyester resin — experimental acrylic modified unsaturated	57.4	18	A
HPE	Polyester resin, styrenated halogen modified	14.4	16	B
SPF wood	Compressed spruce, pine, fir slab	48.7	19	A

[a] From Figure 1

[b] From the Product Research Committee (PRC) sample bank at the National Bureau of Standards and (21)

protocol, a standard was used first and attempts were made to obtain 50% mortality at exactly a specified duration of exposure, such as 30 minutes, as in (20). This was impossible to achieve and the investigators had to settle for a time close to it. For example, when Douglas fir was used as the standard, 50% mortality occurred at 22 minutes instead of the desired 30 minutes (20, 21). However, once the results for the standard are obtained, all other materials can be rated against it for both LC_{50} and LT_{50}.

UNDERSTANDING THE LIMITATIONS OF THE DATA IN TERMS OF REDUCING FIRE FATALITIES DUE TO SMOKE INHALATION

Toxicity Data

Fire is one of the most serious problems affecting modern life and our ability to minimize its effects has improved little over the past 50 years (1). Cullis & Hirshcler (1) placed things in perspective when they pointed out that during the period from 1961 to 1972 fires killed over three times more Americans (143, 550) in the United States than died in the Vietnam War. The US has the worse fire-fatality record of the industrialized nations (1). Only motor vehicle accidents and falls rank higher as a cause of death (23). Recently, most attention has focused on the toxicity of smoke, since approximately 80% of fire victims die from smoke inhalation rather than burns (24). Three major recent examples where this was the case are the fire at the MGM Hotel in Las Vegas, when 85 persons died, most from smoke inhalation (25); the fire at a jail in Biloxi, Mississippi, where 29 prisoners died, all from inhaling the smoke from the wall padding of a single cell (26); and the fire at the Westchase Hilton Hotel in Houston, Texas (27).

The main reason for undertaking the toxicological testing of materials under thermal stress is to provide information on how to select those that will reduce fatalities due to smoke inhalation. Obviously, materials releasing smoke of low toxicity are preferable to materials whose smoke contains potent toxicants.

However, one must also consider that during an actual fire, so much toxicant can be released that nobody survives a 30-minute exposure regardless of the burning materials. Another time, the amount of smoke can be so small or the dilution so great that everyone is likely to survive no matter what materials are involved. For this reason, it makes no sense to regard toxicological data alone, or to think that small differences in LC_{50} or LT_{50} will be important in reducing fire fatalities (20, 21). Developing classifications and rankings for materials on the basis of potency, as presented in Figure 1, can cover only orders of magnitude. Toxicologists have generally recognized a factor of ten as separating different classes of toxic level (8, 9).

Table 9 Amount of materials loaded in the furnace and heated at 20°C/minute resulting in 50% lethality (LC_{50}) within a planned 30-minute exposure period[a]

Foam samples	LC_{50} (grams)	LT_{50} (minutes)	Volume of material at LC_{50} (in^3)
A	34.3	19.5	17
B	7.2	19.3	20
C	10.6	20.5	20

[a] Taken from (29)

A second point to consider is the toxicity of smoke from wood. Although wood is taken as a standard in toxicological testing, smoke from wood is toxic. For example, in one thermal decomposition system a maximum 100 ppm of CO per gram of Douglas fir was easily reached (20), while in another 88 ppm of CO per gram was observed (17). Thus, wood can produce acute lethal effects. If we intend to reduce fire fatalities due to smoke inhalation, it is not enough to use materials whose smoke is less toxic than wood. We must also insist on better fire prevention with measures such as the installation of smoke alarms and sprinkler systems. Some important new developments in synthetic polymeric materials are also worth noting. For example, new inorganic polymers are being developed that do not burn or release toxic gases (28).

The final point to consider is that materials used in building are not used on a weight basis but rather on a volume, surface area, or length basis. For example, three different types of synthetic foam for mattresses have been tested with the Type III method previously described (20); the results are presented in Table 9. A factor of five was found between the most and the least toxic foams when the LC_{50} was given in grams. However, on a volume basis there was no difference among these materials. In order to make the best selection, it is necessary to know how much of each sample is required to obtain the same comfortable mattress on a volume basis. Unless the difference is rather large (i.e. by a factor of ten or so), the choice is difficult. We must consider that smoke's capacity to impair visibility and heat release, which will influence the impact of the fire, are determined by the weight of material, not by its volume. Ease of ignition and flame spread are two other important characteristics of burning material, and these unfortunately are not related to weight or volume. Thus, toxicity is only one of many factors to be considered in the selection of materials.

