NBSIR 85-3139

Polyesters: A Review of the Literature on Products of Combustion and Toxicity

Emil Braun and Barbara C. Levin

U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards
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January 1985

Issued June 1985

Sponsored in part by:
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POLYESTERS: A REVIEW OF THE LITERATURE ON PRODUCTS OF COMBUSTION AND TOXICITY

Emil Braun

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Abstract

The available literature was reviewed to determine the nature and extent of information available on the thermal decomposition products and the toxicity of the combustion products of polyester materials used in consumer applications such as textiles and building construction. This literature review is limited to those publications printed in English through June, 1984.

The thermal decomposition products of polyesters are a function of temperature and oxygen content of the atmosphere. In general, as the temperature increases, the quantity of heavier hydrocarbons decreases and the production of CO and CO_2 increases. The presence of flame retardant additives, such as bromine and chlorine-containing compounds, produce halogenated combustion products. The use of phosphorus and bromine together in the same flame retardant finish increases the concentration of low molecular weight compounds.

Thirteen different test protocols have been used to evaluate the toxicity of various types of polyester. Non-flame retarded polyesters give measured LC_{50} values ranging from 30.5 mg/l to 95.7 mg/l, while flame retarded polyesters, have LC_{50} values ranging from 24.0 mg/l to 38.0 mg/l. Several exceptions, however, are noted. Toxicologists consider these differences to be not significant. In general, the results from large-scale tests are ambiguous because of the presence of other materials in addition to the polyesters.

Keywords: Combustion products; flame retardants; literature reviews; polyesters; pyrolysis; thermal decomposition; toxicity.

1. INTRODUCTION

It is generally agreed that the production of smoke and its toxicity play an important role in determining the likelihood of surviving a building fire. Researchers over the past two decades have become increasingly concerned with the measurement of toxic effects from burning materials under a great many combustion conditions. Recently, many laboratories have attempted to develop standard laboratory-scale toxicity protocols. In the wake of all of this research and testing, much information has been scattered throughout the technical literature on a great many materials. In an effort to collect, compare, and systematize this information, the Fire Toxicology group within the Center for Fire Research at the National Bureau of Standards conducted a literature review on several classes of synthetic materials.

In this report, the literature on polyesters was reviewed to determine the nature and extent of information available on these materials as they are used in consumer applications such as textiles and building construction.

This review is limited to those publications in English through June 1984. A total of 10 databases (Chemical Abstracts, Environmental Abstracts, Excerptica Medica, FRIS Library, Medline, NTIS, RAPRA, RTECS, TRIS, Toxline) were searched for pertinent publications.

The primary purpose of this review was to determine the possible products of combustion that polyesters would yield under various fire conditions and to evaluate the toxicity of these products of combustion. In general, fire investigators, either combustion scientist or toxicologist, do not specifically identify the exact formulation of polyester used in their respective studies. This severely limits the validity of any comparison of results between different investigators. Differences in experimental procedures may be overshadowed by the use of different polyesters. Nevertheless, a range of values can be obtained that are descriptive of the class of materials called polyesters. This includes thermophysical properties as well as products of combustion and, therefore, toxicity.

2. CHEMICAL STRUCTURE AND THERMOPHYSICAL PROPERTIES

The term polyesters is applied to many different types of resins. Three reactions are generally used for the synthesis of polyesters: (1) the polyesterification of dicarboxylic acids with diols or their functional derivatives; (2) self-polyesterification reactions of hydroxycarboxylic acids and their derivatives; (3) ring opening polymerization reactions of lactones and cyclic esters. These hydrocarbon resins can be made in unsaturated and saturated forms.

Unsaturated polyester resins are less flexible and less compatible with aromatic cross-linking agents. These polyesters are primarily used in composite structures where they can be reinforced with fillers such as glass fibers. Polyester resins made by polyesterification of maleic and phthalic anhydrides and propylene glycol increase resin flexibility. Unsaturated glycols can be used to increase the rigidity of the cured resin by permitting additional cross-linking.

Saturated polyester resins are most frequently used in the manufacture of fibers and films. The most prevalent of these polyesters is poly(ethylene terephthalate). This is a linear polyester that is prepared by transesterification of the dimethylester of terephthalic acid and ethylene glycol [1,2][1]. The resulting polymer is chemically resistant to moisture, acids, and organic solvents. Its chemical structure is shown in figure 1. Polyesters have a relatively simple structure composed only of carbon, oxygen, and hydrogen atoms in a benzene ring with CH_2 attached via carbon-oxygen bonds. This formula indicates that upon thermal decomposition the gaseous products would be various hydrocarbon compounds and oxygenated hydrocarbons as well as CO, CO_2, and water. The addition of cross-linking agents, fillers, and flame retardants would modify the nature of the combustion products.

The thermophysical properties of polyesters can vary depending on the exact formulation and form of the material. Table 1 summarizes the range of values found during this review. Polyester has a melting point that ranges from approximately 250-300°C [2], while its self-ignition or autoignition temperature has been found to be between 450-500°C [3,4,5]. Patten [3], using

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[1] Numbers in brackets denote references listed at the end of this report

the piloted ignition test ASTM E136-58, reported a flash ignition temperature of 400°C.

Miller and Meiser [65] measured the flame temperature above burning polymers. Their results showed that while polyester did not have the lowest measured ignition temperature it did have the lowest flame temperature, 750°C, among a group of polymers that included wood and nylon. This compares to a stoichiometric flame temperature of 1977°C reported by Hilado [64] for an unsaturated polyester. While these values do not appear to be correct (stoichiometric polymer flame temperatures are approximately 1250°C), they are included for the sake of completeness.

Goldfarb and McGuchian [6,7] determined that the thermal decomposition activation energies of several aliphatic and aromatic polyesters ranged from 160-190 kJ/mole and that the activation energies of the aliphatic compounds were slightly lower than that of the aromatic compounds. Throne and Griskey [8] reported heats of combustion values of 25-30 MJ/kg for saturated and unsaturated compounds.

Hilado [64] reports Oxygen Index values for various polyesters ranging from 20 to 60. The higher values represent flame retarded compounds.

3. DECOMPOSITION PRODUCTS

A burning polymer undergoes thermal degradation by a complex series of chemical reactions. These reactions occur either in the condensed phase or in the gas phase above the polymer substrate. In general, the initial thermal degradation of polyester appears to be due to random scission of the ester linkage and pyrolysis of the simple esters produced. Newly formed end groups decompose by secondary reactions [6,7,9].

Learmouth and Nesbit [10] have shown that polyester degradation follows a two step reaction scheme that does not appear to be affected by the presence of halogenated additives. The principal decomposition products (acetaldehyde, water, carbon oxides, and the acid and anhydride end groups) and the kinetics of degradation suggest a random chain scission [1]. The initial scission has been found to occur at an alkyl-oxygen bond. Since the presence of oxygen accelerates the decomposition of the polymer, a mechanism of radical formation is required to explain the results [1]. The experimental work on thermal reactions of this type has been done either in vacuum or in inert gas atmospheres. This research has been aimed at deducing the chemical mechanisms and energies involved in each reaction step. Studies under normal atmospheric conditions of 21% O_2 are limited to describing the nature of the combustion products.

In the next few sections of this report we will describe the gaseous products that evolved during thermal decomposition in each of three environments - vacuum, inert atmospheres, and air. While it may not appear relevant to the real fire situation to review work done under oxygen-free conditions, it must be realized that studies such as these provide information about the effect of well controlled conditions on the nature and amounts of volatile products of thermal decomposition. As will be seen, some of these volatile products survive the passage through the flame and appear ultimately as products of incomplete combustion during atmospheric burning of the polymer.

3.1 Vacuum Pyrolysis

Goldfarb and McGuchian [6,7] have done extensive work on the thermal degradation of aliphatic, aromatic, and semiaromatic polyesters. They studied eight aliphatic, three semiaromatic, and four aromatic polymers. Thermal characterization of these polymers involved vacuum pyrolysis followed by analysis of the volatiles by mass spectrometry (MS).

Table 2 is a tabulation of the gaseous combustion products detected during vacuum pyrolysis of various polyester compounds [6,7,11]. The symbols in the table give relative concentrations of these compounds. It should be pointed out that not every polyester produced all the listed compounds. All polyesters produce large quantities of CO_2 but only the aliphatic polyesters produce large quantities of water. Aromatic and semiaromatic polyesters produce moderate quantities of CO and small amounts of water. Aromatic polyesters produce fewer higher molecular weight hydrocarbons than aliphatic polyesters and moderate amounts of benzene.

3.2 Inert Atmosphere Pyrolysis

Studies by Woolley and Fardell [12] at the British Fire Research Station using a gas chromatograph/mass spectrometer (GC/MS) system and a tube furnace showed that polyesters, like wood, decompose in nitrogen atmospheres into CO, hydrocarbons, and oxygenated species. They also note that the same decomposition products are found when decomposition is carried out in air.

Madorsky [13] cites the work of Goodings who exposed poly(ethylene terephthalate) to temperatures ranging from 283-306°C in nitrogen atmospheres. Under isothermal conditions, this polymer slowly decomposes into low molecular weight fragments such as C_2H_4, 2-methyldioxolan, CH_4, C_6H_6, and CH_3CHO in addition to CO, CO_2, and H_2O. The primary decomposition product was CH_3CHO representing 80 mole percent of the total gases.

Characterizing the pyrolysis products of a group of adhesives, Noble et al. [14] decomposed polyester based adhesives in a nitrogen atmosphere in a curie point pyrolyzer set to produce a 10 second "burn" at 610°C. The unsaturated polyester was copolymerized with a styrene monomer. A major feature of the pyrograms was the strong presence of styrene.

