AD-A084 028 ARMY ARMAMENT RESEARCH AND DEVELOPMENT COMMAND ABERD--ETC F/G 21/2
FIRE AND FLAMMABILITY CHARACTERISTICS OF MATERIALS USED IN RAIL--ETC(U)
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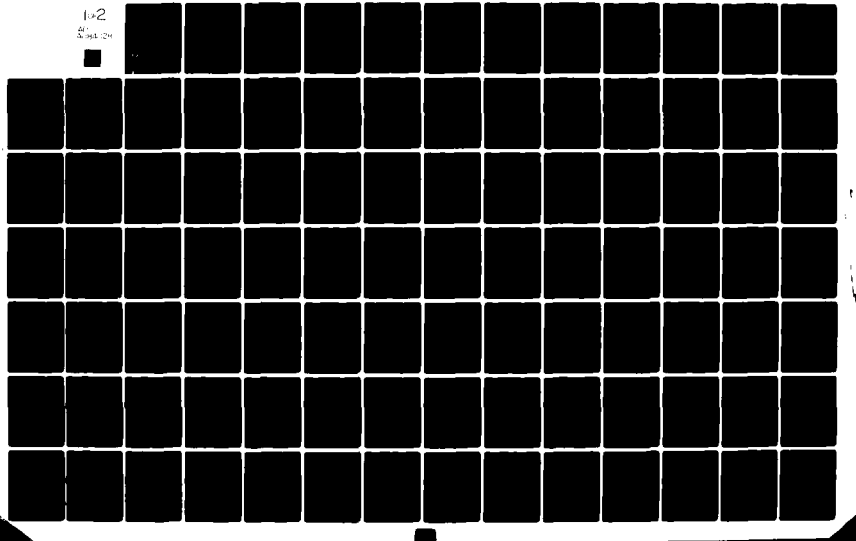

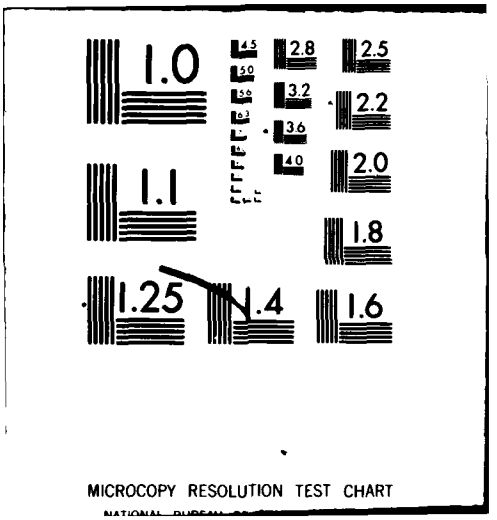
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MEMORANDUM REPORT ARBRL-MR-03009

FIRE AND FLAMMABILITY CHARACTERISTICS OF MATERIALS USED IN RAIL PASSENGER CARS. A LITERATURE SURVEY

John A. Rakaczky

April 1980

US ARMY ARMAMENT RESEARCH AND DEVELOPMENT COMMAND
BALLISTIC RESEARCH LABORATORY
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REPORT DOCUMENTATION PAGE	READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER: MEMORANDUM REPORT ARBRL-MR-03009	2. GOVT ACCESSION NO.: AD-A084028
3. RECIPIENT'S CATALOG NUMBER	
4. TITLE (and Subtitle): FIRE AND FLAMMABILITY CHARACTERISTICS OF MATERIALS USED IN RAIL PASSENGER CARS. A LITERATURE SURVEY.	5. TYPE OF REPORT & PERIOD COVERED: Final
	6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s): John A. Rakaczky	8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS: U.S. Army Ballistic Research Laboratory (ATTN: DRDAR-BLT) Aberdeen Proving Ground, MD 21005	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: N/A
11. CONTROLLING OFFICE NAME AND ADDRESS: US Army Armament Research and Development Command US Army Ballistic Research Laboratory (ATTN: DRDAR-BL) Aberdeen Proving Ground, MD 21005	12. REPORT DATE: APRIL 1980
	13. NUMBER OF PAGES: 100
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	15. SECURITY CLASS. (of this report): UNCLASSIFIED
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

This work was funded by Department of Transportation under Contract No. AR-8179.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Fire, flammability, ignition temperature, flame spread rate, rate of combustion, rate of heat liberation, smoke emission, combustion products, toxicity, pyrolysis, plastics, polymers, synthetic fibers, flammability test methods.

20. ABSTRACT (Continue on reverse side if necessary and identify by block number) (mba)

A literature search was conducted to provide information on the flammability characteristics of materials that are used, or have potential use, in furnishing the interiors of rail passenger cars. Among the characteristics of interest were the ignition temperature, time to reach ignition, the rate of flame spread, the rate of combustion or rate of material loss, rate of heat liberation, heat transfer from flames, the evaluation of smoke, the measurement of smoke density, and the evolution and toxicological effect of the products of combustion. In addition, information was collected on flammability test methods, fire

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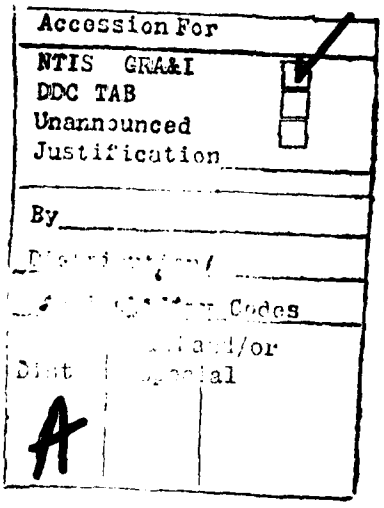
prevention standards or codes, and statistical data concerning accidents involving vehicle fires of interior origin. The information compiled is to be used to assist the Federal Railroad Administration, Department of Transportation (FRA/DOT) in establishing safety standards regarding the flammability of materials used in the interiors of rail passenger cars. 226 references are given.



