

# Acrylonitrile-Butadiene-Styrene Copolymers (ABS): Pyrolysis and Combustion Products and their Toxicity—A Review of the Literature

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A review of the literature was undertaken to ascertain the current knowledge of the nature of the thermal decomposition products generated from ABS and the toxicity of these evolved products *in toto*. The literature review encompasses English language publications available through June 1984. This literature surveyed showed that the principal ABS thermooxidative degradation products of toxicologic importance are carbon monoxide and hydrogen cyanide. The experimental generation of these and other volatile products is principally dependent upon the combustion conditions and the formulation of the plastic. The toxicity of ABS thermal degradation products has been evaluated by five methods. The  $LC_{50}$  (30 min exposure + 14 day post-exposure period) values for flaming combustion ranged from  $15.0 \text{ mg l}^{-1}$  to  $28.5 \text{ mg l}^{-1}$ . In the non-flaming mode of combustion, the  $LC_{50}$  values ranged from  $19.3 \text{ mg l}^{-1}$  to  $64.0 \text{ mg l}^{-1}$ . Therefore, no apparent toxicological difference exists between the flaming mode and the non-flaming mode. The toxicity of ABS degradation products was found to be comparable with the toxicity of the thermal decomposition products of other common polymeric materials.

**Keywords:** ABS plastics; carbon monoxide; combustion products; hydrogen cyanide; literature reviews; thermal decomposition; toxicity.

## INTRODUCTION

Although the hazard posed by toxic gases and vapors generated in a fire environment has long been recognized,<sup>1</sup> information regarding the toxic agent(s) generated from ABS which are responsible for fire deaths not attributable to burns is relatively sparse. The growth of the science of combustion toxicology over the last ten years has resulted in the generation of a large quantity of information regarding the thermal decomposition products of many natural and synthetic materials, and the relative toxicity of those materials' decomposition products *in toto*. This paper is a review of the English literature, available through June 1984, on the thermal decomposition products from acrylonitrile-butadiene-styrene (ABS) terpolymers and an evaluation of the toxicity data from animals exposed to those products.

The ABS plastics are of particular interest since they are found in numerous household items, such as telephones, appliances, luggage and piping, as well as in automobile and aircraft interior structures.

## CHEMICAL STRUCTURE AND THERMOPHYSICAL PROPERTIES

ABS polymers are synthesized from three monomeric chemicals: acrylonitrile, butadiene, and styrene (Fig. 1); from which the acronym is derived. The atomic components of these three chemical compounds are, exclusively, carbon, nitrogen and hydrogen, with carbon being the

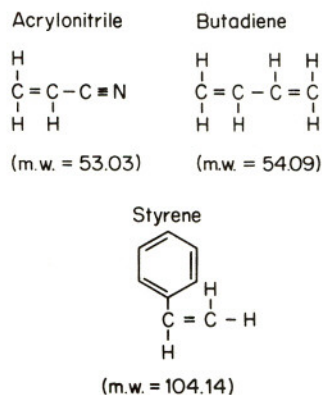


Figure 1. Chemical structure of ABS monomers.

predominant atomic species (atomic weight/molecular weight). The only source of nitrogen in the plastic is acrylonitrile, which contains approximately 26% nitrogen. The weight percentage of hydrogen is relatively small.

Acrylonitrile is a colorless liquid characterized by a strong odor. The boiling point of acrylonitrile is  $77.3^\circ\text{C}$  and its freezing point is approximately  $-83.55^\circ\text{C}$ . Acrylonitrile is soluble in most solvents, both polar and non-polar. Water solubility increases with temperature.<sup>2</sup> Acrylonitrile is capable of undergoing many chemical reactions, the majority of which occur at the carbon-carbon double bond. It is at this site that the homopolymerization of the acrylonitrile monomer occurs. This reaction takes place readily in the presence of initiators through either a free radical mechanism or an anionic mechanism of polymerization.<sup>3</sup> The resultant polymer, polyacrylonitrile, is a crystalline-type compound, which is not soluble in

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most common solvents, e.g. acids, greases, oils, water and hypochlorite solutions. It will, however, degrade when exposed to concentrated cold or hot dilute alkaline solutions, as well as warm 50% sulfuric acid. Although the acrylonitrile monomer is significantly toxic by either ingestion of the liquid or inhalation of the vapor, the homopolymer is considered essentially non-toxic.<sup>3</sup>

1,3-Butadiene is a colorless gas. The boiling point of butadiene is  $-4.5^{\circ}\text{C}$  and its freezing point is  $-108.96^{\circ}\text{C}$ . It is soluble in organic solvents.<sup>4</sup> Due to the presence of two double bonds, butadiene is a very reactive compound, allowing a variety of polymer structures to be formed. All polymerizations require either an initiator or catalytic factor and occur by a free-radical, an ionic or a coordinate mechanism. The end result, polybutadiene, is a rubber polymer formed by addition polymerization.<sup>5</sup>

Styrene is a colorless to yellowish, oily liquid which has a penetrating odor. The boiling point range of styrene is  $145$  to  $146^{\circ}\text{C}$  and the freezing point is  $-30.6^{\circ}\text{C}$ . Styrene is only slightly soluble in water; however, it is soluble in alcohol, ether, methanol, acetone and carbon disulfide. Styrene is not considered very toxic upon ingestion but is a significant irritant when applied to the skin, eyes and mucous membranes. The rate of polymerization of the styrene monomer is slow at room temperature and increases with heat. Since the polymerization is an exothermic process, the reaction can become self-accelerating. Styrene homopolymerization can occur either by free-radical or ionic reactions. The resultant polymer, polystyrene, is a clear, crystalline-type compound.<sup>6-8</sup>

ABS polymers (Fig. 2) can be produced by two general methods, each of which generates a different type of plastic. Type A ABS polymers are produced by a mechanical blending of a styrene-acrylonitrile copolymer resin with a butadiene-based elastomer (butadiene-acrylonitrile rubber). The production of Type B ABS involves a grafting of styrene and acrylonitrile onto polybutadiene. The Type B polymer also contains a styrene-acrylonitrile copolymer and ungrafted polybutadiene. The types of plastics are varied further by differences in the relative proportions of the monomer components. The styrene-acrylonitrile copolymer, for either type of production procedure, can be composed of 65–76% styrene and 24–35% acrylonitrile.<sup>9,10</sup> Since the formulations of ABS plastics are rarely the same and poorly defined in most of the studies examined for this review, it is difficult to generalize or compare ABS samples.

The temperatures at which ABS processing occurs range from  $325$ – $550^{\circ}\text{C}$ , depending upon the type and grade of plastic being produced as well as the technique being used. The melting point range for extrusion grades of ABS is  $88$ – $120^{\circ}\text{C}$  and for the injection molding grades of ABS,  $110$ – $125^{\circ}\text{C}$ .<sup>11</sup> The autoignition temperature of

the finished products, generally termed ABS, has been reported as  $466^{\circ}\text{C}$ <sup>12</sup> and between  $500$  and  $575^{\circ}\text{C}$ .<sup>13</sup> ABS polymers burn readily with the generation of dense smoke, which is characteristic of polymers containing aromatic rings.<sup>14</sup>

In general, the ABS plastics exhibit good durability and resilience, as well as mechanical strength. In addition, these thermoplastic polymers demonstrate a favorable combination of thermal, electrical and mechanical properties. The different properties may be selectively enhanced for specific applications by modification of the composition and/or relative proportions of the components. Such selective production is usually at the expense of one or more of the other properties.<sup>9,10,15</sup>

## THERMAL DECOMPOSITION

The type and quantity of the thermal degradation products from ABS plastics depends upon the combustion chamber utilized and the existing combustion conditions, as well as the composition of the plastic. The majority of the studies of the chemical analysis of the decomposition products of ABS has employed a combustion tube with a ring furnace to decompose the material. This type of combustion system is similar to that used in the DIN 53 436 toxicity test method (see below). This apparatus has the advantages of being easy to set up and operate and requiring only a small sample for testing. The combustion atmosphere is easily changed, allowing for pyrolysis studies under inert conditions as well as thermoxidative degradation experiments. This type of furnace may be programmed either to provide a constant temperature zone or to heat at a fixed rate. The disadvantages within this type of system also must be considered. One of the most important limitations is the large internal surface area on which combustion products may adsorb or react. In addition, the small sample size, listed as an advantage above, may also be considered a disadvantage since it does not provide enough material to be conducive to a flaming test mode. During the actual combustion, air and/or other gases are fed into the system in a manner which is contrary to the natural convective flow of air observed under natural combustion conditions.<sup>16</sup>

Other furnace systems have been used less frequently in combustion product generation and analysis. Therefore, their pertinent advantages and limitations will be addressed when the experiments conducted in these particular systems are initially discussed.