Butt and Cotter [15] pyrolyzed a silicone rubber/poly(ethylene terephthalate) cable insulation material in an inert atmosphere of helium at 800°C. The thermal decomposition products were identified by combined gas chromatography - mass spectrometry (GC/MS). They detected the presence of CO, CO_2, CH_4, ethylene, propylene, butadiene, benzene, and toluene, all of which were attributed to the poly(ethylene terephthalate), and two cyclic compounds, $[(CH_3)_2SiO]_3$ and $[(CH_3)_2SiO]_4$, which were attributed to the silicone rubber.

Using a micropyrolysis furnace and helium or nitrogen atmospheres, Calcraft et al. [16] conducted experiments on three formulations of polyester resin. Different alkyd resins were used in each formulation with styrene as the cross-linking agent. Two formulations had added flame retardants, either trichloroethylphosphate or antimony oxide. Varying the furnace temperature from 150 to 800°C, they found that the yields of the lower boiling point components (i.e., CO, CO_2, CH_4, ethylene, and acetylene) increased with temperature. Chlorine-containing materials produced HCl. The maximum concentrations of the higher boiling point compounds of toluene and styrene appeared between 600 and 700°C, while naphthalene was only detected above 700°C. When the non-flame retardant polyesters were tested, the concentration of benzene increased linearly with temperature and showed a peak around 700°C.

Green et al. [17] tested a set of polyester resins with the same formulations used by Calcraft. They used a quart microreactor and helium atmosphere over a range of 450 to 1000°C. The results of Green tended to agree with Calcraft for the low boiling components; however, the results for the higher boiling point components showed that Green observed maximum yield of toluene at a higher temperature, 1073°C, than Calcraft, 700°C. Styrene yield increased with temperature in Calcraft's work while Green reports a maximum yield at 873°C. Table 3 summarizes the results of Green and Calcraft in terms of temperature effects on the production of decomposition products.

Using a flash pyrolysis/gas chromatography system, Bednas et al. [18] investigated the products of pyrolysis of five commercial polyester fabrics, four of which were treated with flame retardant additives. Tests were conducted with the flash pyrolysis unit set at 700°C or 900°C and with helium as the carrier gas. Approximately 28% of the mass of each fabric sample was consumed at 700°C and an 86% weight loss was observed at 900°C. This mass loss was independent of the presence of a flame retardant. Results indicated the presence of at least 43 compounds in the thermal decomposition products of polyester. All of the compounds were identified except five of the higher molecular weight compounds (Table 4). A greater number of compounds were detected at 900°C than at 700°C. Most notably, water was detected in trace amounts at 900°C, but not detected at all at 700°C. Also, CO became the principal product of pyrolysis at 900°C, while CO_2 was the principal pyrolysis product at 700°C. Methane was produced in appreciable concentrations at the higher temperature, but not observed at 700°C. On the other hand, the observed concentration of acetaldehyde was lower at 900°C than at 700°C. This work indicates that phosphorus-bromine-containing flame retardant systems increase the concentration of the more volatile species as compared to the untreated polyester. The phosphorus only flame retardant systems behaved very similarly to the untreated polyester.

As an extension of the previous work, Day et al. [19] employed a similar pyrolytic system to identify the products of thermal decomposition of Dacron polyester before and after the application of either tris (2,3-dibromopropyl) phosphate, tripropyl phosphate, or 2,3-dibromopropanol. Considering only the 10 major products of combustion designated in the third column of table 4, Day et al. observed that the addition of phosphorus-bromine flame retardants greatly increase the concentrations of the low molecular weight nonaromatic combustion products at the expense of the higher molecular weight aromatic compounds.

3.3 Combustion in Air

Various methods exist for the thermal decomposition of materials in oxygenated atmospheres. Two specific approaches have been applied to polyesters - tube furnace and NBS smoke chamber (NFPA-258 [20] or a variant). Tube furnace experiments are conducted under either isothermal conditions or ramped heating with the rate of heating varying from 5 to 50°C/min. Tube furnace experiments represent a dynamic flow system where combustion products are carried away from the decomposing substrate by a flowing stream of gas, in this case, air.

The NBS smoke chamber can be used to expose a material to purely radiant energy or a combination of radiant and open flame heating. In either case, the external thermal load is constant during exposures. Natural convection within the chamber mixes the combustion products with the air already present.

3.3.1 Tube Furnace Results

Boettner et al. [21] determined the decomposition products from two gram samples of polyester film placed in a tube furnace programmed to heat the material 5 to 50°C/min over a temperature range of 100°C to 1000°C. Quantitative measurements were not taken; however, the presence of CO, CO_2, methanol, and acetaldehyde were detected by infrared (IR) spectroscopy. Methane, ethane, and benzene were identified by GC/MS. Active decomposition was seen at 350°C and combustion was completed at 500°C.

Both Felger and Olsen [22] and Speitel et al. [23] evaluated polyester materials at fixed tube furnace temperatures. Felger and Olsen conducted their tests at 350°C and 450°C, while Speitel et al. used 600°C. Felger and Olsen examined 0.5 gram samples of two types of polyester, a cast magnet wire enamel film and a highly oriented poly(ethylene terephthalate) film. GC and IR analysis of the combustion products showed the presence of only small quantities of aldehydes at 350°C. However, at 450°C, the concentration of aldehydes were 50 times greater than that detected at the lower temperature. Also, large quantities of CO for the cast enamel film and moderate amounts of CO for the oriented film were found at 450°C. Only small quantities of benzene were detected at the higher temperature.

Speitel et al. did not evaluate the combustion products of pure or simple materials. They evaluated wool pile carpeting with a polyester backing and latex back coating for the presence of specific gaseous products. They detected large quantities of CO, HCl and HCN with smaller amounts of H_2S, SO_2 and HCHO. The addition of a urethane foam pad did not substantially change the amounts of low molecular weight gaseous combustion products. However, because of the large quantity of wool present in the sample, none of the detected compounds can be attributible solely to the polyester material. In a similar vein, Hartstein and Forshey [24] evaluated several neoprene polymers reinforced with polyester and found the same types of compounds as Speitel et al.

3.3.2 NBS Smoke Chamber

The NBS Smoke Chamber is a well established method for measuring the opacity of smoke produced when a material is burned. In addition, several researchers have used this test apparatus to generate combustion products from burning polyester prior to their identification.

One of the earliest attempts at characterizing combustion products produced in the NBS Smoke Chamber was done by Gross et al. [25]. They used colorimetric or gas detector tubes in an attempt to measure amounts of specific low molecular weight compounds found in the chamber's atmosphere. [See ASTM E 800-1 [26], Standard Guide for Measurement of Gases Present or Generated During Fires for cautionary notes on the use of gas detector tubes.] They tested a total of 141 aircraft interior materials, eleven of which contained a polyester. A description of the polyester containing materials and concentrations of resulting gases per mass of material tested are presented in table 5. It is interesting to note that with two exceptions, HCl was detected in all samples. This may be indicative of flame retardant additives.

In a similar set of experiments, Speitel et al. [23] decomposed materials in the flaming mode in an NBS Smoke Chamber and determined the presence and concentration of low molecular weight compounds in the combustion gases. They compared colorimetric detector tubes with instrumental methods of analyses. A wool pile, polyester backed carpet was tested with and without a urethane foam pad. The results are reported in terms of mass of gas per mass of consumed material (mg/g)(Table 6). It can be seen that, in general, colorimetric detector tubes overestimate the gas concentrations of a particular species. However, in one case, the instrumental methods detected the presence of H_2S, while the colorimetric detector tubes did not. In the case of HCHO, the reverse was true.

A qualitative comparison can be made between the results of sample 17 (Table 5) of Gross et al. [25] and those of Speitel et al. [23] (Table 6). The comparison can only be qualitative because Gross does not report mass consumed nor can one expect the materials in both reports to be identical. Sample 17 under flaming conditions produced no measureable quantities of HCl while the wool carpet with a urethane foam pad tested by Speitel et al. produced large quantities of HCl. Based on colorimetric detector tubes, there was nearly as much HCl produced as CO. The detection of HCl in the latter material may be indicative of the presence of a flame retardant additive. The quantities of HCl measured as compared to CO appear high. However, they should not be taken as absolute values because of the large potential error associated with the HCl colorimetric detector tube in the presence of small amounts of H_2S [25].

Adams [27] studied the combustion gases produced by a brominated polyester in a modified NBS Smoke Chamber. In this modification the sample was mounted horizontally instead of vertically thereby preventing thermoplastic material from melting and flowing away from the source of heat. The incident radiant flux was maintained at 2.5 W/cm^2. Adams used a mass spectrometer to measure the gas constituents collected in grab sample bulbs. Carbon monoxide was monitored continuously with an infrared analyzer. Adams reports his result in terms of mass of gaseous compound per mass of material consumed (Table 7). Carbon dioxide and carbon monoxide were produced in the largest amounts. As expected, bromide compounds were detected as well as styrene and ethylbenzene both of which somehow survived the transition through the flame zone.

Stauffer et al. [28] and Miller et al. [29,30] investigated the effects of increasing levels of flame retardants on the smoke and toxic gases produced by polyester resins decomposed in the NBS Smoke Chamber. Stauffer et al. observed that as the brominated flame retardant increased, the production of CO_2 declined, while the production of CO, HBr, and total hydrocarbons increased. The results of Miller et al. were identical. They also found that, based on the amount of material decomposed, O_2 consumption also decreased with increasing bromine concentration in the substrate.