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I. INTRODUCTION

A. Background of Problem

Most of the materials used in the interiors of vehicles employed in the transportation of people are of a combustible nature and, as such, present a potentially severe fire hazard to the occupants. An increase in the use of synthetic fibers and plastic materials in the interiors of railroad passenger cars has led to the interest of the Federal Railroad Administration, Department of Transportation (FRA/DOD), in establishing safety standards regarding the flammability characteristics of these materials. Through an interagency agreement the Ballistic Research Laboratory (BRL) has initiated a program to assist the FRA/DOT in formulating these standards.

The overall program has been divided into several phases or tasks. Briefly, these are as follows:

I. A literature survey to collect available information on the flammability characteristics of current, or potential, interior materials;

II. A review of test methods and current regulations to evaluate the techniques and tests presently employed to qualify materials for acceptance;

III. A series of laboratory tests conducted on a set of materials in actual use, or proposed for use, in rail passenger cars;

IV. A full-scale fire test to correlate the laboratory tests with an actual fire.

This report is concerned solely with Task I, the literature survey. Tasks II, III, and IV will be the subjects of subsequent reports, as progress warrants.

While performing the literature search, areas of interest to which particular attention was directed included the following:

a. Test data on the flammability of interior materials;

b. Flammability test methods used or recommended for use by governmental agencies, manufacturers, or other specified authoritative groups;

c. Fire prevention standards relating to vehicle interior materials;

d. Statistical information concerning accidents that involve vehicle fires of interior origin;

e. Criteria used for the acceptability of interior materials.

With respect to flammability test data, there are several factors and parameters that must be considered in evaluating the fire hazard of interior materials. Among these are:

a. Time to ignition;

b. Ignition temperature;

c. Rate of flame spread;

d. Rate of combustion, or rate of material loss;

e. Rate of heat liberation;

f. Heat transfer from flames;

g. Opacity and rate of smoke production;

h. Identity and rate of evolution of the combustion products;

i. Toxicological effect of the gaseous combustion products.

These parameters are not fixed properties of a material, but are dependent upon the conditions of use or exposure of the material. Examples of these conditions are thickness, geometry or orientation, adjacent or near-by materials, and ventilation considerations, such as the air supply and air flow or turbulence.

It is apparent that there are a considerable number of variations possible in the flammability characteristics of interior materials. Therefore, a careful selection of materials, based upon their individual flammability properties and the manner in which they are finally used, could significantly reduce any fire hazard.

B. Objectives

The aim of the literature search was to furnish sufficient data and information that would enable the following objectives to be accomplished:

1. Select methods suitable for evaluating the flammability characteristics of rail passenger car interior materials:

2. Use these methods to measure the flammability properties of currently employed materials, or materials proposed for use;

3. Provide a data base that would serve as a guide to the FRA for setting reasonable material performance standards.

During the course of collecting and reviewing reports on the flammability of interior materials it became apparent that there was a

limited amount of information available that related specifically to the flammability problem of rail passenger cars. The bulk of the work reported on the flammability of transportation vehicle interiors was concerned primarily with aircraft, with a few reports dealing with buses and automobiles. A significant number of reports were concerned with the flammability properties of furniture upholstery materials. In addition, several reports were concerned with the flammability of classes or types of materials in general, and were not tested with any specific end use in mind. All these were reviewed, however, so as to gather as much information as possible in the time allotted. It seemed reasonable to assume that there would be useful flammability data from all these sources, regardless of the ultimate uses to which the materials might be put.

Most of the tests conducted were of small-scale or laboratory-scale size, full-scale tests being extremely expensive. While small-scale tests would provide useful data for screening or comparative purposes, it should be pointed out that there are frequently substantial variations in the performance of materials in large-scale or actual fire environments. Small-scale tests are not adequate in predicting the behavior of materials in actual, full-scale situations.

For purposes of organization the collected information was divided into relatively broad categories which are presented in the following sections. There was no intention to provide an exhaustive, detailed analysis of each article reviewed. General, basic information is presented. For more specific details the reader is referred to the original article or report.

II. FLAMMABILITY CHARACTERISTICS

The fire or flammability characteristics of combustible materials have been divided into several categories. These are (1) ignition related properties or ignitability, (2) flame spread or flame propagation, (3) heat release (fuel contribution), (4) smoke emission, and (5) the production of toxic gases (combustion or pyrolysis products). Each of these is reviewed in the following sections.

A. Ignition Properties/Ignitability

The difficulty required to ignite a material, or conversely the ease of ignition, can provide a relative measure of the fire hazard presented by that material under given conditions of temperature, pressure, and oxygen concentration. A material with a substantially lower ignition temperature than another material would obviously be a more likely fire hazard than the material with the higher ignition temperature, all other parameters being equal. The simplest ignition tests are performed under fixed conditions of heat, oxygen, and time; the test sample either ignites or does not ignite.