In the following sections, the results of the chemical analyses of the combustion atmospheres of ABS are separated according to the prevailing experimental conditions; i.e. inert or oxidative atmospheres. Although real fires occur normally under oxidative conditions, very often (especially in large fires) little or no  $\text{O}_2$  reaches the polymer surface. Therefore, the study of the volatile products generated under inert atmospheres provides information on the molecular mechanisms of thermal degradation under controlled experimental conditions. Also, information may be obtained on potential decomposition products that could be generated under vitiated atmospheres or at the polymer surface in real fires.

A summary of all the decomposition products of ABS

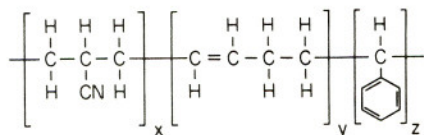


Figure 2. Representative chemical structure of an ABS polymer.



**Table 1. Degradation products of ABS**

Product	Atmosphere <sup>a</sup>	References
Acetophenone	I, O	19
Acids (—COOH)	O	24
Acrolein	I, O	19, 23, 24
Acrylonitrile	I, O	19, 23, 24
Aldehydes (total) (HCHO)	O	24
Benzaldehyde	I, O	19, 23
Carbon dioxide	O	13, 17
Carbon monoxide	O	13, 17, 18, 21, 24
Cresol	I, O	19
Dimethylbenzene	I, O	19
Ethanal	I, O	19
Ethylbenzene	I, O	19
Ethylmethylbenzene	I, O	19
Formaldehyde	O	24
Hydrogen cyanide	I, O	13, 17, 21, 24
Isopropylbenzene	I, O	19
$\alpha$ -Methylstyrene	I, O	19
$\beta$ -Methylstyrene	I, O	19
Nitric oxide	O	21
Nitrogen dioxide	O	21
Phenol	I, O	19
Phenyl cyclohexane	I, O	19
2-Phenyl-2-propanol	I, O	19
3-Phenyl-1-propene	I, O	19
n-Propylbenzene	I, O	19
Styrene	I, O	19, 23, 24
4-Vinyl-1-cyclohexene	I, O	19

<sup>a</sup>I = Inert pyrolysis atmosphere.

O = Oxidative combustion atmosphere.

identified under all the described experimental conditions is presented in Table 1, in which the combustion atmosphere (inert or oxidative) is indicated as are the studies which identified each product. The data indicate that the majority of the products generated are characteristic of both inert and oxidative conditions.

### Thermal degradation in inert atmospheres

This section will cover experiments performed in atmospheres devoid of oxygen. This experimental atmosphere, in effect, limits the type of degradation products formed, as oxidative decomposition is prevented.

Sumi and Tsuchiya<sup>17</sup> measured the amount of hydrogen cyanide (HCN) generated when chopped ABS pipe was exposed to a temperature of 800 °C in a combustion tube furnace with a nitrogen flow of 11 min<sup>-1</sup>. The evolved HCN was collected in a 0.4% sodium hydroxide (NaOH) trap and quantified with a cyanide ion (CN<sup>-</sup>) specific electrode. The maximum concentration of HCN generated under these experimental conditions was 0.034 g HCN g<sup>-1</sup> ABS sample. The generation of HCN under nitrogen did not differ quantitatively from that generated under oxidative conditions (see below).

The amount of carbon monoxide (CO) generated by pyrolysis of an ABS sample in a helium atmosphere was determined by Michal.<sup>18</sup> A horizontal combustion tube was used with a moving ring oven set at 550 °C. Helium gas was fed into the combustion chamber at a flow rate of 30 ml min<sup>-1</sup>. The ABS used was identified as Forsan 752E (Kaucuk, Kralupy, Czechoslovakia).<sup>a</sup> The results indicated that CO (as measured by gas chromatography)

was not detectable when this ABS sample was decomposed under the described inert pyrolysis conditions.

Hoff *et al.*<sup>19</sup> analyzed by gas chromatography-mass spectrometry the volatile products generated from two different ABS samples decomposed under an inert atmosphere. The two ABS samples were identified as Ugikral RA 10331 (Ugine Kulman; referred to as ABS-1) and Cycolac AM 25139 (Borg-Warner; referred to as ABS-2). ABS-1 and ABS-2 were pyrolyzed at 210 °C in a Pyrex glass degradation tube with a nitrogen gas flow of 20–30 ml min<sup>-1</sup>. The two ABS polymers demonstrated different properties upon thermal degradation. ABS-2, the less thermostable of the two, decomposed considerably faster and formed nearly three times as much styrene as ABS-1 (Table 2). ABS-2 also released higher amounts of other volatiles common to both plastics as degradation products, such as 2-phenyl-2-propanol, acetophenone,  $\alpha$ -methylstyrene and isopropylbenzene. ABS-1 did not generate any volatile products other than styrene in quantities greater than 100  $\mu$ g g<sup>-1</sup> of ABS sample pyrolyzed. Some of the degradation products from the ABS samples pyrolyzed under inert conditions contain oxygen, indicating the presence of oxygen-containing additives.

The extensive list of volatile products identified by Hoff *et al.*<sup>19</sup> (Table 2) may be a result of the experimental methodology. The decomposition products evolved during the thermal degradation of the polymer were removed from the furnace/combustion site by the nitrogen gas flow (20–30 ml min<sup>-1</sup>), potentially reducing their further degradation. Also, the temperature used is typical of those in industrial processing and, at most, may represent the temperature conditions during the early phase of a fire. The different amounts of styrene evolved from the two ABS plastics may be related to a difference in the acrylonitrile content of the plastic, as it has been shown that an increase in acrylonitrile content of styrene-acrylonitrile polymers favors a higher styrene yield during degradation.<sup>20</sup>

**Table 2. Thermal degradation products of two types of ABS decomposed in nitrogen<sup>19</sup>**

Degradation product	ABS-1 <sup>a</sup>	ABS-2 <sup>b</sup>
Styrene	2400 <sup>c</sup>	7400
2-phenyl-2-propanol <sup>d</sup>	20	580
Acetophenone <sup>d</sup>	23	420
$\alpha$ -Methylstyrene	12	230
Iso-propylbenzene	42	190
4-vinyl-1-cyclohexane	13	88
Benzaldehyde <sup>d</sup>	33	75
Ethylbenzene	23	54
Ethylmethylbenzene	11	39
n-Propylbenzene	18	32
$\beta$ -Methylstyrene	<10	18
Acrylonitrile	15	<10
Cresol <sup>d</sup>	48	—
Phenol <sup>d</sup>	33	—
Phenylcyclohexane	18	—
Di-methylbenzene	14	—
3-Phenyl-1-propene	<10	—

<sup>a</sup>Ugikral RA 10331, Ugine Kulman.<sup>b</sup>Cycolac AM 25139, Borg-Warner.<sup>c</sup>Values are micrograms of product evolved per gram of material pyrolyzed.<sup>d</sup>Oxygen-containing products.



### Thermooxidative degradation

When sufficient oxygen ( $O_2$ ) is present in the atmosphere, the primary gases formed during the combustion of most materials, including ABS, are CO and carbon dioxide ( $CO_2$ ). Hydrogen cyanide generation from nitrogen-containing materials occurs during thermooxidative degradation as well as during thermal degradation under inert atmospheres. Other thermooxidative products from ABS are listed in Table 1.

Table 3 summarizes the quantitative data in the literature on the generation of CO,  $CO_2$  and HCN from ABS decomposed under oxidative conditions. Although variations in test methods and ABS samples do not allow for direct, quantitative comparisons between studies, generally more CO and  $CO_2$  were generated in the flaming mode than in the non-flaming one. The production of HCN is approximately the same in both modes. The following sections will discuss the experimental studies on each of these primary gases separately.