While the exact products of decomposition depend on the specific polyester, several generalizations can be made regarding the effects of atmosphere and temperature on the decomposition of these polymers. Data indicate that vacuum and inert atmosphere pyrolysis result in polyesters decomposing into a large number of high and low molecular weight fragments. Increasing the temperature of pyrolysis increased the amount of low molecular weight fragments at the expense of the higher molecular weight fragments.

The use of air as the decomposition atmosphere also resulted in the decreasing production of high molecular weight fragments with increasing temperature. An increase in the production of CO, CO_2, H_2O, and CH_4 was observed. At high temperatures, 450°-500°C, CH_4 would also decompose to H_2O and CO_2. The presence of flame retardant additives, such as bromine and chlorine, produced halogenated combustion products. The use of phosphorus and bromine in the same flame retardant finish increased the concentration of low molecular weight compounds.

4. TOXICITY

At least 13 different toxicity protocols have been used to evaluate polyester materials. These protocols are briefly summarized in table 8. The protocols are divided into three classes. The first class (no. 1-5) of protocols represent widely recognized procedures for evaluating combustion product toxicity. These procedures were developed for the purpose of providing information on a broad range of materials. At least one has undergone interlaboratory evaluation (no. 4) and one is currently under consideration by the State of New York (no. 5) for use in developing a data bank on material toxicity. With the exception of the U.S. Testing Company procedure (no. 9), the second group of protocols (no. 6-11) were developed on an ad hoc basis to evaluate the combustion product toxicity of selected materials. It appears not to have been the intent of the researchers to design a general purpose test protocol that could be used for material toxicity evaluations. The U.S. Testing Company toxicity protocol does not precisely fit this description. It appears to have been developed as a general purpose test protocol. However, it has not received the same recognition as the first group of protocols. It was designed to allow fire investigators to simulate several different protocols in one apparatus.

The final group of protocols are those that employ a combustion system from a standard test method, with the animal exposure system as an addendum to the standard test apparatus. These represent exploratory uses of a standard test method to generate combustion products for animal toxicity evaluation.

Those protocols marked with an asterisk in table 8 are described by Kaplan et al. [31]. In addition to Kaplan et al., citations will be provided for a more complete description of each test protocol.

4.1 Laboratory-Scale Protocols

4.1.1 DIN 53 436

The DIN 53 436 test method was developed in the Federal Republic of Germany. It provides a steady output of combustion products and uses a horizontal moving tube furnace to decompose the sample in a flowing air stream [32]. The combustion air stream is diluted with room air and introduced into an animal exposure chamber. The combustion products flow past the animals and are exhausted out of the system. Material is introduced into the combustion system based on equal specimen volume or weight per unit length.

Herpol and Minne [33] and Herpol [34] exposed three male and three female rats per test to the combustion products generated by two glass fiber reinforced polyester materials. One sample was flame retarded. All of the tests were conducted for 30 minutes with combustion air flowing at 200 l/h. When 10 grams of material were decomposed at a furnace temperature of 600°C, the flame retarded polyester produced 100% mortality while the non-treated polyester produced 0% mortality. The mean COHb for the dead animals was found to be 72%, while surviving animals had a 30% COHb level in their blood. For reference purposes, beechwood decomposed under the same conditions produced a mortality rate of 54% and COHb levels of 33% and 62% for alive and dead animals, respectively. However, the COHb values for live animals depends largely on the time interval between the time of the end of exposure and the time when the blood samples are taken. Doubling the amount of the untreated glass fiber reinforced polyester to 20 grams resulted in 100% mortality and a 65% COHb level.

Herpol and Minne also conducted tests at 800°C with 10 grams of material. No fatalities were seen with the untreated glass fiber reinforced polyester and no attempt was made to determine an LC_{50} value. All samples exhibited some flaming combustion. The animals were monitored for changes in respiration. The results were presented as the mean respiration frequency during the experiment expressed as a percent of the mean normal value before the experiment. In general, the respiration rate of the surviving animals during the test varied from 58% to 120% of normal, while for those dying during the test, the respiration rate steadily declined. The respiration rates were higher at the end of the 30 minute experiments than during the earlier part of the exposure. Male rats exhibited a higher than normal respiration rate when compared to females. These results are summarized in figure 2.

Hoffman and Sand [35] investigated the toxicity of an unsaturated polyester resin with and without a flame retardant finish. Using the DIN 53 436 protocol, they varied the furnace temperature and dilution volume. Five grams of material were placed in the furnace with the combustion air flowing at 100 l/hr. They found that the toxicity increased with increasing decomposition temperatures and the flame retardant treated material was more toxic than the untreated material (Table 9).

Kimmerle and Prager [36] also used the DIN 53 436 protocol, but they determined LC_{50} values for a flame retardant glass fiber reinforced polyester (7%-Sb_2O_3) and a polyester fiber specimen. They were decomposed under conditions of varying furnace temperatures, dilution volumes and exposure times. The mass of material was fixed at approximately 36 grams or 0.12 g/cm, the furnace flow rate was set at 100 l/h and rats were mounted in the head-only configuration. Dilution values are reported as the total flow through the animal exposure chamber. Their results on these two materials are listed below. They report a critical degradation temperature, T(C), below which death will not occur and a calculated temperature, $T(LC_{50})$, at which 50% of the animals died with a 100 l/hr dilution. For the polyester fabric, $T(LC_{50})$ is an extrapolation of the data. With the furnace temperature fixed at 600°C, a critical dilution rate, DC_{600}, above which deaths did not occur was determined. At the same furnace temperature, the dilution rate, D_{600}, and mass loading, LC_{50}, at which 50% of the animals died were also calculated.

Material	T(C) (°C)	$T(LC_{50})$ (°C)	DC_{600} (l/hr)	D_{600} (l/hr)	LC_{50} (mg/l)
FR Glass Fiber Reinforced Polyester	450-500	600	300-400	150	48
Polyester Fabric	500-600	650	200-300	100	72

4.1.2 FAA TOXICITY PROTOCOL

Crane et al. [37], at the Federal Aviation Administration (FAA), have developed a small-animal inhalation toxicity system that uses a tube furnace and provides recirculation of the system atmosphere from the tube furnace to the animal exposure chamber and back again. Three albino rats are used in a whole body exposure with time to incapacitation, as measured on an exercise wheel, and time to death as the biological endpoints. The samples tested were commercially available aircraft interior materials. The tube furnace was set at 600°C and the animals were exposed for a maximum of 30 minutes. Sample mass was fixed at 750 mg which is equivalent to a concentration of 60 mg/l if completely consumed. Crane et al. report three sets of time values. One set was the actual time to effect, while the other two were normalized values based on a 200 gram animal and sample weight of 1 gram, where sample weight was either that charged to the system or that consumed during the test. Data based on charged weight was called "standard" and that based on consumed weight was called "loss." Of the 75 materials tested by Crane et al., five contained polyester, their descriptions are listed in table 10 and the test results are presented in table 11. Sample 10, a glass fiber reinforced polyester, appears more toxic than a wool pile carpet with a polyester backing, 33 and 34. Normalizing the data does not change the toxic order of the five materials.

4.1.3 NASA/USF TOXICITY PROTOCOL

The NASA/USF Toxicity Protocol was developed for the National Aeronautic and Space Administration (NASA) and used extensively by Hilado at the University of San Francisco (USF). This method exposes four Swiss-Webster male mice to the combustion products developed in a horizontal tube furnace. The animals are allowed to move freely about in a 4.2 liter animal exposure chamber. The exposure chamber is connected to the furnace by a glass tube. The furnace can be operated at fixed temperatures or ramped at a rate of 40°C/min. Movement of the combustion products is due to thermal expansion except under flow-through conditions when a pump is used to move air through the system at 3 l/min. Damant et al. [38] used this protocol to evaluate the toxicity of several home furnishing materials. One was a resinated polyester batting. With the tube furnace heating the sample at 40°C/min from 200 to 800°C, Damant et al. varied the sample weight and determined a lethal loading value where 50% of the animals died (LL_{50}) at 85 mg for a 30 minute exposure plus 14 days post exposure observation period. With a system volume of approximately 4.2 l, an LC_{50} of 20 mg/l was computed.

Hilado and his coworkers were concerned with the determination of time to incapacitation (T_i) and the time to death (T_d) as a function of sample heating rate and mass charged to the furnace or mass consumed. Hilado [39,40,41] evaluated the toxicity of three polyester fiber batting samples (Table 12). T_i varied from 8.0 to 15.7 minutes, while T_d varied from 8.8 to 21.5 minutes. On a sample consumed bases, no appreciable differences in the time to incapacitation or the time to death were observed for samples A and B when the heating rate was increased from 40°C/min to 60°C/min. Sample C showed a slight decrease in toxicity (i.e. increase in the T_i and the T_d) as the heating rate was increased.

Hilado and Brauer [42] evaluated the toxicity of a polyester material at a fixed temperature of 800°C, while Hilado [43] measured the toxicity of what appears to be an identical material at a heating rate of 40°C/min. In both cases, 1 gram of material was placed into the furnace. T_d was reported to be 6.0 minutes for the fixed temperature tests and 19 minutes for the ramped heating rate. In addition, the CO and CH_4 concentrations were measured at the end of the test and found to be:

Heating Mode	T_d (min)	CO (ppm)	CH_4 (ppm)
800°C	6.0	12,680	7,680
40°C/min	19.0	7,600	4,330

Table 13 summarizes Hilado's [39,44,41,43] results on polyester and polyester blend fabrics. For polyester/cotton blends, reducing the polyester fraction appears to reduce the toxicity of the blended fabric. Data are also presented comparing toxicity results at a 60°C/min heating rate with the chamber sealed as compared to an unsealed or flow-through chamber. Based on mass consumed, the unsealed system appears less toxic because no animals died during the exposure. The times to incapacitation were approximately the same for the sealed and unsealed systems.