In some cases, the toxicological data on synthetic polymers used on a weight, volume, surface area, or length basis is of such a nature that we must question their employment in large quantities or in areas likely to be exposed to high heat without proper fire prevention systems. The use of polymers showing extremely high toxicity of their thermal decomposition products will probably

be the exception rather than the rule. Indeed, during the past ten years, only two types of materials were found, both at the University of Pittsburgh (10, 20, 21) and at the National Bureau of Standards (17), to fit this category: fluoropolymers and polylvinyl chloride. During recent testing at Arthur D. Little (R. C. Anderson, personal communication), a third material was found with a toxicity at least ten times higher than that of the fluoropolymers.

A recent series of tests on the decomposition of communication cables using the Type III method of testing indicated the toxicity of fluoropolymers. The results of these tests are presented in Table 10. The LC_{50} values (in grams or inches) given there are only good approximations of the LC_{50}, since it was not technically possible to cut these wires into smaller quantities, permitting a full series of experiments to statistically calculate the LC_{50}. Nevertheless, these cable amounts and lengths are extremely small. The tests showed that carbon monoxide clearly was not the toxicant produced by the burning cables, nor can hydrogen cyanide be involved, since these polymers contain no nitrogen. As in the case of another fluoropolymer, polytetrafluoroethylene (20), the extremely toxic gas released during the tests was probably perfluoroisobutylene (30), whose acute inhalation toxicity (31) is of the same level as the nerve agent Soman (32). We do not know the mechanism of action of this toxic gas nor do we know an effective treatment for it. These polymers have been attractive as

Table 10 Amount of materials loaded in the furnace and heated at 20°C/minute resulting in 50% lethality (LC_{50}) within a planned 30-minute exposure period[a]

	Wiring samples	
Observations	High-temperature coaxial cable covered with Teflon®-FEP[b]	High-temperature telephone cable with 25 pairs of wire covered with Teflon®-FEP
LC_{50} (grams)	0.29	1.96
LC_{50} (inches)	0.25	0.5
LT_{50} (minutes)	28	28
Temperature at initial decomposition and exposure of animals (°C)	325	325
Temperatures between which major decomposition occurred	400–500	400–500
Maximum CO reached in exposure chamber during decomposition (ppm)	< 50	< 50
Residue after burning (mostly wire) (mg)	42	760

[a] Taken from (29)
[b] ®Registered trademark of E.I. DuPont de Nemours for fluoropolymers

building materials because their flame spread (if any) is extremely low, their heat release is 25% that of wood, and they release no smoke to impair visibility (1). Nevertheless, the toxicity of their thermal decomposition products is so high that it must be a primary factor in determining their use.

Extrapolation from Animals to Humans

Two factors must be considered in extrapolating test data to real conditions. The first one is that laboratory animals, mice or rats, are used for testing. The second one is that the principal toxicants in the decomposition products of various materials are not always the same. These factors greatly complicate our task in extrapolating toxicity test results to humans.

When wood burns, carbon monoxide is the main toxicant (17, 20), and carbon monoxide is the main toxicant in other polymeric materials as well. The relative toxicity ranking established for carbon monoxide in laboratory animals can justifiably be extrapolated to humans because the mechanism of toxicity in both is the same. This gas is absorbed in mice or rats in the same manner as it is in humans; the only difference is that it is absorbed faster, and thus acts more quickly, in animals due to their higher minute ventilation/body weight (33). The same is true with hydrogen cyanide. However, if material A, in which the principle toxicant is hydrogen cyanide, is found to be ten times more toxic in mice than material B, whose principal toxicant is carbon monoxide, can we then extrapolate that material A is also ten times more toxic than material B if humans are exposed? From the data on the relative acute toxicity of hydrogen cyanide and carbon monoxide in mice (12) and the best approximations of their lethal levels for humans (34), such an extrapolation is justified, since the potency ratio between CO and HCN is similar for mice and humans.