Among the methods most frequently employed to measure the ease of ignition of materials are the following: (a) ASTM Method D-2863, Limiting Oxygen Index Test; (b) ASTM Method D-1929, also known as the Setchkin Ignition Test; and (c) ASTM Method E-136. The first of these (Limiting Oxygen Index) appears to be the most often mentioned and used in recent years. The method is based on a procedure developed by Fenimore and Martin in 1966[1]. The oxygen index of a material is taken as the lowest percentage concentration of oxygen in an oxygen-nitrogen mixture which will support sustained combustion of that material.

Basically the apparatus consists of a vertical, heat resistant (Pyrex), glass tube having a minimum diameter of 75mm (2.95 in) and a minimum height of 450mm (17.7 in). Test samples are placed in a vertical position, secured by a clamp at the bottom. Sample sizes are 70-150mm (2.75-5.9 in) long, 6.5mm (0.26 in) wide, and 3.0mm (0.12 in) thick. An oxygen-nitrogen mixture of known composition is directed into the bottom of the glass tube into which a bed of glass beads has been placed. These beads are 3-5mm (0.12-0.20 in) in diameter and the layer is 80-100mm (3.1-3.9 in) deep. Passage through the bed of glass beads smoothes out the flow of gas, which is flowing at a rate of 4 ± 1 cm/sec (1.6 ± 0.4 in/sec). The sample is ignited on its upper end by a flame which is then withdrawn. By adjusting the composition of the oxygen-nitrogen gas mixture the limiting oxygen index (LOI) can be determined. This is the minimum concentration of oxygen (in the gas mixture) that will just permit the sample to burn for a minimum duration of 3 minutes, or for a length of 50mm (2.0 in). There have been modifications made to the apparatus and variations in the procedure given above, and some of these will be discussed below.

The Oxygen Index flammability test was discussed in detail by Isaacs[2] in a 1970 article. This article described the test, gave some typical results for the various types of materials which were investigated using the method, and compared the results of these tests with the results obtained from other flammability tests. Considered to be major advantages of this test were the precision with which the oxygen index can be measured (better than 1%), and the reproducibility of the method (better than 2%). The method also was reported to be utilized to study the flammability of such materials as gases and volatile liquid fuels, rigid and non-rigid plastics, cellular materials, fabrics, rubber, wood, and coated materials. Limited testing indicated that there was no correlation between the results from the ASTM D-655 test or the Underwriters Laboratory Bulletin 94 Test and this test, and only partial correlation with the ASTM E-84 Tunnel Test.

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[1] *C. P. Fenimore and F. J. Martin, "Flammability of Polymers," Combustion and Flame, 10, (3), 135-139 (June 1966).*

[2] *J. L. Isaacs, "The Oxygen Index Flammability Tests," J. Fire & Flammability, 1, 36-47 (January 1970).*

DiPietro and Stepniczka[3] investigated the influence of temperature on the flammability of flame-retarded and untreated polymer systems by using the Oxygen Index Method. The polymers studied in their work were high-impact polystyrene, cross-linked polyester, and high-impact ABS (acrylonitrile-butadiene-styrene). From their work the authors concluded that the oxygen indices of the samples increased with higher flame retardant levels. They also noted that when the samples were exposed to heat the oxygen indices decreased, which indicated an increase in the flammability of the materials. In addition, the authors reported the amount or degree of decrease in the oxygen index value was dependent upon the type of flame retardant used.

Batorewicz and Hughes[4] investigated the applicability of the Oxygen Index Method in evaluating urethane foams. The authors' primary concern was to find a reliable small-scale method with which to evaluate the relative activity of various flame retardants in a foam substrate. The foams investigated in this work were (a) a rigid foam based on crude diphenylmethane diisocyanate (MDI), and (b) a flexible foam based on toluene diisocyanate (TDI), both having an approximate density of 32.04 kg/m^3 (2.0 lb/ft^3). It was reported that within a gas flow rate of 115 to 220 cm^3/sec the oxygen index was independent of flow rate. Also, it was noted that a considerable variation between the thicknesses of samples could be tolerated. The authors reported a maximum average deviation of 1.3% for the rigid urethane foam, and a maximum average deviation of 1.5% for the flexible urethane foam. The sensitivity of the test was reported to allow the clear establishment of the relative order of the activity of flame retardants. An attempt to compare the results of the Oxygen Index Test with data from ASTM D-1692 tests and the Bureau of Mines Flame Penetration Test proved inconclusive.