**Carbon monoxide.** Gross *et al.*<sup>21</sup> measured the amount of CO generated during the combustion of two generic samples of ABS. The composition ratio of the monomers in the plastics was the same for both samples; however, the samples did differ in their physical characteristics and appearance. ABS sample 1 was 0.045 inches thick, weighed  $1.33 \text{ kg m}^{-2}$  and was a semi-rigid sheet with a dark gray matte finish. The second ABS sample was 0.08 inches thick, weighed  $2.35 \text{ kg m}^{-2}$  and was a rigid sheet with a green polished surface. Each ABS sample was placed in an  $18 \text{ ft}^3$  chamber and was subjected to thermal irradiation at a level of  $25 \text{ kW m}^{-2}$  to the normal-use exterior (or front) surface. Gas analysis during the course of experimentation was performed using colorimetric indicator tubes.<sup>b</sup> The maximum value from two separate determinations was reported; if these values differed by a factor of two, additional measurements were performed.

A ten-fold increase in the maximum generation of CO was demonstrated under flaming conditions as compared with the CO levels generated in the non-flaming or smoldering conditions (Table 3).

Similar findings are evident in the data from the interlaboratory evaluation (ILE) of the National Bureau of Standards (NBS) Toxicity Test Method (Table 3).<sup>13</sup> Four laboratories used the same ABS material and essentially the same combustion conditions. However, variations in the results can be attributed to individual laboratory modifications of the designed experimental protocol. An ABS copolymer in pellet form was thermooxidatively degraded in a crucible (or cup) furnace. The amount of air flow around the test sample in the furnace is unknown and not controlled. This may affect the formation of secondary combustion products and the completeness of combustion of evolved products. In the ILE of this test system, toxic gas analysis was performed by continuous flow, non-dispersive infra-red analysis or gas chromatography for CO and  $CO_2$  and either gas chromatography or specific ion electrodes were used for HCN measurement. The observed CO levels generated in the flaming mode generally exceeded levels measured in the non-flaming mode of combustion of the ABS; however, the differences were not as great as those found by Gross *et al.* (i.e. ten-fold).<sup>21</sup> One of the four ILE participating laboratories who examined ABS reported no significant difference in mean CO levels (laboratory #3). The reason for the differences between the data of Gross *et al.*<sup>21</sup> and of Levin *et al.*<sup>13</sup> is unknown.

Sumi and Tsuchiya<sup>17</sup> used gas chromatography to measure the amount of CO generated from chopped ABS pipe subjected to a series of increasing temperatures in a combustion tube furnace (Table 3). An initial increase in CO production was observed when the temperature was raised from 500–600 °C. Further elevation of temperature in 100° increments up to a maximum of 800 °C resulted in a decrease in CO levels. However, when the  $O_2$  con-

**Table 3. Primary toxicants from experimental ABS thermooxidative degradation**

Reference	Apparatus	Combustion atmosphere	Temperature or radiant flux	Sample	Mode	CO <sup>a</sup>	HCN <sup>a</sup>	CO <sub>2</sub> <sup>a</sup>
21	Radiant heating	Air	$25 \text{ kW m}^{-2}$	Sample 1	F <sup>b</sup>	21	0.8	—
					NF <sup>c</sup>	2.0	0.6	—
				Sample 2	F	29	0.8	—
					NF	3.2	0.7	—
17	Combustion tube	Air	500 °C			48	19	223
			600 °C			55	21	272
			700 °C			36	25	254
			800 °C			27	36	297
			800 °C			52	44	58
13	Cup furnace	Air:N <sub>2</sub> 50:50	800 °C					
		Air	550 °C	1 <sup>d</sup>	F	$62 \pm 26^e$	$9 \pm 1$	$900 \pm 342$
			500 °C		NF	$17 \pm 14$	$2 \pm 0.5$	$414 \pm 144$
			725 °C	3	F	$126 \pm 75$	$12 \pm 1$	$954 \pm 396$
			530 °C		NF	$160 \pm 184$	$6 \pm 1$	$954 \pm 756$
			694–700 °C	5	F	$76 \pm 14$	—	$792 \pm 160$
			475 °C		NF	$15 \pm 2$	—	$270 \pm 86$
			600 °C	6	F	$86 \pm 18$	$7 \pm 3$	$990 \pm 104$
			525 °C		NF	$25 \pm 3$	$6 \pm 0.5$	$306 \pm 27$

<sup>a</sup>Expressed as milligrams per gram of sample.

<sup>b</sup>Flaming combustion.

<sup>c</sup>Non-flaming combustion.

<sup>d</sup>The numbers respond to the laboratory code of those laboratories participating in the interlaboratory evaluation.

<sup>e</sup>Values are the mean  $\pm$  standard deviation.



centration was decreased by 50% by nitrogen, the CO level increased two-fold over that found at 800 °C in air alone. The authors provide no indication of whether or not the specimens flamed during their tests. However, as noted above, the quartz tube furnace is not conducive to flaming combustion.

**Hydrogen cyanide.** The generation of HCN, like that of CO, is dependent upon the combustion conditions. The data from the previously described work of Gross *et al.*<sup>21</sup> and Levin *et al.*<sup>13</sup> (laboratory #6 of the ILE) demonstrate no difference between the evolution of HCN gas during flaming combustion and during non-flaming thermal degradation (Table 3). However, some data (laboratories 1 and 3 of the ILE) indicate a somewhat greater production of HCN in the flaming mode of combustion than in the non-flaming one (Table 3).<sup>13</sup> Sumi and Tsuchiya<sup>17</sup> demonstrated an increase in HCN production as the temperature increased from 500 to 800 °C. The incidence of flaming combustion, however, was not noted. For the 300 °C increase in temperature, the generation of HCN increased approximately two-fold. At 800 °C, a 50% decrease in the O<sub>2</sub> content of the combustion atmosphere increased HCN production by approximately 20%.

**Carbon dioxide.** Sumi and Tsuchiya<sup>17</sup> examined the effect of temperature on the production of CO<sub>2</sub>. Carbon dioxide production was approximately five- to ten-fold greater than CO production (Table 3). The CO<sub>2</sub> production at all temperatures was approximately the same, ranging from 223 to 297 mg g<sup>-1</sup> sample. The occurrence of flaming combustion was not reported. In a combustion atmosphere of air and nitrogen (50/50; 10% O<sub>2</sub>), the yields of CO and CO<sub>2</sub> were of the same order of magnitude (52 and 58 mg g<sup>-1</sup> sample, respectively).

The data reported by Levin *et al.*<sup>13</sup> also demonstrated a preponderance of CO<sub>2</sub> over CO generated in the combustion of ABS (Table 3). Except for the results reported by one of the participating laboratories (laboratory #3), CO<sub>2</sub> production was greater in the flaming mode than in the non-flaming one. The mean CO<sub>2</sub> values differed between combustion modes by a factor of two to three.

**Organic volatiles.** The classes of organic volatiles and the summed quantities of the individual agents generated during the experimental thermooxidative degradation of various samples of ABS are presented in Table 4 and discussed below. Some of these compounds, such as acrolein and styrene, have known irritant properties and may be present in high enough concentrations to compound the hazard of the fire environment by affecting the mucous membranes and respiratory tracts of exposed individuals.

Zitting and Heinonen<sup>23</sup> measured the levels of styrene, benzaldehyde, acrolein and acrylonitrile when Cylolac T 10000 (Borg Warner) was decomposed in air at 250, 300 and 350 °C in a combustion tube furnace with an air flow of 0.5 l min<sup>-1</sup>. Styrene and benzaldehyde were measured by gas chromatography, acrolein by high pressure-liquid chromatography (HPLC) of its 2,4-dinitrophenylhydrazide derivative and acrylonitrile by colorimetric indicator tubes.<sup>b</sup> The aromatic hydrocarbon yield (in this case, styrene) increased with each 50 °C increase in temperature, as did the aldehydes (benzaldehyde and acrolein) and acrylonitrile (Table 4). The amount of benzaldehyde present exceeded the measured amount of acrolein one hundred-fold.

Zitting and Savolainen<sup>24</sup> determined the quantity of various organic volatiles when Cylolac T 1000 was thermooxidatively degraded at temperatures of 300 and 330 °C. Gas chromatographic analyses of styrene (listed as an aromatic hydrocarbon in Table 4) indicated that the concentration doubled with the 30 °C increase in degradation temperature. The same relative increase was seen with acrylonitrile and the organic acids which were measured by back titration with NaOH. The aldehyde concentrations (acrolein, formaldehyde and total aldehydes) also increased with the increase in temperature; however, this increase was less than two-fold. Acrolein was measured by the method of Cohen and Altshuler.<sup>25</sup> Formaldehyde concentration was determined by a chromatographic method<sup>26</sup> and total aldehydes by sodium bisulfite titration.