When the principal toxicant is hydrogen chloride, as in polyvinyl chloride (35, 36), 58% of the polymer is chlorine and almost all of it is released as hydrogen chloride (1). In this case a correction factor must be applied in order to extrapolate to humans the results obtained in mice. This is because such gases as hydrogen chloride, hydrogen fluoride, and hydrogen bromide are highly soluble in water and react at the surface of the nasal mucosa. Mice and rats breathe exclusively through the nose; thus, such gases are readily scrubbed by the upper airways and are prevented from reaching the lungs and systemic circulation, reducing their toxic action (37–39). In an actual fire, humans breathe exclusively through the mouth, since smoke is irritating to the nose (40). In order to prevent the nasal mucosa from removing these gases, mice and rats can be exposed to the toxicant via tracheal cannula (37–39).

As shown in Table 11, the toxicity of smoke from polyvinylchloride and from hydrogen chloride differed by a factor of seven to ten between mice breathing through a tracheal cannula and normal mice breathing through the nose. In contrast, carbon monoxide and hydrogen cyanide were equally toxic

Table 11 Acute lethality in mice exposed to thermal decomposition products of various polymers or exposed to hydrogen chloride, carbon monoxide, or hydrogen cyanide. LC_{50} is given in grams loaded in the furnace for the polymers and in ppm for the gases.

Samples	LC_{50} values	
	Cannulated mice	Normal, non-cannulated mice
Polyvinyl chloride A[a,b]	2.2	15.2
GM-41 isocyanurate foam[c]	11.7	6.4
GM-57 phenol formaldehyde foam[b]	2.9	6.3
Hydrogen chloride[d]	1,095	10,157
Hydrogen cyanide[e]	166	166
Carbon monoxide[e]	3,500	3,500

[a] This sample contained 46% polyvinylchloride and inorganic inert filler.
[b] Taken from (20, 37)
[c] Taken from (20)
[d] Taken from (37)
[e] Taken from (12)

no matter which way they were inhaled. The difference in toxicity was small between GM-41 and GM-57, which release hydrogen cyanide and carbon monoxide respectively as the main toxicants during thermal decomposition (20). The LC_{50} of hydrogen chloride in cannulated mice (1095 ppm) is comparable to the predicted lethal concentration (1000–2000 ppm) in humans for a short exposure duration (34). This further reinforces the theory that a factor of seven to ten must be applied in extrapolating the acute lethal effect of this gas, or of smoke where the principal toxicant is hydrogen chloride, from experiments conducted with normal mice.

There may be other instances where such a correction factor is needed. For example, when perfluoroisobutylene is released from fluoropolymers and is the main toxicant in smoke (30), humans may be more or less susceptible to this gas than mice or rats. There are no data in the literature on the acute lethal level of this gas in humans and no correction factor can be applied at this time.

SMALL-SCALE FIRE MODELS AND EXPOSURE SYSTEMS

Criteria for Small-Scale Fires

Various apparatus have been used to evaluate smoke from polymers in a manner comparable to what can happen in an actual fire, and a list of combustion devices and their limitations has been presented (1–4). None of them is perfectly adequate. Testing methods must follow general criteria and investiga-

tors must make a variety of measurements to establish general relationships to real fires. Among the criteria and measurements required for adequate testing we can list the following:

1. The temperature should be high enough to decompose all samples being tested.
2. Sufficient air (oxygen) should surround the samples at all times during decomposition.
3. The temperature or radiant energy used should not be higher than average developing fires, i.e. around 400–800°C, since we do not want to incinerate the samples nor do we want to supply energy greatly in excess of what would occur in an actual fire.
4. Both non-flaming and flaming decomposition products should be investigated, simultaneously or as they follow each other in a fire.
5. The combustion-exposure chamber system should minimize the deposition of gases and particulates on the walls and the reaction of decomposition products with the walls.
6. The residence time of decomposition products at elevated temperature is an important variable. If residence time is very long, the larger molecular-weight organic constituents of the smoke will further decompose to gases such as CO_2, CO, H_2O, HCN, and HCl. Little work has been done on this subject.
7. The combustion system should be large enough to accomodate low-density materials, layered materials, and composite materials in a configuration, horizontal or vertical, appropriate to their intended use.
8. The rate at which the samples decompose must be monitored. This is a most important measurement, since the size of a fire is proportional to the burning rate of the material. Few studies have included this information.
9. Monitoring of at least carbon monoxide, carbon dioxide, and oxygen is necessary; they relate to the size and intensity of the fire. Tests of polymers containing nitrogen may require monitoring the hydrogen cyanide. In halogen-containing polymers, the halogens should also be measured if carbon monoxide or hydrogen cyanide are not the principal toxicants in the smoke.
10. The combustion system must permit the investigation of concentration-response relationships in order that acute lethal effects or other toxic effects can be quantitatively evaluated. This can be accomplished in two ways: (*a*) increase or decrease the size of the sample while keeping the dilution air constant or (*b*) keep the size of the sample constant while changing the dilution air.
11. Two major types of decomposition systems have been used. The first type is a fixed-temperature system. As long as the temperature is high enough to