A report by Brown and Dunn[5] described the use of the Oxygen Index Method to evaluate the relative flammabilities of a number of polymeric materials. The method was reported to provide accurate reproducible data on the efficiency of various fire retardants as well as providing information on the mechanism of fire retardation. It was indicated that oxygen index values were not dependent on specimen size or gas flow rate, within certain limitations. In addition, the results showed that oxygen indices decreased with an increase in temperature. This led to a discussion of a "fire protection temperature" concept, defined as the

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[3] *J. DiPietro and H. Stepniczka, "A Study of Smoke Density and Oxygen Index of Polystyrene, ABS, and Polyester Systems," J. Fire & Flammability, 2, 36-53 (January 1971).*

[4] *W. Batorewicz and K. A. Hughes, "The Application of the Oxygen Index to Urethane Foams," J. Fire & Flammability, 2, 260-270 (October 1971).*

[5] *J. R. Brown and P. Dunn, "The Combustion of Organic Polymeric Materials - Evaluation of Flammability by the Oxygen Index Method," Report No. 561, Department of Supply, Australian Defence Scientific Service, Defence Standards Laboratories, Maribyrong, Victoria, June 1973 (AD-914 237).*

highest temperature at which a material will burn for less than one second in an atmosphere containing 20.9% by volume of oxygen, after removal of the ignition flame. Poor correlation was reported between the results of the Oxygen Index Test and the results of test conducted according to method ASTM D-635 and the Underwriters Laboratories Bulletin 94 Test.

The Oxygen Index Test (ASTM D-2863) was extended by Routley[6] to determine the flammability of materials other than plastics. These materials included wood, hardboard, thin films of polyvinyl chloride and polyethylene sheet, fabrics, and paint films. In order to accomplish this some modifications to the standard apparatus were required. These included the design of a holder to support thin samples of non-rigid materials, and the incorporation of an electrical heating tube to heat the samples to considerably higher temperatures. This latter modification led to the introduction of the "temperature index" concept. The temperature index was taken to be the temperature at which the oxygen index of a material decreased to 20.8. The determination of oxygen index values at ambient temperature was considered to be an indication of the potential hazard of a material at the initial stage of a fire, while the temperature index was considered to be an indication of the flammability of a material in an actual fire situation.

A paper by Mathews and Sawyer[7] reported on their study of a modification to the standard Limiting Oxygen Index (LOI) Test in which they used an opposed flow diffusion flame (OFDF) configuration. In this work the oxygen mole fraction necessary to induce extinction was measured as a function of the oxidant flow velocity for three different commercially available polymers, polymethylmethacrylate, high molecular weight polyethylene, and polyoxymethylene. The authors stated that the OFDF configuration can be more precisely controlled, therefore it can be mathematically modeled to a high degree of accuracy, and thus a more refined interpretation of the results can be made. They also reported that it was just as easy to determine the limiting oxygen index in the opposed flow configuration as it was in the coaxial flow configuration of Fenimore and Martin[1]. Three parameters of interest that are used in assessing polymer flammability, and which can be derived from measurements made from the modified apparatus, are (1) the mass transfer number, (2) the effective heat of gasification (enthalpy of gasification), and (3) the temperature sensitivity of the reaction rate.

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[6] *A. F. Routley, "The Development of the Oxygen Index Concept for the Assessment of the Flammability Characteristics of Materials," CDL Report No. 5/73, Central Dockyard Laboratory, HM Naval Base, Portsmouth, U.K., November 1973 (AD-918 078).*

[7] *R. D. Mathews and R. F. Sawyer, "Limiting Oxygen Index Measurement and Interpretation in an Opposed Flow Diffusion Flame Apparatus," J. Fire & Flammability, 7, 200-216 (April 1976).*

The Oxygen Index Method, ASTM D-2863, was used to investigate a number of organic polymers, composites, and polymeric foams[8]. The variation in oxygen index value as a function of temperature was determined for each material over the temperature range between ambient and 300°C (572°F), i.e., the temperature index. Previous work[3,5,6] had indicated that materials could be ignited at progressively lower oxygen concentrations as the temperature of the environment increased. Thus a material whose flammability characteristics were acceptable at ambient temperatures could become a hazard at elevated temperatures, such as those found in a fire environment. Factors that influence oxygen index values were given as sample uniformity, composition, char formation, the evolution of gaseous components, and dripping of the sample during the test. Results from this work indicated that a temperature index profile (a plot of oxygen index values vs. temperatures) was a more informative and a more complete measure of the flammability behavior of a material than the single oxygen index determination at ambient temperature.

The oxygen index test was modified by Funt and Magill[9] and the resultant method employed to predict the burn rate of polymers. An equation was developed to predict the flame-spread rate in vertically-downward burning. In the work described the equation was employed to predict the burn rate of polystyrene films under conditions in which certain parameters were varied. These included an oxygen index value ranging from 20 to 50%, a gas velocity of 6 to 17 cm/min (2.4-6.7 in/min), a film thickness of 5 to 20 mils, and the use of nitrogen or helium as the inert diluent. Adequate agreement between predicted and measured burn rate was reported.

Flexible polyurethane foams were subjected to Limiting Oxygen Index tests, and the results reported by Damant[10]. Oxygen index values tended to be less for low density foams than for higher density formulations. In addition, oxygen index values for flame-retarded urethanes were consistently higher than for non-flame-retarded urethanes. Also, a decrease in oxygen index values was reported as aging conditions became more severe. This was attributed to a gradual volatilization or migration of flame retardant additives.