Hoff *et al.*<sup>19</sup> thermooxidatively decomposed two ABS plastics, Ugikral RA 10331 (ABS-1) and Cylolac AM

**Table 4. Organic volatiles from experimental ABS thermooxidative degradation**

Reference	Apparatus	Combustion atmosphere	Temp. (°C)	Hydrocarbons	Aromatic hydrocarbons	Alcohols	Ketones	Aldehydes	Acids	Acrylonitrile
19	Combustion tube									
ABS-1		Air	208	10 µg g <sup>-1</sup>	2445 µg g <sup>-1</sup>	72 µg g <sup>-1</sup>	35 µg g <sup>-1</sup>	69 µg g <sup>-1</sup>	—	19 µg g <sup>-1</sup>
ABS-2			197	82 µg g <sup>-1</sup>	8256 µg g <sup>-1</sup>	700 µg g <sup>-1</sup>	450 µg g <sup>-1</sup>	218 µg g <sup>-1</sup>	—	< 10 µg g <sup>-1</sup>
23	Combustion tube	Air	250	—	35 mg m <sup>-3a</sup>	—	—	13 mg m <sup>-3b</sup>	—	< 1 mg m <sup>-3</sup>
			300	—	87 mg m <sup>-3</sup>	—	—	26 mg m <sup>-3</sup>	—	4 mg m <sup>-3</sup>
			350	—	120 mg m <sup>-3</sup>	—	—	43 mg m <sup>-3</sup>	—	9 mg m <sup>-3</sup>
24	Combustion tube	Air	300	—	11.8 ppm <sup>a</sup>	—	—	8.4 ppm <sup>c</sup>	2.1 ppm <sup>d</sup>	2 ppm
			330	—	24.5 ppm	—	—	11.5 ppm	3.9 ppm	4 ppm

<sup>a</sup>Styrene.

<sup>b</sup>Benzaldehyde with small amount of acrolein.

<sup>c</sup>Acrolein, formaldehyde and total aldehydes.

<sup>d</sup>Organic acids (as —COOH).



**Table 5. Thermooxidative degradation products of two types of ABS<sup>19</sup>**

Degradation product	ABS-1 <sup>a</sup>	ABS-2 <sup>b</sup>
Styrene	2300 <sup>c</sup>	7800
2-Phenyl-2-propanol	< 10	700
Acetophenone	35	450
Iso-propylbenzene	35	190
Benzaldehyde	43	130
$\alpha$ -methylstyrene	< 10	120
4-vinyl-1-cyclohexene	10	82
Ethylbenzene	20	56
Acrolein	15	50
Ethymethylbenzene	14	38
Ethanal	11	38
n-propylbenzene	18	35
$\beta$ -methylstyrene	< 10	17
Acrylonitrile	19	< 10
Cresol	37	—
Phenol	25	—
Phenylcyclohexane	16	—
Di-methylbenzene	12	—

<sup>a</sup>Ugikral RA 10331, Uguine Kulman.<sup>b</sup>Cyclac AM 25139, Borg Warner.<sup>c</sup>Values are micrograms of product per gram of material pyrolyzed.

25139 (ABS-2) at 208 °C and 197 °C, respectively, and measured a number of organic volatiles (Tables 4 and 5). Styrene was the principal degradation product measured. ABS-1 generated six times more styrene than the total of all other combustion products combined and ABS-2 generated four times more styrene than the total of all the other volatiles. Thus, the aromatic hydrocarbons were the predominant class of organic volatiles. During the thermooxidative degradation of ABS-1 no other measured compound appeared in the fire atmosphere in quantities equal to or greater than 100  $\mu\text{g g}^{-1}$  of sample. ABS-2 generated significant amounts (greater than 100  $\mu\text{g g}^{-1}$  of sample) of 2-phenyl-2-propanol, acetophenone, isopropylbenzene, benzaldehyde and  $\alpha$ -methylstyrene in addition to styrene; the other measured compounds appeared in quantities less than 100  $\mu\text{g g}^{-1}$  of sample (Table 5). Comparison of Tables 2 and 5 indicates that similar degradation products evolved during the degradation of ABS-1 and ABS-2 under both inert and oxidative conditions, which demonstrates no significant oxidative effect on the products. Therefore, either no oxidation occurs under the described thermooxidative combustion conditions or the combustion apparatus prevented oxidation from occurring.

## COMBUSTION PRODUCT TOXICITY

In laboratory experiments designed to assess the toxicity of combustion products of either natural or synthetic materials a number of factors must be considered, including the experimental design, the physical apparatus, the combustion conditions and the material sample. A review of the literature on ABS combustion product toxicity is presented below with appropriate consideration given to these important factors.

The variety of ill-defined material formulations, experimental systems and conditions that have been used to assess ABS combustion product toxicity makes inter-

laboratory comparison of data difficult. However, sufficient toxicity data obtained using different test methods exist to compare the toxicity of the thermal degradation products of ABS to those of other materials such as Douglas fir. (Although it is recognized that Douglas fir is not a substitute for ABS in commercial products, the large realm of toxicological data on wood provides a point of reference with which the relative toxicity of materials can be compared.) Certain other characteristics of the combustion product toxicity can also be inferred. A brief description of each test system will precede a discussion of the data.

## National Bureau of Standards (NBS) toxicity test method

The NBS test method<sup>27</sup> utilizes a static exposure system in which the combustion products accumulate in the exposure chamber for the duration of the exposure. The system employs a cup furnace which generates combustion products directly into the 200 l exposure chamber. The material to be tested is decomposed at a cup furnace temperature 25 °C above (flaming mode) and below (non-flaming mode) the predetermined autoignition temperature of that particular material. The experiments may also be performed at furnace temperature of 440 °C if the autoignition temperature exceeds 490 °C. The design of the exposure chamber provides for head-only exposure of six rats, as well as sampling of the chamber atmosphere for chemical analyses. Carbon monoxide, CO<sub>2</sub> and O<sub>2</sub> are monitored continuously. Hydrogen cyanide is measured approximately every 3 min when a nitrogen-containing material is tested.

The biological/toxicological endpoints that have been used with this test method are incapacitation and lethality. Incapacitation is determined by the hind limb flexion conditioned avoidance response for which an  $EC_{50}$  value is determined. For lethality, an exposure  $LC_{50}$  value (the mass loading of material per unit volume of the chamber necessary to cause 50% of the test animals to die) is determined, as well as an  $LC_{50}$  value for both the exposure and post-exposure observation periods. The procedure also calls for the observation of toxic signs during the 30-min exposure period and the 14-day post-exposure period, during which daily animal body weights are recorded. Carboxyhemoglobin (COHb) levels are measured before, during exposure and just before the end of the exposure period in two animals, which are cannulated 24 h prior to exposure.

The toxicity data from Levin *et al.*<sup>13</sup> and Anderson *et al.*<sup>28</sup> show that the degradation products from ABS may be more toxic when decomposed under flaming thermooxidative conditions than non-flaming ones (Table 6). The within-exposure ( $LC_{50}$  (30 min)) and the within plus post-exposure ( $LC_{50}$  (30 min + 14 days)) results are equivocal in the comparison of toxicity under the two modes of combustion. The animal deaths did occur during both the exposure and post-exposure periods. The incapacitation data ( $EC_{50}$ ) demonstrate that the flaming and the non-flaming modes produced combustion products of approximately equal toxicity. In addition, Anderson *et al.*<sup>28</sup> reported that some animals demonstrated a degree of corneal opacity when ABS was degraded in the non-flaming mode.