4.1.4 NBS TOXICITY PROTOCOL

The National Bureau of Standards (NBS) toxicity protocol has been described in detail by Levin et al [45] and Kaplan et al. [31] . The sample is introduced into a cup furnace set at 25°C above or below the sample's autoignition temperature. It is a static system in that all of the combustion products are contained in an exposure chamber that holds six male rats in a head only exposure. The exposure lasts for 30 minutes at which time the animals are withdrawn and survivors held for 14 days of observation. Sample mass is varied in order to determine an LC_{50} value based on the amount of material loaded in the furnace divided by the volume of the exposure chamber (200 l). Levin et al. [4] found that a polyester fabric in the non-flaming mode at 475°C had a 30 minute LC_{50} of 39.0 mg/l. In the flaming mode at 525°C, the polyester had a 30 minute LC_{50} value of 37.5 mg/l. Similar tests [46], using a polyester fiberfill material with an autoignition temperature of 525°C, resulted in a 30 minute LC_{50} of 28 mg/l and 31 mg/l for the nonflaming and flaming modes, respectively. All values include deaths occurring during the 30 minute exposure plus a 14 day post-exposure observation period.

4.1.5 University of Pittsburgh

This test protocol has been used by several researchers [47,48,49] to evaluate combustion product toxicity. It is a dynamic flow-through system that uses a Lindberg furnace and a programmed controller to heat the sample at a fixed linear heating rate (20°C/min). Air and combustion products are flushed through the furnace, diluted with cooled air, and passed through an exposure chamber at a total airflow rate of 20 l/min. In each experiment, four mice are exposed in the head-only mode. Typical endpoints are the LL_{50}, the lethal loading that kills 50% of the animals during a fixed exposure time (usually 30 minutes); the LT_{50}, the time needed to kill 50% of the animals exposed to the LL_{50}; and the RD_{50}, the concentration that reduces respiration rate of the animals to 50% of normal. In the University of Pittsburgh method the concentration is denoted by the amount of material placed in the furnace.

In evaluating polyester batting, Alarie et al. [48] calculated a 30 minute LL_{50} of 28.0 ± 1.15 grams and an LT_{50} of 19.5 minutes. The LL_{50} can be roughly converted to a volume base by using the total flow for a 30 minute exposure. This yields 46.7 mg/l for the 30 minute LC_{50} of polyester batting. Fiber glass reinforced polyester was examined by Anderson and Alarie [49] under similar conditions, and the LL_{50} and LT_{50} were found to be 67.5 ± 7.1 grams and approximately 20 minutes, respectively. Converting this LL_{50} value to a volumetric base yields 112 mg/l. While there is a factor of four difference between the two LC_{50} values, it should be pointed out that both are based on the amount of material loaded in the furnace. In the case of the reinforced polyester, a large portion of the mass of material was fiberglass which does not contribute to the toxicity.

Alarie et al. [50] evaluated the toxicity of three polyester resins. One was a commercially available acrylic modified unsaturated polyester resin, another was an experimental version of the same polyester resin, and the third was a styrenated, halogen modified polyester resin. The most toxic material was the halogenated polyester resin, while the least toxic was the experimental resin.

Material	LL_{50} (g)	LC_{50} (mg/l)	RD_{50} (mg)
Commercial Resin	34.8	58.0	119
Experimental Resin	57.4	95.7	121
Halogenated Resin	14.4	24.0	50

In all of these reports, the LL_{50} and LC_{50} values are based on a 30 minute exposure plus a 10 minute recovery period.

Barrow et al. [47] measured RD_{50} values for a fiberglass reinforced polyester using a slightly modified procedure. While he maintained a constant linear heating rate of 20°C/min, he varied the total air flow from 10 l/min to 220 l/min and the sample weight from 5 mg to 200 mg. In addition, he varied the duration of exposure from 3 to 7 minutes. Using various combinations of these three test parameters, Barrow developed a dose-response curve by which an RD_{50} value could be determined. He obtained an RD_{50} value of 0.14 mg/l based on amount of material consumed.

4.1.6 Miscellaneous Protocols

Dufour [11] conducted a general literature review of combustion product toxicity and the various means used for measuring a material's toxicity. He cites the work of: Truesdail (1953); Snell, Corbett, and Gee (1957); and Whitely (1958). Truesdail and Whitely used almost identical protocols to evaluate the toxicity of polyester resins.

Truesdail used six albino rats placed on a mesh wire screen inside of a 14 inch diameter vertical glass cylinder. The glass cylinder had a one inch square vent at the top. The material was burned in a horizontal section below the animal location. Combustion products flowed from the combustion zone past the animals (whole body exposure) and out the vent. Strips of self-extinguishing polyester resin reinforced with chopped glass fiber were burned. After a two hour exposure, Truesdail observed no visible effects on the behavior of the rats. Whitely used six white mice in a 10.5 inch diameter glass cylinder (similar construction). After a 30 minute exposure, the mice showed signs of nasal irritation, lachrimation, and unconsciousness, but all recovered during the post-exposure observation period. The dose could not be determined from the description of the test results.

Snell et al. exposed rats in a 4 cubic foot chamber that was ventilated at the rate of six changes per hour. A mixing fan was used to prevent stratification of the combustion products produced by two stainless steel electrically heated plates in contact with the test material. All samples were heated for five minutes. Some tests were conducted with a fixed area of sample (22.5 in^2), and varying exposure times (5, 10, 15, 30 minutes), while other tests used fixed sample weights with a 30 minute exposure. For the fixed area tests, at least a 15 minute exposure to the decomposition products of a sample described as phthalic polyester was required before one death occurred. A 30 minute animal exposure to the decomposition products from 22.7 grams of the phthalic polyester produced three post-exposure deaths but none during exposure. A fire retarded polyester produced two exposure deaths and one post-exposure death when 45.4 grams were thermally decomposed during a 30 minute animal exposure. Snell et al. measured the oxygen, nitrogen, CO_2, CO, and HCl concentrations in the atmospheres produced when 22 grams of three polyesters were thermally decomposed (Table 14).

Grand [51] used a system developed at the U.S. Testing Company. It consisted of a 20 liter glass combustion chamber connected to a 40 liter animal exposure chamber by 5/8" glass tubing. A rotating wheel (6 rpm) was used to determine the incapacitation times of the exposed rats. Mortality was also an endpoint. Two combustion modes were used in these tests. Non-flaming combustion was achieved by an electrical radiant heater, while flaming combustion used four small butane burners. Exposures were vented (i.e., 8 l/min of fresh air were mixed continuously with the combustion products to total a circulation flow rate through both chambers of 16 l/min) or nonvented (only the combustion products were recirculated). Non-flaming vented and non-vented tests had animal exposure times of 15 and 30 minutes, respectively. Flaming exposures were 20 minutes. Both fire retarded and non-fire retarded fiber glass reinforced polyesters were tested. The results (Tables 15, 16, 17) showed that the fire retarded material was more toxic based on the estimated LC_{50} values (Table 18). In both the vented and non-vented tests, the toxicity of the fire retarded polyester was similar to that of Douglas fir which was greater than the non-fire retarded polyester.

Nunez et al. [52,53] compared toxicity results of the combustion products from 100% cotton and 50/50% cotton/polyester fabrics some of which were treated with flame retardant compounds. His system was composed of an 8.6 l combustion chamber that had radiant glow bars heated by a gas burner connected to a 449 l exposure chamber holding 10 rats in a whole body exposure. The test procedure resulted in flaming combustion of all samples. Air flow through the combustion chamber was 10 l/min. Three minutes after ignition, the burner was turned off and the entire system was sealed. Animal exposure continued for 2 hours. The results of this work are shown in table 19. It can be seen that the untreated materials had about the same LC_{50} value of about 21.7 mg/l. The flame retardant materials showed an increase in toxicity. The addition of polyester to the cotton did not increase the level of toxicity.

Yamamoto [54] evaluated the toxicity of polyester fibers. A stainless steel sample holder was placed on an electrically heated hot plate. The hot plate was turned on to its maximum setting. Yamamoto reported that it took about 20 minutes to reach its maximum temperature of about 500°C. The hot plate was placed in a combustion chamber of about 45 l. This chamber was connected by a flexible hose to a 13 l exposure chamber. In each test, ten grams of material were placed in the furnace holder and a single male rat exposed. In 4 out of 5 tests, the polyester fiber burst into flames 7 minutes after the furnace was turned on. Time to incapacitation was measured based on observed animal activity. The maximum exposure time was 30 minutes. At the time of incapacitation, the animal was withdrawn and %COHb measured. Only flaming conditions produced incapacitation. The following data were obtained:

Sample Size (g): 10

Max. CO(ppm): 2900-5300

Min. O_2 (%): 15.6-19.1

COHb (%): 20-30

Time to Incapacitation (min): 15-19

Yoshida et al. [55] used an airstream flowing at 2.5 l/min through a 2.18 l stainless steel reaction vessel. With the sample in place, the furnace was started at ambient temperature and allowed to heat as rapidly as possible to 550°C. The entire flow was collected in a plastic bag. At the end of the combustion experiment, the collection bag was connected to a 1.5 l chamber where three male mice were exposed in a whole body mode. The duration of the exposure was one hour and was followed by a 7 day post-exposure period. The polyester material began to decompose at 300°C. Yoshida et al. determined a 60 minute plus 7 day LC_{50} value of 30.5 mg/l. Their gas analyzers detected 3000 ppm of CO, 1000 ppm of acetaldehyde and traces of benzene.