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[8] *D. P. Macaione and R. Dowling, II, "Flammability Assessment Tests for Organic Materials - The Oxygen Index/Temperature Index Concept," Report No. AMMRC-TR-77-19, U.S. Army Materials and Mechanics Research Center, Watertown, Massachusetts 02172, September 1977 (AD-A047 830).*

[9] *J. M. Funt and J. H. Magill, "Application of a Flame-Spread Model to the Oxygen Index Test," J. Fire & Flammability, 4, 174-184 (July 1973).*

[10] *G. H. Damant, "Flammability Aspects of Flexible Polyurethane Foams Commonly Used in Upholstered Furniture," J. Consumer Product Flammability, 3, 73-127 (June 1976).*

The apparatus employed in both the ASTM D-1929 and ASTM E-136 ignition tests is essentially the same. A vertical furnace tube having a length of 25.4 cm (10 in) and an inside diameter of 10.2 cm (4.0 in) is heated by current passing through nichrome wire in an asbestos sleeve (which surrounds the tube). The test sample is positioned inside an inner refractory tube which is 25.4 cm (10 in) long with an inside diameter of 7.6 cm (3 in). Air is passed into the apparatus at a controlled rate, and the temperature of this air is monitored by thermocouples.

The ASTM D-1929 test, which is also known as the Setchkin ignition test, requires a sample of 3 grams. The sample is exposed to air at progressively increasing temperatures until ignition is observed. The flash-ignition and self-ignition temperatures of a sample material are determined by this method. The flash-ignition temperature has been defined[11] as the lowest initial temperature of air passing around the specimen at which an amount of combustible gas sufficient to be ignited by a small external pilot flame is evolved. Self-ignition temperature has been defined[11] as the lowest initial temperature of air passing around the specimen at which, in the absence of an ignition source, the self-heating properties of the specimen lead to ignition or ignition occurs of itself as indicated by an explosion, flame, or sustained glow.

The ASTM E-136 ignition test requires a sample 5.1 cm (2.0 in) long x 3.8 cm (1.5 in) wide x 3.8 cm (1.5 in) thick. The sample is positioned in a stream of air at 750°C (1382°F) and moving at a rate of 3 m/min (9.8 ft/min). The temperature of the test sample should not increase by more than 30°C (86°F) and there should be no flaming of the sample after the first 30 seconds of exposure.

Thermal properties, including ignition data have been determined for a variety of plastic and rubber materials using 1000-watt tungsten lamps and pilot flames for ignition sources[12,13]. The information reported for each material included its name or type, the manufacturers, its

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[11] *C. J. Hilado, "Flammability Tests, 1975: A Review," Fire Technology, 11, (4), 282-293 (November 1975).*

[12] *R. G. Rein, J. R. Welker, and C. M. Sliepcevich, "Susceptibility of Potential Target Components to Defeat by Thermal Action," Ninth Quarterly Progress Report, Report No. OURI-1578-QPR-9, Contract No. DAAA-15-67-C-0074, Department of the Army, Edgewood Arsenal Research Laboratories, Physical Research Laboratory, Edgewood Arsenal, MD 21010, January 1969 (AD-853 427).*

[13] *J. R. Welker and C. M. Sliepcevich, "Susceptibility of Potential Target Components to Defeat by Thermal Action," Tenth Quarterly Progress Report, Report No. OURI-1578-QPR-10, Contract No. DAAA-15-67-C-0074, Department of the Army, Edgewood Arsenal Research Laboratories, Physical Research Laboratory, Edgewood Arsenal, MD 21010, March 1969 (AD-853 423).*

chemical structure, specific heat, thermal conductivity, density, and a description of the behavior of the sample during the ignition tests. Also given was a plot of the ignition time as a function of incident radiation for both types of ignition sources.

The combustibility of materials employed in space vehicle cabins was investigated by Stevens, Fisher, and Breen[14]. They were concerned with defining the spontaneous ignition temperature of individual materials under dynamic atmospheric conditions, and with the determination of the burning characteristics of materials as a function of atmospheric and gravitational environments. Another part of this program was concerned with the flame spread behavior of materials. The ignition and flammability behavior of materials were reported to be definable in terms of time to ignition, the amount of energy required for ignition, spontaneous ignition temperature, burning time, and burning rate.

An article by Welker[15] discussed various phases of ignition. This included the techniques used in the experimental investigation of ignition, and the techniques used in the mathematical modeling of ignition data. Several terms were defined and a detailed discussion of ignition modeling and the ignition of polymers was presented. A simplified mathematical analysis indicated that there were several factors of prime importance that required consideration in ignition studies. The factors are (a) the thermal properties of the sample, density, specific heat and thermal conductivity, (b) the ignition temperature, (c) sample thickness, (d) spectral absorbance of the sample, (e) the spectral distribution of the radiant energy source, and (f) incident irradiation.

Screening tests were conducted on insulation and building materials in order to determine their ignitability[16]. Heat fluxes used in this determination were 5.8, 8.1 and 10.5 watts/cm^2. Ignition times were found to decrease as heat flux levels increased. Results of these tests indicated that lower density materials had a tendency toward greater surface ignitability than higher density materials.