Table 6. ABS toxicity data—NBS toxicity test method<sup>13,28</sup>

Laboratory	$EC_{50}$ (mg l <sup>-1</sup> )		440 °C	$LC_{50}$ (30 min) (mg l <sup>-1</sup> )		$LC_{50}$ (30 min + 14 d) (mg l <sup>-1</sup> )		440 °C
	F <sup>a</sup>	NF <sup>b</sup>		F	NF	F	NF	
1 <sup>c</sup>	10.6 (7.4–15.2) <sup>e</sup>	~ 21.0 <sup>d</sup> [15.1–25.2]	~ 20.2 [15.1–25.2]	17.4 (13.9–21.9)	22.0 (17.6–27.5)	15.0 (12.3–18.3)	19.3 (13.9–26.9)	30.0 (26.5–34.0)
3	6.0 (4.1–8.9)	5.8 (2.8–8.4)	9.0 (4.7–17.3)	15.6 (13.2–18.4)	> 38.0	15.6 (13.2–18.4)	> 38.4	> 38.0
5	~ 17.0 [15.0–20.0]	~ 23.0 [18.5–27.5]	< 37.6	20.8 (18.9–22.9)	33.0 (22.8–47.8)	20.8 (15.9–27.2)	33.3 (23.1–47.9)	> 37.6
6 <sup>f</sup>				22.1 (20.1–24.4)	> 32.5	19.3 (16.7–22.3)	30.9 (21.2–45.0)	N.D. <sup>g</sup>
ADL <sup>h</sup>						28.5 (23.6–34.5)	64.0 (54.2–75.5)	

<sup>a</sup>Flaming mode of combustion.<sup>b</sup>Non-flaming mode of combustion.<sup>c</sup>The numbers respond to the laboratory code of those laboratories participating in the NBS interlaboratory evaluation.<sup>13</sup><sup>d</sup>Estimated value; numbers in brackets used for estimate.<sup>e</sup>95% confidence limits.<sup>f</sup>NBS large furnace.<sup>g</sup>Not determined.<sup>h</sup>Data from Anderson *et al.*<sup>28</sup>Table 7. ABS toxicity data: NBS toxicity test method—carbon monoxide, COHb and HCN<sup>13</sup>

Laboratory	CO (ppm) <sup>a</sup>		$LC_{50}$ (30 min) COHb (%) <sup>b</sup>		HCN (ppm) <sup>a</sup>		CO (ppm) <sup>c</sup>		$EC_{50}$ (30 min) COHb (%) <sup>b</sup>		HCN (ppm) <sup>c</sup>	
	F <sup>d</sup>	NF <sup>e</sup>	F	NF	F	NF	F	NF	F	NF	F	NF
1 <sup>f</sup>	900	330	23	—	130	50	550	320	< 23	—	80	~ 50
3	1500	> 850	60	> 22	180	> 160	590	130	26	6	70	24
5	1500	420	44	18	—	—	1200	290	37	18	—	—
6 <sup>g</sup>	1800	> 700	44	> 28	160	> 160	—	—	—	—	—	—

<sup>a</sup>Average calculated for 30 min exposure at  $LC_{50}$  (30 min).<sup>b</sup>COHb values measured just prior to end of 30 min exposure.<sup>c</sup>Average calculated for 30 min exposure at  $EC_{50}$ .<sup>d</sup>Flaming mode of combustion.<sup>e</sup>Non-flaming mode of combustion.<sup>f</sup>Numbers respond to the laboratory code of those laboratories participating in the NBS interlaboratory evaluation.<sup>13</sup><sup>g</sup>NBS large furnace.Table 8. Relative toxicity of ABS and Douglas fir—NBS test method<sup>13</sup>

Laboratory	ABS						Douglas fir					
	$LC_{50}$ <sup>a</sup> (mg l <sup>-1</sup> )	Flaming CO <sup>b</sup> (ppm)	HCN <sup>b</sup> (ppm)	$LC_{50}$ (mg l <sup>-1</sup> )	Non-flaming CO (ppm)	HCN (ppm)	$LC_{50}$ (mg l <sup>-1</sup> )	Flaming CO (ppm)	HCN (ppm)	$LC_{50}$ (mg l <sup>-1</sup> )	Non-flaming CO (ppm)	HCN (ppm)
1	17.4	900	130	22.0	330	50	35.0	3100	—	21.7	3000	—
3	15.6	1500	180	> 38.0	> 850	> 160	~ 24.9	2700	—	37.3	3900	—
5	20.8	1500	—	33.0	420	—	38.4	3600	—	> 46.5	> 4400	—
6 <sup>c</sup>	22.1	1800	160	> 32.5	> 700	> 160	39.8	3400	—	29.0	3400	—

<sup>a</sup> $LC_{50}$  for the 30 min exposure period.<sup>b</sup>Average CO calculated for the 30 min exposure at the  $LC_{50}$  (30 min).<sup>c</sup>NBS large furnace.

The concentrations of CO and HCN in the combustion atmosphere are measured according to the protocol of the NBS test method and the results are presented in Table 7. More CO was generated in the flaming than the non-flaming exposure atmospheres and correspondingly higher COHb levels were noted in the exposed animals; however, the amount of CO was not sufficient to account for the lethality of the animals.<sup>29</sup> On the other hand, the measured HCN concentrations in the exposure atmospheres were sufficient by themselves or with the additional CO to account for the deaths that were observed in laboratories 1, 3 and 6 in the flaming mode. In the non-flaming mode, laboratory 1 reported HCN and CO levels

that either individually or together were too low to account for the observed within-exposure deaths. Whereas, laboratories 3 and 6 reported HCN levels sufficiently high enough to have caused within-exposure deaths, in actuality, no deaths were observed (Table 7).

Under flaming conditions, the  $LC_{50}$  values for ABS were lower than those found for Douglas fir by approximately a factor of two (Table 8). This difference may not be regarded as toxicologically significant. There is no significant difference in toxicity between ABS and Douglas fir when combusted in the non-flaming mode, even though the wood generates a significantly greater amount of CO under both combustion conditions. These results



support the earlier implication of the involvement of another toxicant (presumably HCN) in the toxic action of ABS combustion products.

### University of Michigan test methods

Two test systems, one static and one dynamic, each with distinct characteristics, were developed by Cornish and coworkers.<sup>30-32</sup> The static system consists of a 1500 l stainless steel exposure chamber in which mice are exposed in a whole-body fashion to the combustion products for a period of 4 h. Combustion products are generated by placing the test material in a Vycor tube wrapped with resistance wire which produces a combustion temperature of 700–800 °C in 1–2 min. The  $LC_{50}$  is determined after a 7-day observation period. Additional animals may be tested and sacrificed following exposure for histological/pathological examination.

The dynamic University of Michigan test system consists of a flow-through Pyrex glass tube chamber with side ports for the head-only exposure of rats. The combustion products are generated from materials placed in ceramic boat in a combustion furnace. The furnace temperature is programmed to increase 3 to 5 °C per minute to a maximum temperature of 700–800 °C. Carrier air is passed through the combustion apparatus at a rate of 1 l min<sup>-1</sup> and an additional diluting air stream of 2 l min<sup>-1</sup> is added before the combustion products enter the exposure chamber. The exposure period parallels the time course of combustion product generation during the degradation of the material sample.

The amount of material consumed which kills 50% of the exposed animals ( $LA_{50}$ )<sup>c</sup> from a number of studies on ABS decomposed in both the static and the dynamic test systems are listed in Table 9. The specimens were not identified sufficiently to determine if the ABS material tested was identical in all three studies. The data provide some information on the relative toxicity of fire retardant (unspecified) treated ABS (ABS-FR) and non-fire retarded ABS samples and other materials used in these studies. Because of the great differences in design and operation of the static and dynamic exposure systems the specific toxicity of any one material in either system should not be compared. However, the relative toxicities of different materials studied within one system should be comparable with that found in others. This does not always hold.<sup>32</sup>

In the static exposure system red oak is a factor of two more toxic than ABS and ABS-FR (Table 9). However,

the results of the experiments with the dynamic exposure system rank both ABS and ABS-FR of approximately equal toxicity with red oak (Table 9). When one considers the relative toxicities of ABS and polypropylene in the static exposure system, polypropylene is equal in toxicity to ABS; whereas in the dynamic exposure system it is more toxic (Table 9).<sup>32</sup> Therefore, these data indicate that a change in combustion systems will affect different materials differently.