Keller et al. [56] and Moreci et al. [57] modified the NBS smoke chamber (NFPA-258) to accommodate animal exposures to the combustion products produced during sample decomposition. Moreci attached an animal exposure chamber to one side of the NBS smoke chamber. The animal exposure system exposed the whole bodies of four male mice and only the head of one mouse. They monitored the behavior (i.e., level of activity) of the free moving mice, recorded survival time, and the percent surviving. A 100% cotton and a 50/50 cotton/polyester fabric were exposed to a 2.5 W/cm^2 radiant heat source and the results were as follows:

	Mass Pyrolyzed (g)	Survived (%)	Survival Time (min)	Peak CO (ppm)
100% Cotton Muslin	38.1	0	34	7000
50/50 Cotton/Polyester	29.8	60	33	6500

Keller et al. [56] placed 8 rats (4 male/4 female) into the NBS smoke chamber and set the radiant heat source at 5 W/cm^2. With the animals in the smoke chamber, approximately five gram samples of untreated and fire retardant treated polyester single knits were tested. A five minute sample burn was followed by a 15 minute holding period for a total exposure time of 20 minutes. An additional 30 minute post-exposure period was used to determine recovery. The biological endpoint was the time for each rat to leave a 25 cm circle (exploration time). The materials tested contained three concentrations of fire retardants (1.2%, 5.6%, 15.9%). No appreciable differences were noted between the untreated and the 1.2% and 5.6% fire retardant treated polyester. Exploration times were approximately 5-6 seconds. However, addition of the 15.9% fire retardant showed a slightly longer exploration time, 13 seconds. In all cases, all animals survived and showed normal activity throughout the 14 day observation period.

Pryor et al. [58] utilized the test described by ASTM E-84 [59] as a combustion system to evaluate the toxicity of fiberglass reinforced polyester. An exposure chamber was connected to the ASTM E-84 system by a one inch pipe. The exposure chamber was approximately 295 l and held 10 mouse cages. Smoke was drawn from ASTM E-84 and trapped in the exposure chamber. The animals were exposed to this atmosphere for 4 hours. One out of 10 animals died during the exposure. The chamber was at 100°F and contained 1025 ppm of CO. The concentration of CO was determined by colorimetric detector tubes. Prior testing showed that exposure to 1500 ppm of CO for 4 hours is lethal.

5. LARGE-SCALE TESTS

Several researchers have combined large scale fire testing (i.e., room size or larger) of furnishings and/or finishing materials with animal exposures or with detailed analysis of combustion products. In most cases, polyester materials were tested in combination with other materials. This makes it very difficult to assess the toxic contribution of one material as compared to another since the toxicity is a result of the total combustion products. However, comparisons between tests that differ in only one or two components can be made.

Hafer and Yuill [60] and Yuill [61] conducted a series of room tests that were designed to measure fire performance of an innerspring mattress with various combinations of blankets and pillows after cigarette or match ignition. During all of these tests, they measured CO_2, CO, and O_2 concentrations. The innerspring mattress had a rayon ticking and was covered with a cotton sheet. A blanket (cotton, polyester, acrylic, or wool) or pillow (feather or polyester) was added to each test. The maximum CO_2 and CO concentration and minimum O_2 concentration as measured in the test chamber (12' x 14' x 8') along with the time of occurrence of the maximum CO value are tabulated in table 20. The data appears to indicate the extent of burning rather than any intrinsic property of the test materials.

In a similar way, Moore [62] measured CO, CO_2, and O_2 levels produced from burning curtains and drapes in a room (10' x 16' x 7 1/2') having one doorway. He measured gas concentrations at the top of the doorway. The results of the polyester curtain tests are listed in table 21. With the drapes drawn back, higher levels of CO were produced than with the drapes extended.

Woolley et al. [63] conducted a series of bedroom fire tests. One of the mattress configurations used a polyester filled quilt with a cotton cover fabric on a polyurethane core mattress covered with a layer of nylon fabric and a PVC covering over the nylon fabric. Using an L-shaped facility with an internal volume of 300 m^3 and a ceiling height of 3 m, they ignited a wood crib (Crib No. 7 as defined in Tests for the Ignitability of Upholstered Seating British Standard Institution Draft for Development DD58:1978) placed on one of 3 beds located in the burn room. Gas analyses were recorded from within the burn room (1 m high) and adjacent simulated corridor (1 m high). They monitored CO, CO_2, and O_2 continuously and used colorimetric detector tubes to measure HCℓ and HCN. In the burn room, CO concentration did not begin rising until after the fire involved the major part of the quilt and, in all likelihood, had penetrated into the polyurethane core. CO reached a maximum of 800 ppm, CO_2 reached 3%, and O_2 decreased to 18%. In the adjacent corridor, CO_2 was 3-4% and O_2 was 18%. At both locations, HCN and HCℓ concentrations were 5 and 17 ppm, respectively.

Alarie et al. [50] conducted room corner tests that included animal exposures to the combustion products. Three grades of fiberglass reinforced polyester were tested in the room corner test. A thirty pound wood crib was used as the ignition mechanism. During each test, smoke was drawn from the corner of the room and distributed via a manifold to four exposure chambers, each holding four mice. Each exposure chamber received combustion gases diluted to different concentrations. In this way, Alarie was able to develop concentration-response relationships. His data is summarized in table 22. It shows that an experimentally modified polyester resin was less toxic than the commercially available resin. However, a halogenated polyester resin was more toxic in comparison because it required a 40% dilution before it became non-lethal. A decrease in respiratory rate followed a similar pattern. Comparing these results to Alarie's small-scale results previously cited (see section 4.15), one can see excellent agreement in the rank ordering of these three materials.

Alarie et al. [48] also used a similar approach in evaluating the toxicity of combustion products produced by smoldering upholstery chairs in a closed room. Chair number 5 was covered with a heavy cotton fabric and filled entirely with polyester batting. The chair was placed on a load cell in a closed room with dimensions of 3 x 3 x 2.4 m. A lighted non-filter cigarette was placed into the crevice formed by the seat cushion and right sidearm. The cigarette was covered by a piece of cotton sheeting. This assembly smoldered during the entire test. Three groups of four mice each were exposed to the combustion products at different times and dilution rates. The first group of animals were exposed to the room atmosphere for the first 70 minutes of the test. The second group was exposed from 73 minutes until 105 minutes and the third group was exposed beginning at 113 minutes. The test continued until 180 minutes. Although respiratory depression was noted with the first two groups of animals, no deaths were observed, even with undiluted air. From a toxicological point of view, the third group of animals were exposed to the highest concentrations of CO, CO_2, and hydrocarbons. One death was observed within this group at a 25% dilution level. No exposures were conducted at 0% dilution. The oxygen concentration was approximately 17.5%. The CO_2 concentration was 5% and CO concentration was in excess of 3000 ppm.

6. CONCLUSION

Pyrolysis products of a given polyester are a function of temperature and atmosphere. As the temperature was increased, researchers observed a decrease in the quantity of heavier hydrocarbons with an increase in the production of CO and CO_2. The presence of flame retardant additives, such as bromine and chlorine, produced halogenated combustion products. The use of phosphorus and bromine in the same flame retardant finish increased the concentration of low molecular weight compounds.

Thirteen different protocols were found that evaluated the toxicity of various types of polyester. In general, non-flame retarded polyesters were found to be less toxic than flame retarded polyesters. LC_{50} values for non-flame retarded polyester ranged from 30.5 mg/l [55] to 95.7 mg/l [50]. This variation could be due to differences in polyester formulations used by various researchers as well as the effects of dyes and other finishing compounds. Halogen compounds are usually employed to limit the thermal hazard of polyester end-products, as defined by specified test methods. Flame retarded polyesters had LC_{50} values of 24.0 mg/l [50] to 38.0 mg/l [51]. Most toxicologists consider less than an order of magnitude difference in LC_{50} not to be significant. Therefore, the above differences do not necessarily indicate that flame retarded polyesters represent a significantly more toxic atmosphere than non-flame retarded polyesters.

The overall toxicity, as measured by an LC_{50}, of polyesters appear to be within the range of many other commercially available materials. Douglas fir, for example has been found to have an LC_{50} for 30 minute exposure of 21 mg/l to 50 mg/l [45]. Acrylonitrile butadiene styrene, polyphenylsulfone, and polystyrene all have the same order of magnitude LC_{50} values [45] as the polyesters. Several researchers, in fact, found some polyester materials to be more toxic than materials known to produce toxic combustion products. Crane et al. [37] found that fiberglass reinforced polyester was more toxic than a wool carpet containing a polyester backing and a PVC/polyester fabric. These results may, in part, relate to differences in polyester formulations. More likely, they are indicative of the presence of flame retardant or other additives in the fiber glass reinforced polyester. Hilado [39,40,41,42,43,44] also found polyester to be more toxic than cotton and a flame retarded polyurethane foam.

In general, large-scale tests results were ambiguous because of the presence of other materials. However, Alarie has shown that qualitative results can be obtained from a comparison of large-scale and small-scale tests.