decompose the sample, this testing method is valid (17). The second type is a system in which the temperature increases linearly, from 5 to 35°C per minute, until the sample decomposes. This method is equally valid.

12. The latter system requires that particular care be taken in determining the rate of heat increase. During tests of thermoplastic polymeric materials such as polystyrene foam or polymethylmethacrylate, a heating rate of 35°C per minute can cause explosions and flash-overs if these materials are burned in quantities of ten grams or more. A rate of 5°C per minute is probably too low for the adequate testing of thermosetting plastics such as urea-formaldehyde foam. A good working temperature rate for most heat-increase tests is probably around 20°C per minute (20). The criteria listed above reflect personal experience. I offer them as a guide to researchers interested in initiating research work in this field.

Exposure Systems

Investigators testing for toxicity in burning polymeric materials have used both static and dynamic exposure systems. Either is adequate for recreating the conditions of an actual fire. However, the advantages, disadvantages, and results of testing with these systems vary. Given below are the most important differences between the two exposure systems.

STATIC EXPOSURE SYSTEM The static exposure system is most commonly used by the National Bureau of Standards (NBS) (17), which employs a cup furnace to decompose materials, and by Hilado (6), who uses a tube furnace. The NBS uses two temperature settings to test polymeric materials. The first setting produces thermal decomposition products at a temperature just below the ignition temperature of each material; the second setting produces thermal decomposition products in the flaming mode. One weakness of NBS tests done in the past has been their failure to measure the rate of material decomposition. Simple modifications of these exposure systems could allow for this measurement. The decomposition temperature required by NBS protocol seems reasonable. However, a low-oxygen condition has prevailed in the cup furnace during tests of large volumes of low-density samples. This can be rectified by increasing the cup size. The NBS tests have shown sufficiently rapid mixing and minimal deposition of thermal decomposition products on the walls of the exposure system.

By changing the sample size, the NBS investigators obtained concentration-response relationships for acute lethality (11), as did Hilado (16) in later experiments. NBS protocol requires determining the autoignition temperature of the materials being tested prior to establishing the temperatures at which they decompose. This could present problems during the testing of composite or

layered materials; carpets, for example, can have different layers with a wide range of autoignition temperatures.

DYNAMIC EXPOSURE SYSTEMS Two different dynamic exposure systems have been used to test the toxicity of polymeric materials and both yield valid concentration-response relationships for evaluating the acute lethal effects of a variety of polymers. The first system is a standardized method designated DIN53-436 by the German Standards Institution and commonly referred to as the DIN method (41); Herpol has also used this system (42). In the DIN system, samples are placed in a quartz tube. A furnace, set at 300–600°C, moves over the samples at a given rate for a fixed period of time, such as 30 minutes, and gradually decomposes the samples. Smoke escaping from the tube is then directed into the exposure chamber and diluted with room air to vary the toxicity level. A temperature of 600°C is high enough to decompose almost entirely all common polymeric materials. However, this decomposition system does not permit direct measurement of the rate of decomposition. In addition, Herpol reports (42) that tests of a large number of samples in multiple experiments show considerable differences in the behavior of the same samples as they decompose. Because of this drawback a comparison of toxicity between materials has been impossible. Nevertheless, it seems that with some modifications this approach should work. Indeed, LeMoan & Chaigneau (18) have obtained valid concentration-response relationships for several polymers, as listed in Table 4, using a similar decomposition system that changes the sample size rather than the dilution air to produce different levels of toxic effects.