The  $LA_{50}$  values from the experiments using both the dynamic and the static systems<sup>30,31</sup> do not show much difference between the apparent toxicities of the combustion products of ABS and those of ABS-FR (Table 9). However, the specific mortality results, taken in a separate study,<sup>32</sup> do indicate a difference. For example, when rats were exposed in the static system to the combustion products of a 20 g sample of ABS-FR, 14 out of 15 animals (93%) died. Three of four rabbits also died when subjected to the same exposure conditions.<sup>32</sup> This mortality is somewhat greater than anticipated, since a 20 g sample is essentially equivalent to the reported  $LA_{50}$  value.<sup>30,32</sup> In contrast, no rats or rabbits died from the exposure when a 20 g sample of non-fire retarded ABS was decomposed,<sup>32</sup> although the reported  $LA_{50}$  value is also approximately 20 g<sup>30,31</sup> or slightly greater (33 g).<sup>32</sup> These inconsistencies which are evident between the mortality data<sup>32</sup> and the  $LA_{50}$  values<sup>30-32</sup> for ABS and ABS-FR are not explained.

### University of Pittsburgh (PITT) method

This dynamic test system was developed by Alarie and Anderson.<sup>33</sup> A Lindberg furnace programmed to heat at 20 °C min<sup>-1</sup>, starting at room temperature, is responsible for the generation of combustion products. The test material starts in the non-flaming mode and will flame when the material's autoignition temperature (under these combustion conditions) is exceeded. Animal exposure begins in the non-flaming mode when 0.2% of the material has decomposed. An air flow of 1 l min<sup>-1</sup> is maintained through the furnace during the combustion of the material. Total air flow entering the exposure chamber amounts to 20 l min<sup>-1</sup> following dilution of the combustion gases with cooling air. The 2.3 l glass exposure chamber accommodates four mice in the head-only exposure mode. The biological endpoints/parameters which are determined include the  $RD_{50}$  (i.e. the concentration of smoke that produces a 50% decrease in respiratory rate), a sensory irritation stress index (SISI), asphyxiant effects, lethality and histopathological changes. Analyses of the combustion atmosphere for primary toxicants and O<sub>2</sub> depletion are also performed.

A very limited amount of ABS toxicity information derived from this test system is available. Alarie and Anderson<sup>34</sup> determined an  $LC_{50}$  of 6.3 g (10.5 mg l<sup>-1</sup>)<sup>d</sup> where the  $LC_{50}$  is the amount of material loaded in the furnace that is required to kill 50% of the animals within an exposure period of 30 min and a post-exposure period of 10 min. The ABS sample used was only described as 'standard acrylonitrile-butadiene-styrene'. The  $LT_{50}$ , the time at which 50% of the animals die at the sample weight killing 50% of the animals (or the sample weight nearest above it), was recorded as 9 min. According to the

Table 9. Toxicity data—University of Michigan test method

Material	$LA_{50}$ values <sup>a</sup>		Reference
	Static	Dynamic	
ABS	18	1.7	30
	22	1.8	31
	33	2.2	32
ABS-FR <sup>b</sup>	20	2.2	30
	21	2.3	32
Red oak	9	3.6	32
polypropylene	28	0.9	32

<sup>a</sup>Amount (grams) of material consumed necessary to cause the death of 50% of the exposed animals.

<sup>b</sup>Fire-retarded treated sample.



evaluation criteria incorporating both the concentration-response and time-response, the ABS is classified as being more toxic than wood (i.e. Douglas fir) and toxic actions occur faster upon exposure to ABS combustion products than upon exposure to the combustion products of wood.

Anderson *et al.*<sup>28</sup> also tested ABS using the PITT method in their report to the New York State Office of Fire Prevention and Control. An  $LC_{50}$  value<sup>d</sup> of  $9.3 \text{ mg l}^{-1}$  was obtained for the ABS sample used. The  $LT_{50}$  range during which the deaths occurred was 0–40 min with an additional death reported during the period of 49 h to 14 days post exposure. Again, the ABS also proved to be more toxic than Douglas fir.

#### DIN 53 436 method—Federal Republic of Germany

This apparatus was developed in the Federal Republic of Germany and adopted as a standard test method by the German Commission of Standards.<sup>35</sup> The combustion apparatus consists of a silica tube with a ring oven which moves along the combustion tube at a rate of  $10 \text{ mm min}^{-1}$ . In these flow experiments the key parameters are residence time in the heated zone and air/fuel (gas) ratio. Air flow through the combustion tube is provided at a rate of  $1001 \text{ h}^{-1}$  in a direction counter to the movement of the oven. The combustion products are diluted, cooled and carried into the exposure chamber by a total air flow of  $2001 \text{ h}^{-1}$ . Various exposure chambers can be used to provide for either whole body or head-only exposures. The toxicological endpoint is animal death. In addition, the animals are observed for toxic signs during and following the exposure. Gross pathological examinations are performed when appropriate. The typical protocol consists of a 30-min exposure period and a 7–14-day post-exposure observation period.

Kimmerle<sup>36</sup> used the head-only exposure system to evaluate the toxicity of two samples of ABS, a solid and a foam. The mortality data are presented in Table 10. It appears that a substantial increase in mortality occurred when the decomposition temperature of the solid ABS sample was increased from 350–400 °C. Although the CO concentration at 400 °C was increased more than two-fold

in the atmosphere, the level was too low to account for the deaths. The carboxyhemoglobin levels in the rats exposed to solid ABS being degraded at 400 °C were also higher than the other groups but still well below toxic levels, which were shown by Levin *et al.* to be above 80%.<sup>29</sup> The increased HCN concentration from 100 to 150 ppm, however, was enough to cause lethality in 30 min.<sup>29</sup>

An ABS foam differed from the above described solid ABS in that the increase in mortality at the elevated temperature was much less for the foam. No change in CO concentration was recorded when the foam was degraded at the higher temperature, and the five-fold increase in HCN concentration resulted in a final concentration of only 100 ppm. It is, therefore, not surprising that fewer rats died in the 30-min exposure to the combustion products of the ABS foam as compared with the solid. These results show that the solid ABS combustion products appear to be more toxic than those of the ABS foam when exposed to temperatures of 400 °C. At this temperature, lethal levels of HCN are generated from the solid ABS sample while sublethal levels are produced from the ABS foam. In both cases, HCN concentrations increased at the higher temperature. The differences in toxicity between the two ABS samples can be attributed to possible variations in the formulation of the solid and foam.

Herpol<sup>37</sup> also utilized the DIN test apparatus to evaluate the toxicity of an ABS sheet. However, the chamber system was modified to allow for individual whole-body exposure of the rats. This ABS sample was degraded at three different temperatures (400, 600 and 800 °C) and the mortality found at each temperature is given in Table 11. The toxicity of ABS increases with an increase in combustion temperature. However, at the two higher temperatures more material degraded. This temperature phenomenon was also described to some degree by Kimmerle<sup>36</sup> (see above). A significant mortality was evident at 400 °C and not at 350 °C in the results for the ABS solid.<sup>36</sup> However, Herpol did not observe any animal deaths until a temperature of 600 °C was reached.<sup>37</sup> This may reflect a difference in material concentration, formulation or any number of possible variations in the experimental conditions. Herpol<sup>37</sup> demonstrated an increase in the CO and CO<sub>2</sub> indices as the temperature increased from 400–600 °C. These indices are calculated by summing the recorded values at each minute and indicate the amount of gas liberated by the test material during the test period. A slight decrease was evident when the temperature was further increased to 800 °C (see Table 11). In pure CO experiments, Herpol<sup>37</sup> found that the CO index necessary to cause death during a

Table 10. ABS toxicity data—DIN 53 436 method<sup>36</sup>

Sample	Temp. (°C)	Mortality (# dead/# tested)	CO (ppm)	COHb (%)	HCN (ppm)
ABS solid	350	0/20	150	5.8	100
	400	13/20	350	14.2	150
ABS foam	350	0/20	100	6.2	20
	400	2/20	100	7.3	100

Table 11. ABS mortality and toxicity data—DIN 53 436 method<sup>37</sup>

Temp. (°C)	Number of tests	Sample <sup>a</sup> wt (g)	Weight loss of sample (%)	Mortality (# dead/# exposed)	Mean COHb <sup>b</sup> (%)	CO index <sup>c</sup> (ppm. min)	CO <sub>2</sub> index <sup>c</sup> (%v/v. min)
400	3	10.0	48	0/18	—	2950	2.0
600	4	10.0	90	3/24	56	69550 <sup>d</sup>	110.9
800	5	10.0	90	9/29	40	51940 <sup>d</sup>	86.0

<sup>a</sup>Wt of sample charged.