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Table 1

Thermophysical Properties of Polyester

Property	Measured Value	Reference
Melting point:	250-300°C	2
Heat of combustion:	25-30 Mj/kg	8
Activation energy	160-190 Kj/mole	6,7
Ignition temperature		
flash ignition:	~ 400°C	3
self ignition:	450-500°C	3,4,5
Flame temperature:	750°C	65
Stoichiometric flame temperature:	1977°C	64
Oxygen index:	20-60	64

Table 2 - Thermal Degradation Products Produced by Vacuum Pyrolysis of Aliphatic, Aromatic, and Semiaromatic Polyesters [6,7]

Compound	Aliphatic	Semiaromatic	Aromatic
Acetaldehyde	+++		
Acetic Acid	-		
Acetone	+		
Acetylene	+		
Acrolein	+		
Allyl Alcohol	+		
Benzaldehyde	-		-
Benzene			+
Benzoic Acid			-
Butadiene	+++	+	
Butanaldehyde	+		
Butane		+	
Butene	+	+	
CO_2	+++	+++	+++
CO	++	++	
Cyclobutanone	+		
Cyclohexadiene	-	-	
Cyclohexane	+		
Cyclohexanone	+		
Cyclohexene	+	++	
Cyclopentanone	+++		
Cyclopentene		-	
Ethene	+	+	
1,5 Hexadiene		++	
Hydrogen		-	-
Methane		+	-
Olefin	+		
1,3 Pentadiene	+		
1,4 Pentadiene	+		
Pentene	+	+	
4-Pentene-1-ol	+		
Phenol			-
Propanaldehyde	++		
Propene	+	+	
Quinone			+
Tetrahydrofuran	+		-
Toluene			-
Water	+++	+	+

+++: more than 20% of total gaseous products

++: 10% to 20%

+: 1% to 10%

-: trace or minor amounts

Table 3

Decomposition Products of Inert Atmosphere Pyrolysis of Polyesters (450°-1200°C) as a Function of Temperature

Compound	Temperature of Maximum Concentration	
	Calcraft [16] (°K)	Green [17] (°K)
CO	↑	↑
CO_2	↑	↑
CH_4	↑	↑
Ethylene & Acetylene	↑	↑/1073
Benzene	↑/800	↑
Toluene	700	1073
Styrene	↑/600	873
Naphthalene	↑	↑/1073
Ethylbenzene & Xylene	-	↓/873
Biphenyl	-	1073
Fluorene	-	873/1073
Phenanthrene & Authracene	-	1073/1173
Methylanthracenes & Methylfluorenes	-	1073

↑ Shows the general trend of compound yield as a function of temperature. No maximum detected before peak test temperature.

↑/°K At least one sample had a maximum concentration before peak test temperature.

°K/°K Sample dependent maximums.

Table 4

Identified Combustion Products Resulting from the Flash Pyrolysis of Untreated Polyester Fabric at 700°C and 900°C

Compound	700°C [18]	900°C [18]	900°C [19]
Carbon Monoxide	+	+	+
Methane	+	+	+
Carbon Dioxide	+	+	+
Ethylene & Acetylene	+	+	+
Ethane		+	
Water		+	
Propylene	+	+	
Acetaldehyde	+	+	+
Acetone	+	+	
Propenal	+	+	
Ethanol	+	+	
Benzene	+	+	+
Toluene	+	+	
Ethylbenzene	+	+	
Styrene	+	+	
p-Vinyl Toluene		+	
Benzaldehyde		+	
p-Ethyl Toluene		+	
Acetophenone		+	
Methyl Benzoate		+	
Vinyl Benzoate	+	+	+
Ethyl Benzoate	+	+	
p-Methyl Acetophenone	+	+	
Benzoic Acid	+	+	+
p-Methyl Vinyl Benzoate	+	+	
p-Vinyl Acetophenone		+	
Propyl Benzoate		+	
p-Ethyl Vinyl Benzoate	+	+	
p-Vinyl Vinyl Benzoate	+	+	
Biphenyl		+	
1-Hydroxy Ethyl Benzoate	+	+	
Diacetyl Benzene	+	+	
p-Acetyl Vinyl Benzoate	+	+	
Divinyl Terephthalate	+	+	+
Ethyl Vinyl Terephthalate	+	+	
p-Acetyl Benzoic Acid	+	+	
Methyl 1-Hydroxyethyl Terephthalate	+	+	
Ethylene Dibenzoate	+	+	+

Table 5

Specific Combustion Products Detected and Concentrations
Found During NBS Smoke Chamber Tests
of Materials Containing Polyester [25]

Sample #	Sample Weight (g)	Description	Exposure	Gas Concentration (ppm/g)			
				CO	HCl	HCN	NO + NO_2
6	5.0	Polyester plasticizer on cotton	F	70	40	0.6	
			N	80	60	0.4	
7	12.2	Modacrylic/acrylic pile w/polyester back & urethane foam pad	F	41	7.4	1.6	
			N	10	2.5	2.5	
13	5.4	PVC & PVA base w/ABS polyester film	F	37	56	0.6	
			N	11	50	0.4	
17	15.2	Wool pile w/polyester back & urethane pad	F	21	0	1.0	1.6
			N	20	0	3.9	
20	13.0	PVA covered w/polyester on aluminum sheet	F	22	7.7	0.2	
			N	1.5	6.2	0	
22	1.3	Polyester face & vinyl acetate, PVC copolymer	F	69	54	0	
			N	7.7	23	0	
30	12.3	Polyester coated glass fabric paper honeycomb/glass fabric	F	23	3.7	0.6	
63	2.0	Modacrylic/polyester fabric	F	140	75	23	
			N	40	50	20	
67	4.7	Polyester plastic filled glass fiber fabric	F	49	4.3	0	
			N	6.4	1.7	0	
75	3.9	Cotton/nylon/polyester fabric	F	46	0	1.3	
			N	31	0	1.3	
160	13.1	Styrene/polyester fiber glass panels	F	38	15.3	0	
			N	9.5	11.5	0	

F = Flaming exposure
N = Nonflaming exposure
PVC = Poly Vinyl Chloride
PVA = Poly Vinyl Alcohol
ABS = Acrylonitrile Butadiene Styrene

Table 6

Comparison of Colorimetric Detector Tubes and Instrumental Methods for Analyzing Gases Generated from the Thermal Decomposition of Wool Pile, Polyester-Backed Carpets in the NBS Smoke Chamber [23]

		Gas Concentration (mg/g)						
Carpet	Analysis Method	CO	HCl	HCN	H_2S	HCHO	SO_2	NO_2
No Pad	CDT[a]	32.3	17.5	3.2	ND	1.7	24.6	9.72
	IMA[b]	27.2	7.1	3.0	3.0	ND	17.0	0.14
Pad	CDT	38.0	31.8	2.6	ND	2.9	22.4	8.92
	IMA	36.0	11.8	2.6	0.5	ND	15.8	0.13

[a] Colorimetric detector tubes
[b] Instrumental methods of analysis
ND: Not detected.
Pad: Urethane foam

Table 7

Concentration of Various Gas Species Produced by a Brominated Polyester in a Modified NBS Smoke Box [27]

Compound	Gas Concentration (mg/g)
CO	15.59
H_2O	1.56
CO_2	24.77
CH_3OH	1.65
Styrene	0.64
Ethylbenzene	0.44
Methyl Bromide	0.78
Ethyl Bromide	1.57
Ethylene Bromide	2.71
Ethylene Bromohydrin	1.80

Table 8

Summary of Toxicity Protocols

No.	Protocol Name	Animal	Exposure Time (min)	Endpoint	Animal Exposure	Combustion System	Combustion Flow System
1	* DIN	rats	30		WB[b]/NO[c]	tube furnace	vented
2	* FAA[a]	rats	30	1) incapacitation 2) death	WB	tube furnace	recirculated
3	* NASA/USF	mice	30	1) incapacitation 2) death	WB	tube furnace	non-vented
4	* NBS	rats	30	1) incapacitation 2) death	HD[d]	cup furnace	non-vented
5	* Pittsburgh	mice	30	1) incapacitation 2) death 3) respiration	HD	tube furnace	vented
6	* Nunez	rats	120	death	WB	radiant coils	non-vented
7	Snell	rats	5-30	death	WB	electric hot plate	non-vented
8	Truesdail	mice	30,120	behavior	WB	flaming	vented
9	*U.S. Testing Company	rats	15,20,30	1) incapacitation 2) death	WB	electric heater	vented/non-vented
10	* Yamamoto	rats	30	incapacitation	WB	plate heater	non-vented
11	Yoshida	mice	60	death	WB	preheated air	non-vented
12	ASTM E-84	mice	240	death	WB	preheated air	vented
13	NFPA 258	rats	20+	exploration time	WB	radiant	non-vented

*Described by Kaplan et al. [31]

[a] Animals in an exercise wheel during exposure

[b] WB = whole body exposure

[c] NO = nose only exposure

[d] HD = head exposure

Table 9

Results of Toxicity Tests of Untreated and Flame Retardant Treated Unsaturated Polyester Resin and Glass Fiber Structure [35]

Temp °C	FR	Dilution (cp:air)	COHb (%)	Mortality (%)
300	-	1:1	<15	0
	+	1:1	<10	0
	+	1:4	<10	0
	+	1:9	<10	0
400	-	1:1	23	25
	+	1:1	28	100
	+	1:4	<10	100
	+	1:9	<10	67
500	-	1:1	54	83
	+	1:1	76	100
	+	1:4	59	100
	+	1:9	22	100
600	-	1:1	63	8
	+	1:1	85	100
	+	1:4	76	100
	+	1:9	58	100

All samples weighed 5 grams.
The combustion airflow was 100 liters per hour.
CP = Combustion products.
FR = Flame retardant.