The second dynamic-exposure system was originally developed by Barrow et al (43) and adapted to test a wide variety of polymers (20, 21, 44). This method is now known as the University of Pittsburgh protocol. In this method, the sample is placed in a furnace and heated, beginning at room temperature, at an established rate of 20°C per minute. Air flowing through the furnace at a rate of 11 liters per minute carries the smoke toward the exposure chamber. Cool air is also added to prevent excessive oxygen depletion and temperature increase. A schematic of this system is presented in Figure 2. The system generates smoke that continuously changes in chemical composition as the temperature increases. Animals are exposed to the smoke when 0.2 or 1% weight loss is recorded and continue to be exposed for 30 minutes, less if they all die prior to this time. Since initial polymer decomposition temperatures are seldom less than 200°C, the final temperature reached is 800°C, high enough to decompose all materials. Thus, the animals are first exposed to thermal decomposition products produced during pyrolysis at low temperature and then to products occurring during flaming conditions, if flaming ignition occurs. During exposure, CO, CO_2, and O_2 are monitored continuously. Depending on the nature of

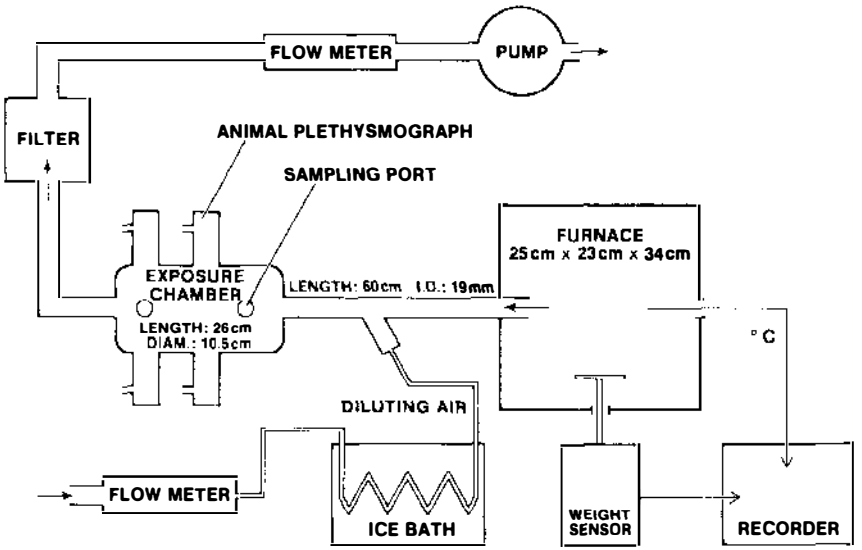

Figure 2 Experimental method to study the toxicity of thermal decomposition products from synthetic and natural polymers decomposed by increasing heat from room temperature at a rate of 20°C per minute. Taken from (20).

the polymer, formaldehyde, hydrogen cyanide and hydrogen chloride are also measured.

Some examples of the results obtained with this method are presented in Figures 3 and 4. Figure 3 illustrates the differences in toxicity observed between two cellulosic materials, Douglas fir and a heavily flame-retarded cellulose insulation fiber sample. The variation between these two cellulosic substances is clear. When the Douglas fir was heated, release of CO occurred at the point of flaming ignition and was responsible for the deaths of the animals. The flame retardant prevented flaming ignition of the cellulose fibers, but decomposition released a much larger amount of CO. Thus, although both samples were mainly cellulose, one was six times more toxic because it produced much more CO. Figure 4 illustrates the difference between two thermosetting plastics so difficult to ignite that they did not do so under experimental conditions. Urea-formaldehyde foam insulation released large amounts of HCN, but only above 450°C. Moreover, less than 20% of the 2.49 grams of urea-formaldehyde loaded in the furnace produced toxic smoke. The principal toxicant of phenol formaldehyde is carbon monoxide, which is released at temperatures above 300°C. Both samples released formaldehyde at fairly low temperatures. However, the amount of formaldehyde released was considerably lower than the lethal level for this chemical (45).