<sup>b</sup>Mean COHb levels of those animals which died.

<sup>c</sup>The CO and CO<sub>2</sub> indices are calculated from the measurements at each minute interval and summing the values. The indices provide an estimate of the total amount of toxicant liberated during the exposure period.

<sup>d</sup>CO index at the moment of death.



30-min exposure was 120 000 ppm.min (equivalent to a 30-min exposure to 4000 ppm). A CO<sub>2</sub> index of 300%.min (equivalent to a 30-min exposure to 100 000 ppm) will result in the inhibition of respiration. It is evident from the data (Table 11) that the CO was not present in amounts that can solely account for the observed mortality. These data suggest, as has the work of other authors, that CO is not the only toxicant involved.

#### University of San Francisco (USF) method

The apparatus for this method consists of a Lindberg horizontal tube furnace which is either programmed to heat at a rate of 40 °C min<sup>-1</sup> from 200 °C to a maximum of 800 °C or set at a fixed temperature. The toxic combustion products which are generated are carried into the exposure chamber with or without a forced air flow. The exposure chamber is a 4.2l hemisphere constructed of polymethylmethacrylate and provides for whole-body exposure of four mice. The biological endpoints which are used in this system are time intervals to various observed signs of intoxication, such as incapacitation, staggering, convulsions, collapse or death. The mortality is recorded. Analysis of CO and CO<sub>2</sub> in the chamber atmosphere is performed at the conclusion of the experiment. Oxygen levels, however, are monitored periodically during the exposure.

The principal disadvantage to this system is that all endpoints are based on the subjective measurements of the one individual conducting the test. In addition, these endpoints provide no insight into the cause of the observed response. Since CO and CO<sub>2</sub> are measured at the end of the exposure period, limited inference can be made concerning the role of these gases in the observed toxic effects. Moreover, time to effect is not a true toxicologic parameter and, in this case, is related to both the time necessary for material degradation and that required for the toxic insult to take effect. Toxicity is based on the quantity of a substance required to elicit a certain measurable effect. The 'time to effect' is more appropriately considered important in the overall hazard assessment of a material in a particular use rather than being an index of toxicity.

Hilado and co-workers have amassed a sizeable amount of data on the toxicity of materials, including

ABS. Only selected representative work by Hilado *et al.*<sup>38,39</sup> will be presented here in an effort to avoid redundancy.

The data for ABS toxicity are presented in Table 12. The endpoints used by Hilado are the following:

- (1) Time to incapacitation (the first observation of staggering, prostration, collapse or convulsions);
- (2) Time to staggering (the initial observation of loss of equilibrium);
- (3) Time to convulsions (the first observation of convulsive-type movement);
- (4) Time to collapse (the first observation of muscular support loss); and
- (5) Time to death (the time at which cessation of movement and respiration are observed).

The mean values and standard deviations of times to specified animal responses presented in the studies by Hilado *et al.* are derived from the means of two or more replicate tests and reflect between-experiment variation rather than individual animal variability. The ABS material used by Hilado *et al.* was identified as Dylel 702, natural, lot A54000 from Sinclair-Koppers, Co., Kobuta, PA. The data in Table 12 compare various experimental conditions and their influence on the toxicity of ABS. The amount of ABS pyrolyzed under each set of experimental conditions was approximately 1.0 g. From these results it is evident that the determination of the relative toxicity of ABS depends largely upon the test conditions used. With this test system the most toxic exposure condition is a fixed furnace temperature of 800 °C with forced air flow, at which animals respond most rapidly. This short animal response time is most likely due to the more rapid generation of toxic decomposition products at this temperature. The addition of a forced air flow through the combustion system into the exposure chamber also augments the degree of toxicity, as reflected in the shorter time to response at 600 and 800 °C. The apparent CO concentration (ppm) in the animal chamber at the end of the exposure period did not correlate with the time to response. In fact, at 800 °C with forced air flow, the amount of CO was lower at the shorter response times, an observation that was not evident at a furnace temperature of 600 °C.

In another study of ABS by Hilado and Huttlinger<sup>39</sup> a material sample size-dependent phenomenon was de-

Table 12. ABS toxicity data—USF method<sup>38</sup>

Temp. (°C)	Air Flow (l min <sup>-1</sup> )	Experimental conditions					Mortality number (# dead/# exposed)	CO (ppm)
		Time to incapacitation (min)	Time to staggering (min)	Time to convulsions (min)	Time to collapse (min)	Time to death (min)		
800 <sup>a</sup>	0	13.52 ± 3.46 <sup>b</sup> (5) <sup>c</sup>	16.48 ± 6.44 (2)	15.53 ± 4.09 (5)	18.09 (1)	17.62 ± 4.77 (5)	20/20	—
600 <sup>d</sup>	0	5.83 ± 2.10 (2)	6.50 ± 2.83 (2)	8.39 ± 1.90 (2)	7.71 ± 3.68 (2)	18.52 ± 5.08 (2)	8/8	2975 (2)
600 <sup>d</sup>	1	2.84 ± 0.06 (2)	—	3.39 ± 0.41 (2)	3.41 ± 0.30 (2)	4.53 ± 0.16 (2)	8/8	2405 (2)
600 <sup>d</sup>	3	2.30 ± 0.04 (2)	—	2.93 ± 0.21 (2)	—	5.96 ± 2.61 (2)	8/8	3700 (1)
800 <sup>d</sup>	0	3.09 ± 1.57 (2)	4.46 ± 1.99 (4)	5.50 ± 1.25 (4)	5.02 ± 0.72 (4)	9.51 ± 4.09 (4)	16/16	3600 (1)
800 <sup>d</sup>	1	1.69 ± 0.05 (2)	—	1.72 ± 0.09 (2)	1.72 (1)	3.80 ± 1.53 (2)	8/8	2435 (2)
800 <sup>d</sup>	3	1.47 ± 0.49 (2)	1.12 (1)	1.76 ± 0.26 (2)	2.03 ± 0.08 (2)	3.47 ± 0.39 (2)	8/8	1695 (2)

<sup>a</sup>Ramped heating mode.

<sup>b</sup>Means ± S. D.

<sup>c</sup>Number in parentheses represents the number of experiments from which the means were used to calculate the means ± S. D.

<sup>d</sup>Fixed heating mode.



monstrated under fixed and ramped temperature conditions in the time to death of the animals (Table 13). Two samples of ABS, Dylel 702 natural Lot A54000, Sinclair-Koppers Co., Kobuta, PA (ABS-1), and Lustran, Monsanto Co., St Louis, MO (ABS-2), were tested. As the mass of the pyrolyzed sample increased, the mean time to death of the experimental animals decreased, a result which is not surprising since the amount of toxic gases produced is directly correlated with the amount of sample decomposed. The decrease is directly correlated with the amount of sample decomposed. The decrease in time of death observed with both samples under ramped and fixed temperature conditions was comparable.

Hilado and Huttlinger compared the relative toxicity of ABS to various woods under ramped temperature conditions and no air flow.<sup>41</sup> The results are presented in Table 14. The data presented by Hilado<sup>41</sup> show that the CO concentration generated by the ABS sample at the time of death is less than that generated by any of the nine wood samples tested under similar conditions. Also, the concentration-time product for ABS is lower than that of any wood sample tested. The concentration-time product

of CO was calculated to be 31 020 ppm·min, indicating that the amount of CO generated by the thermal decomposition of ABS was barely in the critical range (30 000–45 000 ppm·min for a 30-min exposure period is characteristic of materials whose principal toxicant is CO<sup>41</sup>). (Caution should be used, however, in extrapolating concentration-time products to other exposure times since this value is not a constant.) While CO was found to be an important contributor to ABS combustion product toxicity,<sup>40</sup> Hilado and Huttlinger<sup>39</sup> did not consider it to be the sole toxicant.

## SUMMARY

The processes of pyrolysis and combustion under various atmospheric conditions result in the production of many decomposition products, some which are known toxicants and others whose toxicities have not been investigated. In addition, there may be toxic products generated that have not been identified. The conditions under which decomposition occurs are important in determining which degradation products will be generated and at what concentrations.