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[14] *M. R. Stevens, H. D. Fisher, and P. B. Breen, "Investigation of Materials Combustibility, Fire, and Explosion Suppression in a Variety of Atmospheres," Report No. AFAPL-TR-68-35, Air Force Aero Propulsion Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio 45433, May 1968 (AD-669 349).*

[15] *J. R. Welker, "Ignition of Combustible Solids," University of Oklahoma Research Institute, Norman, Oklahoma 73069, 1972.*

[16] *C. J. Hilado and R. M. Murphy, "Ignitability of Some Insulation and Building Materials," J. Thermal Insulation, 1, 237-240 (April 1978).*

Hilado and Kosola[17] described a laboratory-scale apparatus and method to determine ignition temperatures of materials. Basically, this apparatus consisted of a horizontal tube furnace into which could be placed a glass sample holder and thermocouple. An air supply whose rate was controllable was attached to the system. Tests were conducted on a series of plastic materials and data was obtained for the times and temperatures at which the sample melted, smoked, or ignited. The results of these tests were different than the results obtained for the same materials according to the ASTM D-1929 test. This was attributed to differences between the methods in the type of sample containers used, the geometries of the apparatus, the location at which temperatures were measured, and air flow characteristics. The reported advantages of this system over the ASTM D-1929 method were cost, ease and speed of operation, and safety, in addition to technical advantages of sample exposure, temperature measurement, and visibility of sample during the test.

Ignition tests also have been conducted on various types of home furnishing materials, such as upholstery fabrics, carpeting, wood or wood products, and plastics[18]. The results of the tests indicated that the ease with which the materials were ignited may be a function of the incident heat flux, their physical structure, and their behavior as much as of their chemical composition. The effect of heat flux on the ignition time was found to vary with the material. Part of this variation was attributed to behavioral differences such as charring or melting. Tests were conducted at heat flux densities of 5.8, 8.1, and 10.5 watts/cm^2. Ignition times were determined to decrease with an increase in heat flux density.

A report by Morimoto, et al[19], discussed the design and employment of an apparatus used to measure ignition temperatures and ignition limiting oxygen indices (ILOI) of several commercially available polymers. Ignition limiting oxygen index was defined as the minimum volume fraction of oxygen required for ignition to occur in a slowly rising gaseous atmosphere under a fixed condition of heat. ILOI values were determined for 0.2 g samples of material at a gas flow rate of 2.1 liters/min. at temperatures of 550°C, 600°C, and 650°C (1022°F, 1112°F, and 1202°F). Reproducibility was reported to be within ± 0.1%.

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[17] *C. J. Hilado and K. L. Kosola, "A Laboratory Technique for Determining Ignition Temperatures of Materials," Fire Technology, 14, (4), 291-296 (November 1978).*

[18] *C. J. Hilado and R. M. Murphy, "Ignitability by Radiant Heat of Some Materials in Home Furnishings," J. Consumer Product Flammability, 5, 68-81 (June 1978).*

[19] *T. Morimoto, T. Mori, and S. Enomoto, "Ignition Properties of Polymers Evaluated from Ignition Temperature and Ignition Limiting Oxygen Index," J. Appl. Poly. Sci., 22, 1911-1918 (1978).*

A model has been developed recently[20] that enabled predictions to be made of the radiative ignition time of a vertically oriented fabric in the presence of air. This was the result of a program whose aim was to develop a model that included all the important processes in the ignition of a fabric subjected to a constant radiant heat flux, and to determine the relative influence of the various thermophysical and kinetic parameters on the predicted ignition time. The model was reported to predict values within 15% of measured values at high intensities.

Ignition temperatures and burning rates have been reported[21] for specific fabric materials. Ignition temperatures were reported to be 927°C (1700°F) for a polybenzimidazole fabric, 871°C (1600°F) for a synthetic fiber (Nomex), and 788°C (1450°F) for a flame-retardant-treated cotton fabric. The thermal insulation properties of a fabric were reported to be largely dependent upon the entrapment of still air within the structure of the fabric and a function of fabric thickness.

B. Flame Spread/Flame Propagation

An important characteristic in evaluating the flammability of a material, in fact considered to be the most critical characteristic in transit vehicle fires[22], is the rate of flame spread. This has been defined as the rate of travel of a flame front under given conditions of burning[11]. A determination of a fire hazard can be made from this parameter in that flames can spread from one material surface to adjacent flammable materials and thereby increase the magnitude of the fire. The rate of flame spread also can have an effect on the time required to evacuate a hazardous area. (The slower the spread of the fire, the more time available to evacuate the area.) An indication of flame spread can be obtained by measuring such parameters as the distance of flame travel (per some unit of time) or the rate of combustion or burning.

It appears that there have been more tests developed to measure flame spread than any other flammability property. Tests have been developed for specific classes or types of materials (plastics, cellular plastics, rigid cellular plastics, foams, fabrics, carpets, etc), and for specific specimen orientations (vertical, horizontal, 45° angle, 30° angle, 60° angle). Unfortunately, there also appears to be little

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[20] *C. C. Ndubizu and P. Durbetaki, "Modeling Radiative Ignition of Fabrics in Air," Fire Research, 1, 281-290 (1977/78).*

[21] *W. D. Freeston, Jr., R. J. Coskren, J. Skelton, and R. E. Sebring, Flammability and Heat Transfer Characteristics of PBI Fabric," Technical Report AFML-TR-70-267, Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio 45433, January 1971 (AD-882 360).*

[22] *C. J. Hilado, "Fire Response Characteristics of Non-metallic Materials: A Review of Recent Papers and Reports," J. Fire & Flammability, 7, 539-558 (October 1976).*

or no correlation possible between the various tests.