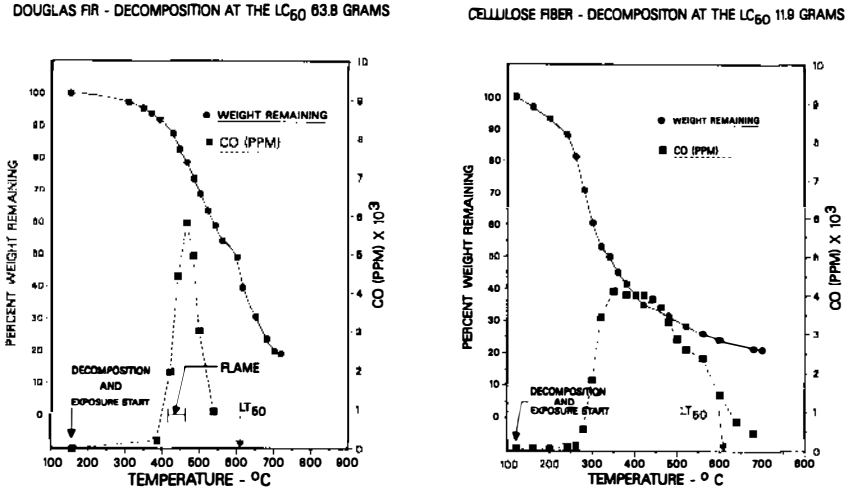

Figure 3 Decomposition patterns of Douglas fir and cellulose insulation fibers treated with flame retardant. Carbon monoxide release and flaming ignition temperature for Douglas fir as indicated. Beginning of exposure and temperature at which 50% lethality occurred as indicated. Both samples were heated at 20°C per minute, beginning at room temperature. Modified from (20).

With the dynamic exposure method of toxicity testing, the measurement of time for 50% mortality (LT_{50}) was calculated from the start of decomposition. This is dependent on the thermal stability of the polymers as well as on the rapidity of action of the toxicant released.

REPRODUCIBILITY OF TOXICITY MEASUREMENTS

The reproducibility of test results is an important aspect to consider when proposing protocols for the evaluation of toxicity. In 1982 the National Bureau of Standards organized a round-robin discussion of protocol among several laboratories. The group judged very good the results of experiments using the National Bureau of Standards testing method (17). More recently, the protocol used by the University of Pittsburgh was tested in three laboratories: the results are presented in Table 12. Considering that the Pittsburgh method contains two sources of variability, i.e. decomposition of the samples and biological variation, the results presented in Table 12 indicate good repeatability. The results obtained within the same laboratory were comparable and reproduced well and the results obtained by other different laboratories were also comparable. In fact, the results presented in Table 12 are well within the variation obtained in one laboratory performing oral LD_{50} tests (46).

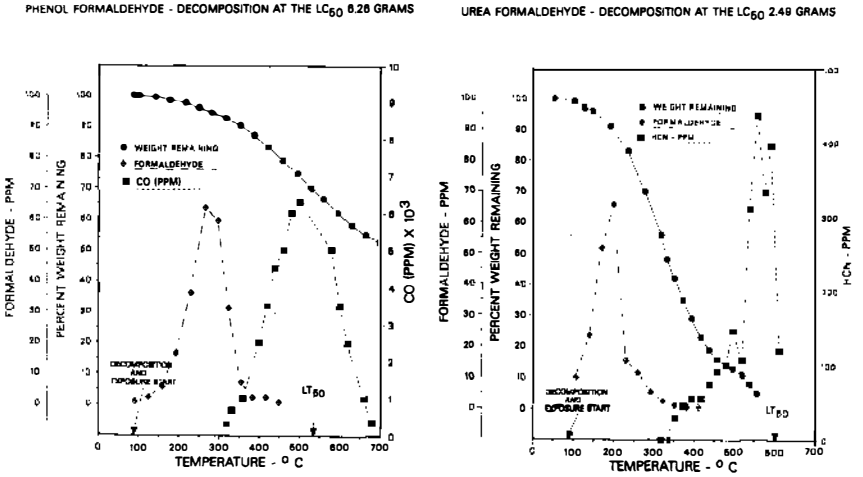

Figure 4 Decomposition patterns of phenol-formaldehyde foam and urea formaldehyde foam insulation with formaldehyde, carbon monoxide, and hydrogen cyanide release. Beginning of exposure and temperature at which 50% lethality occurred as indicated. Both samples were heated at 20°C per minute, beginning at room temperature. Modified from (20).