Table 10

Description of Polyester Materials Tested in FAA Apparatus (37)

Sample Number	Thickness (mm)	Weight (kg/m^2)	Description	Use
10	0.99	1.91	Glassfiber Reinforced Polyester	Cargo Liner
12	13.34	3.07	PVF/Polyester-Chopped Glass/Aramid Honeycomb Polyester-chopped Glass	Panel
33	6.73	1.76	Wool Pile/Polyester Backing/Latex Coating	Floor Cover
34	8.76	1.74	Wool Pile/Polyester Backing/Latex Coating/ Urethane Pad	Floor Cover
97	0.46	0.39	PVC - Polyester	Fabric

Table 11

Tests Results of Materials Described in Table 10 from FAA Protocol (37)

Sample Number	Mean Response Time (min)					
	Measured		Normalized Charged		Normalized Consumed	
	T_i	T_d	T_i	T_d	T_i	T_d
10	5.09	7.89	3.99	6.20	3.6	5.59
12	7.57	-	5.85	-	3.6	-
33	7.07	15.80	5.26	11.73	4.95	11.07
34	7.35	20.43	5.53	15.35	5.13	14.26
97	9.23	13.59	6.97	10.28	6.51	9.60

T_i = Time to incapacitation.
T_d = Time to death.
\- = No responses during 30 minute exposure.
Measured = Mean of observed values.
Normalized Charged = Measured values normalized to a standard 200 g animal and 1 g material based on amount of material placed in furnace.

Normalized Consumed = Same as normalized charged except based on amount of material consumed.

Table 12

Summary of Results for Polyester Fiber Batting
[39,40,41]

Material	Sample Weight (g)	Sample Consumed (g)	Average Mortality (%)			Ti[a] (min)	Td[b] (min)	Ref.
			(10 min)	(20 min)	(30 min)			
Heating Rate = 40°C/min								
A - 6 & 16 denier no resin	5.0	1.5	25	100	100	9.5	10.2	39
	2.0	-	0	100	100	11.3	12.9	40
	1.0	0.85	75	100	100	8.2	9.4	41
B - 6 & 16 denier 13.3% acrylic resin	5.0	0.7	0	100	100	10.5	12.0	39
	2.0	0.6	0	100	100	11.0	14.9	40
	1.0	0.88	67	100	100	8.6	10.2	41
C - 6.5 & 15.0 denier 20.6% acrylic resin	5.0	1.5	0	100	100	12.0	15.2	39
	2.0	0.5	0	100	100	8.9	10.5	40
	1.0	0.9	40	100	100	8.9	10.5	41
Heating Rate = 60°C/min								
A	5.0	2.5	100	100	100	8.1	9.1	39
	2.0	1.8	0	100	100	9.5	10.6	40
	1.0	0.2	0	100	100	10.0	16.9	40
B	5.0	2.6	100	100	100	8.5	9.0	39
	2.0	0.3	0	100	100	9.3	10.8	41
	1.0	0.2	0	100	100	9.3	15.0	40
C	5.0	2.2	100	100	100	8.0	8.8	39
	2.0	0.9	0	0	100	13.3	21.0	40
	1.0	0.9	0	25	100	15.7	21.5	40

- = Value not recorded
a. Time to incapacitation
b. Time to death

Table 13

Polyester and Polyester Blends Tested in NASA/USF Protocol

Material	Sample Weight (g)	Mass Consumed (g)	Ti[a] (min)	Td[b] (min)	Ref.
Heating Rate = 40°C/min		Sealed System			
Polyester	1	0.7	7.4	9.4	40
Polyester	1	0.8	-	19.0	43
Polyester/acetate, 65/35	1	-	7.8	10.6	41
Polyester/cotton, 70/30	5	-	8.0	9.6	39
Polyester/cotton, 50/50	5	-	9.5	9.6	44
Polyester/cotton, 30/70	5	1.3	10.5	11.1	44
Heating Rate = 60°C/min		Sealed System			
Polyester/cotton, 50/50	5	3.0	10.0	11.0	44
	Unsealed System				
Polyester/cotton, 30/70	10.4	6.3	9.5	10.2	44
Polyester/cotton, 50/50	4.8	2.8	10.9	-	44
Polyester/cotton, 50/50	9.8	4.7	9.5	-	44

[a] Time to incapacitation
[b] Time to death

Table 14

Results of Gas Analysis During Thermal Decomposition of Polyesters [11]

Material (Author's Designation)	Sampling Period (min)	Gas Concentration				
		O_2 (%)	N_2 (%)	CO_2 (%)	CO (ppm)	HCl (ppm)
FR Polyester (93LS)	6-20	18.2-18.7	79.3	2.0-2.5	31	93-101
	23-30	18.9-19.3	79.2-79.4	1.5-1.7	-	12-15
FR Polyester (92)	6-20	19.1	78.8	2.1	19	24
	23-30	19.5	78.8	1.7	-	-
Phthalic Polyester	6-20	18.9-19.0	78.7-79.0	2.0-2.4	21-24	-
	23-30	19.5-20.2	78.8-79.0	1.0-1.5	-	-

Note: No chlorine or phosgene detected.

Table 15

Results of Venting Tests on Two Polyester Materials [51]

Glass Reinforced Polyester	Mass Tested (g)	Mass Loss (g)	Mass Loss (%)	Time to Incapacitation (min)	Number Died / Number Tested Within Exp.	Number Died / Number Tested Post Exp.	COHb[1] (%)
Non-Flaming							
NFR	9.5	6.1	64	13.3-14.5	0/6	1/5*	--
	10.0	7.3	73	11.8-14.7	0/6	1/5*	--
	11.5	8.3	72	6.3-8.3	6/6	--	71
	12.3	8.8	72	9.5-10.0	6/6	—	70
FR	5.6	4.2	75	10.0-14.0	0/6	1/5*	—
	5.7	4.2	74	11.7-14.7	0/6	2/5*	--
	6.1	4.6	76	7.9-9.3	4/6	0/2	66
	6.1	4.6	75	8.5-10.0	6/6	—	67
	6.7	4.9	73	7.2-9.3	5/6	0/1	69
Flaming							
NFR	4.8	3.7	77	7.3-9.2	1/6	0/5	67
FR	4.1	3.0	73	8.3-10.2	4/6	1/2	67
	4.1	3.1	76	7.7-10.4	2/6	0/4	80

[1] COHb from dead animals only, averages given when two or more values obtained.
*One animal sacrificed.
NFR: Not fire-retarded.
FR: Fire-retarded.

Table 16

Results of Non-Venting Tests on Two Polyester Materials [51]

Glass Reinforced Polyester	Mass Tested (g)	Mass Loss (g)	Mass Loss (%)	Time to Incapacitation (min)	Number Died / Number Tested Within Exp.	Number Died / Number Tested Post Exp.	COHb[1] (%)
NFR	3.6	2.0	56	--	0/6	2/6	--
	4.7	3.1	66	19.8-23.7	0/6	0/5*	--
	6.3	3.5	56	16.3	1/6	1/5	56
	5.6	3.8	68	14.3-17.2	3/6	0/3	76
	7.2	4.0	56	12.7-16.7	5/6	0/1	66
FR	2.3	1.5	63	--	0/6	0/5*	--
	2.4	1.5	64	--	0/6	2/5*	--
	3.6	2.0	56	--	0/6	0/6	--
	3.1	2.2	72	14.0-16.2	2/6	1/3*	66
	3.2	2.3	70	13.3-14.1	6/6	--	67
	3.6	2.3	62	--	0/6	1/6	--
	3.6	2.3	64	17.4-18.0	3/6	0/6	84
	3.7	2.3	62	16.3-19.5	2/6	3/3*	58
	3.8	2.3	60	16.3-27.0	4/6	1/2	57
	4.1	2.7	66	13.0-14.8	5/6	0/1	60

[1] COHb from dead animals only, averages given when two or more values obtained.
* One animal sacrificed.
NFR: Not fire-retarded.
FR: Fire-retarded.

Table 17

Carbon Monoxide Concentrations and Animal Incapacitation Times [51]

Glass Reinforced Polyester Sample	Mass Loss (g)	Time to Incapacitation		CO x Ti[a] (ppm-min x 10^3)	CO x Mean Ti (ppm-min x 10^3)
		(min)	Mean (min)		
Non-Venting					
FR	2.7	13.0-14.8	13.7	39.5-48.7	43.0
	2.3	13.3-14.1	13.6	41.0-44.5	42.0
	2.3	16.3-27.1	19.3	32.3-64.8	42.0
NFR	4.0	12.7-16.7	14.2	30.5-48.6	37.6
Venting					
FR	4.9	7.2-9.5	8.1	35.4-54.7	43.7
	4.6	7.9-9.3	8.6	32.1-44.4	38.3
	4.6	8.5-10.0	9.7	29.0-41.4	38.5
NFR	8.3	6.3-8.3	7.3	22.8-45.4	34.1
Flaming					
FR	3.0	8.3-10.2	9.1	32.5-40.4	35.8
NFR	3.7	7.3-9.2	8.2	25.5-32.8	29.2

[a] Incapacitation time.
FR: Fire retarded.
NFR: Not fire retarded.

Table 18

Estimated LC_{50} Values[1] For Rats Exposed to Combustion Products from Glass Reinforced Polyester

Fire Retardant	Conditions	LC_{50} (mg/l)
-	Vented[2]	122-138
	Non-vented	63
+	Vented	76
	Non-vented	38

[1] Results estimated from data of Grand assuming a 60 liter combustion and exposure system [51].