Among the most frequently employed tests to measure flame spread are (a) ASTM E-84 25-foot tunnel test, (b) ASTM E-162 radiant panel test, (c) ASTM E-286 8-foot tunnel test, (d) the Union Carbide 4-foot tunnel test, and (e) the Monsanto 2-foot tunnel test. Some examples of other flame spread tests are: the ASTM D-635 test for plastics; the Schlyter test; the Pittsburgh-Corning 30-30 tunnel test; the ASTM D-1692 test for cellular plastics; ASTM D-568 and ASTM D-1433 tests for plastics; ASTM D-3014 test for rigid cellular plastics; Federal Test Method Standard No. 191 for fabrics which includes Methods 5900 and 5906 for horizontal orientation, Methods 5903, 5904, and 5905 for vertical orientation, Method 5908 for 45°-angle orientation; ASTM D-2859 test for floor covering. Several more tests also are available but are not listed here. A brief description of the first two tests is given to illustrate some of the variations between tests.

The ASTM E-84 25-foot (7.62 meter) tunnel test requires a test specimen with a length of 7.62 meters (25 feet) and a width of 50.8 cm (20 inches). The specimen is mounted face down in a manner that will form the roof of a tunnel 44.5 cm (17.5 in) wide x 30.5 cm (12.0 in) high x 7.62 meters (25 feet) long. The ignition source consists of 2 gas burners positioned 30.5 cm (12.0 in) from the fire end of the test specimen and 19.1 cm (7.5 in) below the surface of the sample. The burners are adjusted to provide flame spread on selected red oak flooring 5.9 meters (19.5 feet) from the end of the igniting fire in 5.5 ± 0.25 minutes. The end of the igniting fire is considered to be 1.4 meters (4.5 feet) from the gas burners. This flame length is due to an average air velocity of 73.2 ± 1.5 meters/min (240 ± 5 ft/min). Flame spread classification is determined from a scale on which the red oak flooring is rated as 100 and asbestos-cement board is rated as 0.

The ASTM E-162 radiant panel test employs a vertically mounted, porous refractory panel, 30.5 cm x 45.7 cm (12.0 in x 18.0 in) and maintained at a temperature of 670 ± 4°C (1238 ± 7.2°F) as a radiant heat source. A test specimen 45.7 cm x 15.2 cm (18 in x 6 in) is supported in front of the panel so that the 45.7 cm (18.0 in) dimension is inclinde 30° from the vertical. Ignition is on the top of the sample by a pilot flame, 12.1 cm (4.75 in) away from the radiant panel. The flame front progresses downward along the underside of the specimen exposed to the radiant panel. The increase in temperature is measured by stack thermocouples, above their base level of 204°C (400°F). This temperature rise is used as a measure of the heat emission.

Williams and his colleagues[23] studied the processes involved in the propagation of a fire within a room from the time of ignition to the

[23] *F. A. Williams, F. J. Kosdon, M. Vogel, and C. Buman, "Fire Propagation Mechanisms, Rates and Criteria," DASA Final Report, Contract No. N00228-67-C-0834, U.S. Naval Radiological Defense Laboratory, San Francisco, California, July, 1969 (AD-859 091L).*

time of flashover in order to develop a fundamental understanding of the propagation mechanisms. Their approach was (1) to make an accurate characterization of the time-dependent heat-transfer fields in areas adjacent to burning items, (2) to use these heat-transfer fields to calculate conditions under which adjacent but non-contiguous items would ignite, and (3) to measure experimentally the conditions under which such objects ignited. The necessary tests were made using vertically oriented cellulosic cylinders with diameters ranging from 0.1 - 1.0 inch (0.254 - 2.54 cm) and with length ranging from 1.0 - 6.0 inches (2.54 - 15.24 cm). Experimental data was obtained by photographic means, laser interferometry techniques, and measurements of weight loss, temperatures, and heat fluxes. A discussion of the propagation of flame from one item to another was presented.

The development and application of a "fire propagation" test was reviewed by Rogowski[24]. This test was designed primarily to assess the fire performance of different materials employed as internal wall linings. The properties of structural materials that can effect the initial growth rate of an inclosed fire were given as the ease of ignition, rate of flame spread, and the amount of heat liberated. A detailed description of the test chamber and method was presented.

The mechanism of flame spread was reviewed extensively in an article by Magee and McAlevy[25]. They discussed several factors that influence the rate of flame spread, and also examined the work conducted by several other laboratories. Among the factors discussed were the following: (a) the effect of surface roughness and exposed edges, (b) the effect of sample orientation, (c) the effect of chemical composition, (d) the effect of sample geometry, (e) the effect of pressure, and (f) the effect of the mole fraction of oxygen. In addition, these authors presented a review of the major flame spread theories at the time of the article. Some experimental results were compared to predictions based upon these theories.

A critical review of the theories of flame spread above solid combustible materials was given by Sirignano[26]. Among the factors or

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[24] *B. F. W. Rogowski, "The Fire Propagation Test: Its Development and Application," Fire Research Technical Paper No. 25, Ministry of Technology and Fire Offices Committee, Joint Fire Research Organization, Her Majesty's Stationery Office, London, U.K., April 1970 (AD-872 569).*

[25] *R. S. Magee and R. F. McAlevy, III, "The Mechanism of Flame Spread," J. Fire & Flammability, 2, 271-296 (October, 1971).*

[26] *W. A. Sirignano, "Flame Spreading Across Materials: A Review of Fundamental Processes," in Aircraft Fire Safety, 45th Meeting of the AGARD Propulsion and Energetics Panel held at the Palazzo Aeronautica, Rome, Italy, 7-11 April 1975, Report No. AGARD-CP-166, Document No. AD-A 018 180, U.S. Dept. of Commerce, National Technical Information Service, 5285 Port Royal Road, Springfield, VA, 22161, October, 1975.*

parameters discussed were natural convective flows, orientation of the direction of flame spread with respect to gravity, the thickness of the burning sample, and the values for the conductivity, diffusivities, heats of reaction and pyrolysis, chemical kinetic constants, and ambient oxygen concentration.