Table 12 Repeatability and reproducibility of the acute lethality measurement (LC_{50}) using the University of Pittsburgh experimental protocol described in (4, 20)

Materials	University of Pittsburgh	Biotecs Laboratory[b]	Arthur D. Little[c]
Douglas fir[a]	64	57	50
	78	61	
	56	64	
		59	
Average for Douglas fir ± (SD) = 61.1 (8.2) (n = 8)			
Phenol formaldehyde foam (GM-57)[a]	6.3	7.4	4.8
Polyester-fiberglass PEI[a]	35	36	
Polyester-fiberglass PE II[a]	57	58	
Vinyl coated wire[a]	15		15
Polyurethane foam flexible	13		9
Polyester-fiberglass halogen retardant HPE[a]	14	15	

[a] Samples furnished by the University of Pittsburgh
[b] Data supplied by C. P. Carpenter of Biotecs Laboratory, Mellon Institute, Pittsburgh
[c] Taken from (4)

CONCLUSION

During the past ten years, major advances have been made in the study of the toxicity of smoke from polymeric materials. Such advances have been possible because of the collaboration among toxicologists, analytical chemists, fire technology experts, and polymer chemists. We now recognize that smoke from different polymers will produce acute lethal effects different from the smoke of wood. Below is a summary of our basic findings:

1. Some synthetic polymers will release a much larger amount of carbon monoxide than wood does (17, 20, 21). In these cases the principal toxicant is the same as with wood or cotton, the difference being the yield of carbon monoxide per gram of polymer.
2. Because of their nitrogen content, some synthetic polymers release substantial amounts of hydrogen cyanide. Hydrogen cyanide is much more potent and faster acting than carbon monoxide; this is the reason why the smoke from these polymers is classified as more toxic and faster acting than wood smoke (20, 21). The results of Clark et al (47) indicate that high levels of cyanide are now being found in victims of smoke inhalation. Treatment of this condition will require much more involved procedures than the simple administration of oxygen.
3. Some synthetic polymers release large amounts of hydrogen chloride. This gas is more toxic to humans than carbon monoxide (34) and victims surviving exposure to this gas suffer very serious pulmonary complications (36, 48, 49). As a result, emergency room physicians must try to anticipate this type of toxic effect, which is quite different from intoxication by carbon monoxide or hydrogen cyanide. This is particularly important since polyvinylchloride is a very widely used polymer (1) and is likely to be involved in most fires. Unfortunately, there is no adequate treatment for intoxication by this gas, and recovery from pulmonary injury is extremely slow (36, 49).
4. Some synthetic polymers release CO or HCN at a very fast rate, much higher than the rate at which CO is released from wood or cotton (50). Because of this higher rate of emission, there is less chance for dilution. As a result, the overall exposure concentration will be higher (50), making these polymers more hazardous than wood or cotton in a fire.
5. Some synthetic polymers, the fluoropolymers, release toxicants, probably perfluoroisobutylene and other fluorinated hydrocarbons, that have been shown to be extremely toxic (30, 31). This explains why they fall in the category labeled much more toxic than wood (20, 21). We do not know the mechanism of their toxic action nor what kind of treatment should be used for their victims.

These five reasons explain why, in general, smoke from decomposing

synthetic polymers is faster acting and more toxic than smoke from wood. This can also be seen from the data presented in Figure 2.

Synthetic polymers were introduced into the US in large quantities only about thirty years ago (1). They have been instrumental in raising the American standard of living and their applications in science are useful and widespread. They also present serious problems when they decompose under heat. We must discover how best to use toxicity data in combination with the other properties of these materials to reduce deaths due to smoke inhalation. Clearly we have passed the point of questioning whether smoke from synthetic polymers is more toxic than smoke from wood. The answer obviously is yes. Now our task is to make sure that those who use large quantities of synthetic materials understand the toxicity of their thermal decomposition products and choose substances no more potentially toxic than wood. Combustible building materials, synthetic or natural, should be used with extreme care as replacements for noncombustible materials such as concrete, metals, glass, and ceramics. Finally, only synthetic polymers whose smoke is no more toxic than wood should be used in place of wood; smoke from wood is already toxic enough (20, 21). Only a better selection of building materials, combined with more effective fire prevention, will help improve our record on fire fatalities.

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Figures 1–4 reprinted with permission from Academic Press. Written under Grant 60NANB4D001 from the National Bureau of Standards. The conclusions are those of the author.

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