[2] See text for description.

Table 19

LC_{50} Values for Cotton and Cotton/Polyester Fabrics Untreated and Treated with a Flame Retardant Finish [52,53]

Sample Description	LC_{50} (g)	LC_{50} (mg/l)
Cotton Twill, untreated	9.49 ± 0.61	20.7
Cotton Twill, THPOH/NH_3	1.02 ± 0.05	2.2
Cotton Twill, THPOH/NH_3 & Topped	3.62 ± 0.30	7.9
Cotton Flannel, untreated	10.40 ± 0.60	22.7
Cotton Flannel, THPOH/NH_3	3.80 ± 0.27	8.3
Cotton Flannel, THPOH/NH_3 & Topped	1.22 ± 0.12	2.7
Cotton/Polyester, Untreated	9.89 ± 0.83	21.6
Cotton/Polyester, THPOH/NH_3	2.39 ± 0.14	5.2
Cotton/Polyester, THPOH/NH_3 & Topped	2.87 ± 0.41	6.3

Topped = topping agent was trimethylomelamine
THPOH = Tetrakis (Hydroxymethyl) Phosphonium Hydroxide

Table 20

Gas Results of Large-Scale Mattress Fire Tests of Mattresses
with Rayon Ticking and Cotton Sheets [60,61]

Test Number	Additional Material	Ignition Mode	Max CO (ppm)	Max CO_2 (%)	Min O_2 (%)	Time Max CO (min)
10	Cotton Blanket	Cigarette	4130	5.55	16.7	144
11	Polyester Blanket	Cigarette	3000	2.70	18.2	204
12	Acrylic Blanket	Match	4950	3.35	18.2	51
13	Wool Blanket	Match	3870	2.75	18.4	210
21	Feather Pillow	Cigarette	2230	1.15	20.1	141
22	Polyester Pillow	Match	6730	4.15	17.1	64

Table 21

Maximum Gas Concentrations Found by Burning Polyester Curtains and Drapes in a Room [62]

Test Number	Position	CO (ppm)	CO_2 (%)	O_2 (%)
S14	Extended	500	2.73	18.34
S7	Retracted	800	2.65	18.09

Weight: 3.17 oz/yd^2
Size : 48" x 84" per panel

Table 22

Mortality During Room Corner Test of Three Fiberglass Reinforced Polyester Resins [50]

Material	Dilution (%)	Time to Death (min)	# Deaths / # Exposed
Commercial	0	9.6-12.0	4/4
	18.5	0	0/4
	31.5	0	0/4
	42.0	0	0/4
Experimental	0	0	0/4
	18.5	0	0/4
	31.5	0	0/4
	42.0	0	0/4
Halogenated	0	7.0-8.0	4/4
	18.5	8.4-8.5	4/4
	31.5	11-11.3	3/4
	42.5	0	0/4

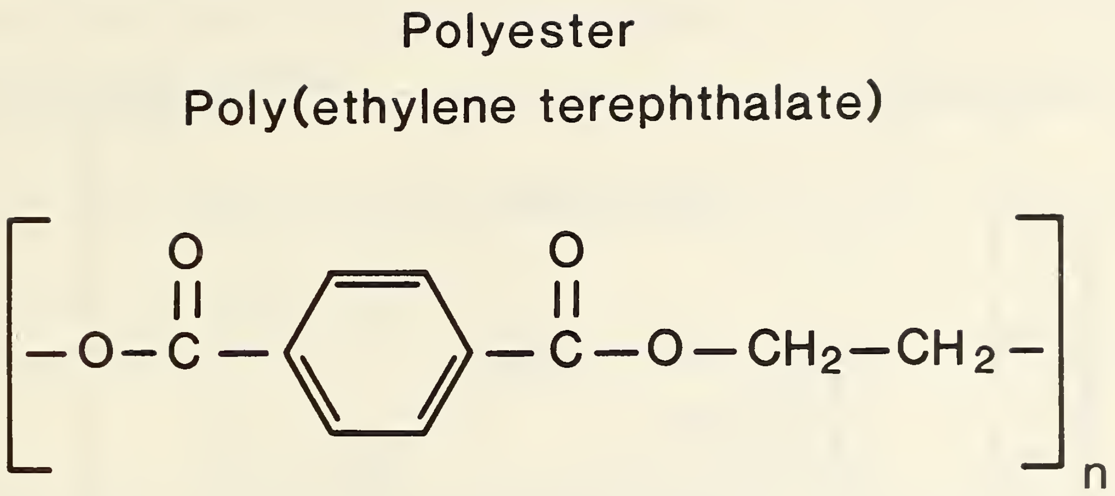

Figure 1. Chemical Structure of Polyesters

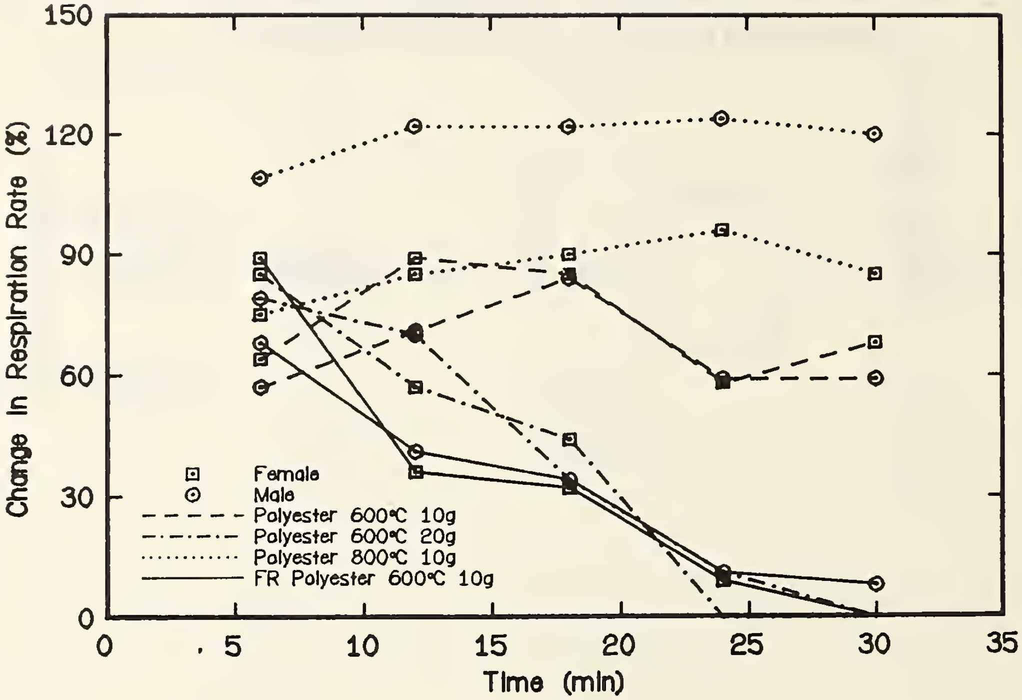

Figure 2. Comparison of the change in respiration rate during a 30 minute exposure to the combustion products of FR treated and nontreated glass fiber reinforced polyester

NBS-114A (REV. 2-80)

U.S. DEPT. OF COMM. **BIBLIOGRAPHIC DATA SHEET** *(See instructions)*	1. PUBLICATION OR REPORT NO. NBSIR-85/3139	2. Performing Organ. Report No.	3. Publication Date June 1985

4. TITLE AND SUBTITLE

Polyesters: A Review of the Literature on Products of Combustion and Toxicity

5. AUTHOR(S)

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6. PERFORMING ORGANIZATION *(If joint or other than NBS, see instructions)*

NATIONAL BUREAU OF STANDARDS
DEPARTMENT OF COMMERCE
WASHINGTON, D.C. 20234

7. Contract/Grant No.

8. Type of Report & Period Covered

9. SPONSORING ORGANIZATION NAME AND COMPLETE ADDRESS *(Street, City, State, ZIP)*

Consumer Product Safety Commission
Washington, DC 20207

10. SUPPLEMENTARY NOTES

☐ Document describes a computer program; SF-185, FIPS Software Summary, is attached.

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

The available literature was reviewed to determine the nature and extent of information available on the thermal decomposition products and the toxicity of the combustion products of polyester materials used in consumer applications such as textiles and construction. This literature review is limited to those publications printed in English through June, 1984.

The thermal decomposition products of polyesters are a function of temperature and oxygen content of the atmosphere. In general, as the temperature increases, the quantity of heavier hydrocarbons decreases and the production of CO and CO_2 increases. The presence of flame retarded additives, such as bromine and chlorine containing compounds, product halogenated combustion products. The use of phosphorus and bromine together in the same flame retardant finish increases the concentration of low molecular weight compounds.

Thirteen different test protocols have been used to evaluate the toxicity of various types of polyester. Non-flame retarded polyesters are less toxic, with LC_{50} values ranging from 30.5 mg/l to 95.7 mg/l, than flame retarded polyesters, whose LC_{50} values ranged from 24.0 mg/l to 38.0 mg/l. Several exceptions, however, are noted. In general, the results from large-scale tests are ambiguous because of the presence of other materials in addition to the polyesters.

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

Combustion products; flame retardants; literature reviews; polyesters; pyrolysis; thermal decomposition; toxicity.

13. AVAILABILITY

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☐ Order From Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402.
☒ Order From National Technical Information Service (NTIS), Springfield, VA. 22161

14. NO. OF PRINTED PAGES

71

15. Price

$10.00