In the case of ABS, twenty-seven chemical compounds have been identified as combustion products.<sup>13,17–19,21,23,24</sup> It is obvious that more combustion products are generated, but have not been identified or investigated to date. The degradation products which appear to be of primary toxicologic concern are CO and HCN.<sup>13,36</sup> These two decomposition products have been detected under a wide variety of experimental conditions and are likely to be generated under real fire situations. Although each toxicant alone may not be present in adequate concentrations to pose a health threat, recent studies at NBS on the interaction of CO and HCN indicate that these two toxicants may act in an additive fashion.<sup>29</sup> The data presented in this review have been evaluated to determine the extent to which CO and HCN together could account for the combustion product toxicity. It appears that the concomitant generation of CO and HCN is responsible for the toxic/lethal effects of the combustion products of ABS. However, the involvement of other toxicants cannot be precluded prior to comprehensive analyses of the degradation products.

In general, the degradation products of ABS from the flaming mode produced  $LC_{50}$  values that were lower than those of wood (either Douglas fir or red oak) (Fig. 3).<sup>13,32,34</sup> however, some findings to the contrary have been noted.<sup>32</sup> The magnitude of the differences in  $LC_{50}$  values ranges from a two-fold difference in a static exposure system<sup>13</sup> to a ten-fold difference in a dynamic test system.<sup>34</sup> The ABS  $LC_{50}$  values for flaming combustion ranged from 10.5 mg l<sup>-1</sup><sup>34</sup> to 22.1 mg l<sup>-1</sup><sup>13</sup> for a 30-min exposure period and 15.0 mg l<sup>-1</sup><sup>13</sup> to 28.5 mg l<sup>-1</sup><sup>28</sup> for the 30-min exposure and 14-day observation period. In the non-flaming mode, both ABS and Douglas fir combustion products are equally toxic.<sup>13</sup> In the non-flaming mode of combustion, the ABS  $LC_{50}$  values ranged from 22.0 mg l<sup>-1</sup><sup>13</sup> for a 30-min exposure to 64.0 mg l<sup>-1</sup> or greater<sup>13,28</sup> for the 30-min exposure and 14-day observation period.

**Table 13. Time to death dependency on sample size—USF test method**<sup>39</sup>

Sample	Temperature	Number of experiments	Weight of sample		Time to death (min)
			Charged	Pyrolyzed (g)	
ABS-1 <sup>a</sup>	ramped	2	0.0500	0.0500	26.66 ± 1.87 <sup>b</sup>
		6	1.00283	0.98413	18.52 ± 4.81
		1	2.00393		10.02 ± 0.36
		1	5.00170	4.87166	9.41 ± 0.25
ABS-2 <sup>c</sup>	ramped	3	0.10384	0.10337	25.28 ± 1.75
		2	1.00080	0.98704	20.58 ± 0.01
		1	2.00271	2.00154	10.88 ± 0.44
		1	5.00262	4.89112	9.96 ± 0.08
ABS-1	fixed	4	1.00011	0.99374	9.51 ± 1.09
		1	2.00355	1.99133	2.58 ± 0.13
		1	5.00227	4.95491	2.27 ± 0.0
ABS-2	fixed	2	0.99974	0.99648	7.10 ± 1.12
		2	2.00144	1.76249	3.17 ± 0.66
		2	5.00481	4.97572	2.65 ± 0.11

<sup>a</sup>Dylel 702 Natural lot A54000, Sinclair-Koppers Co., Kobuta, PA.

<sup>b</sup>Mean ± standard deviation.

<sup>c</sup>Lustran, Monsanto Co., St Louis, MO.

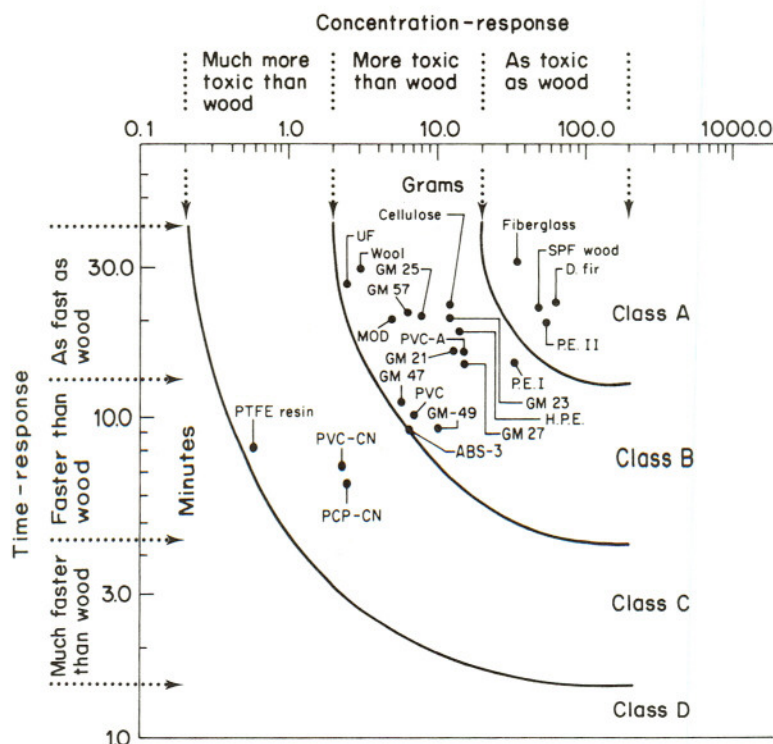
**Table 14. Relative toxicity of ABS compared with various wood**<sup>41</sup>

Sample/material <sup>b</sup>	Time to death (min)	CO (ppm)	Conc. time <sup>a</sup> (ppm·min)
ABS	18.52	6 700	31 020
Aspen poplar	14.06	15 000	52 720
Beech	13.82	11 400	39 390
Yellow birch	15.09	12 000	45 270
Red oak	14.50	10 200	36 980
Western red cedar	14.91	9 100	33 920
Douglas fir	14.76	9 100	33 580
Western hemlock	14.37	13 500	48 500
Eastern white pine	15.42	10 300	39 710
Southern yellow pine	15.56	9 200	35 790

<sup>a</sup>Concentration-time products (ppm·min) for CO.

<sup>b</sup>Samples were pyrolyzed with a ramped furnace temperature at 40 °C min<sup>-1</sup> to a maximum of 800 °C with no forced air flow through the system.





**Figure 3.** Relative toxicity of ABS-Pitt method.<sup>33</sup> Each point represents the amount of material (grams on the X-axis) which produced sufficient smoke to kill 50% of the animals ( $LC_{50}$ ) and the time (minutes on the Y-axis) required to kill 50% of the animals ( $LT_{50}$ ) using that amount of material. Reading the graph vertically, each material is classified in terms of potency while each material is classified in terms of onset of action by reading horizontally. To combine both, parallel quadrants separate classes A-D. (Reproduced with the permission of the authors. Copyright 1981 Academic Press, Inc.)

## CONCLUSIONS

The currently available literature on ABS combustion product toxicity provide a great deal of data; however, these results have only very limited usefulness. The full assessment of the relative toxicity of the combustion products of ABS is complicated by a large number of potential variations in the chemical formulations of ABS and a variety of test systems and experimental protocols. However, the following generalizations are possible:

- (1) Many combustion products are generated during the decomposition of ABS.
- (2) The principal gases which appear to be responsible for the observed toxicity are HCN and CO.

- (3) The thermal degradation products of ABS plastics demonstrate a measureable degree of toxicity. However, the toxicity of ABS combustion products is comparable with the toxicity of the degradation products of other common polymeric materials.

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## NOTES

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

<sup>b</sup> Indicator tubes, such as Draeger Tubes, do provide a convenient and inexpensive indication of the presence of measureable amounts of individual combustion products; however, if interfering gases are present in the test atmosphere, a high degree of precision and accuracy is not attainable.

<sup>c</sup> The use of the convention,  $LC_{50}$  by Cornish *et al.* to describe a value expressed in grams and not grams per unit volume is inappropriate. The convention  $LA_{50}$  (lethal amount<sub>50</sub>) is used as a more appropriate substitute in the discussion of these data.

<sup>d</sup> Alarie reports his toxicological results in grams of material. For comparison purposes the gram units have been converted to  $mg\ l^{-1}$  units by the following equation:

$$\frac{wt\ (g)}{\text{chamber air flow rate}\ (l\ min^{-1}) \times \text{exposure time}\ (min)} \times 1000\ mg/g$$



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