An evaluation of the flame spread potential of foamed plastics by means of the commonly accepted ASTM E-84 tunnel tests produced anomalous results[27]. Foamed plastics were reported to promote fire as readily as those materials with less satisfactory flammability resistance. One reason for the disparity was given as the low thermal inertia of foamed plastics, thermal inertia of a material being defined as the product of thermal conductivity, density, and specific heat. Another reason proposed for the anomaly was that the effective surface area of a foam is much greater than that of conventional materials. The results suggested that the use of a rate index might resolve the anomaly. Also, it was suggested that corner testing might be useful in assessing the flammability of foam plastics in cases where tunnel testing produces uncertain results.

An interlaboratory evaluation of the Radiant Panel Method[28] for the determination of flame spread of samples of two foams (polyurethane and neoprene), and one hardboard was made. Between-lab coefficient of variation on the flame-spread index was 21% for the hardboard, 35% for the urethane, and 45% for neoprene. The higher variability for foam samples reportedly was caused by the rapid melting of the urethane and an unstable flame front for neoprene during the tests. Among some of the sources of errors were the determination of the calibration constants, and the inappropriate use of the base stack temperature correction.

Benjamin and Adams[29] presented background and technical data to aid in establishing criteria to be used with the Flooring Radiant Panel test of the National Bureau of Standards. This test was employed to determine the potential contribution to fire growth of floor covering systems. In the test a 100 cm (39.4 in) sample, mounted in a horizontal position, is subjected to radiant energy from an air-gas panel mounted above the sample at an angle of 30°. A flux profile is thus generated along the

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[27] *M. V. D'Souza and J. H. McGuire, "ASTM E-84 and the Flammability of Foamed Thermosetting Plastics," Fire Technology, 13, (2), 85-94 (May 1977).*

[28] *T. G. Lee, "Reproducibility of the Radiant Panel Test Method (ASTM E-162-67) Using Polyurethane Foam, Neoprene, and Hardboard Specimens," NBSIR-77-1222, Center for Fire Research, National Bureau of Standards, Washington, DC 20234, March 1977 (PB-265 089).*

[29] *I. A. Benjamin and C. H. Adams, "Proposed Criteria for Use of the Critical Radiant Flux Test Method," Report No. NBSIR-75-950, Center for Fire Research, Institute for Applied Technology, National Bureau of Standards, Washington, DC 20234, December 1975 (PB-250 664).*

length of the sample ranging from 1.1 watts/cm^2 to 0.1 watts/cm^2. The distance burned can be converted to W/cm^2 from a calibrated flux profile graph and is reported as the minimum flux necessary to sustain flame propagation.

The effects of resin, fiber reinforcement, fire-retardant additives, and protective barriers on the flammability characteristics of organic-matrix composites were evaluated by Silvergleit, et al[30]. Flame spread index was measured by the radiant panel test, ASTM E-162, using a pilot flame as the ignition source. Fire retardant additives were reported to influence the burning rate of materials by interfering with combustion reactions, making the pyrolysis products less flammable, reducing heat transfer from the flame to the material, and reducing the rate of diffusion of the pyrolysis products to the flame front.

The burn rate of more than 100 aircraft interior materials was determined by means of a horizontal, a vertical, and a radiant-panel flame-spread method[31]. The results indicated that the burn rate determined by the vertical method was 10 times more rapid than the burn rate determined by the horizontal method. Also, the radiant panel test was reported to be the most severe test method employed here.

Another report discussed the measurement of the flammability properties of 140 aircraft interior materials[32]. Included in these properties were ignition times, burn rates, and flame-spread index values. Among the materials investigated were vinyls, acrylics, acrylonitrile-butadiene-styrene (ABS) resins, aromatic polyamides, polyimides, polycarbonate, polysulfone, and fluorocarbons. The test methods employed in this study were a Vertical Flammability Test Method and the Radiant Panel Flame-Spread Method. Analysis of the results indicated that the total heat generated during the combustion of these materials varied with their chemical composition and thickness. Also, it was noted that several important factors must be considered in devising any material rating system. These factors were (a) the minimum heat, temperature, and time required for ignition; (b) the rapidity by which flames

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[30] *M. Silvergleit, J. G. Morris, and C. N. LaRosa, "Flammability Characteristics of Fiber-Reinforced Organic-Matrix Composites," Report No. MAT-77-21, David W. Taylor Naval Ship R&D Center, Annapolis, MD 21402, June 1977 (AD-B019 020L).*

[31] *J. F. Marcy, E. B. Nicholas, and J. E. Demaree, "Flammability and Smoke Characteristics of Aircraft Interior Materials," Report No. FAA-ADS-3, Federal Aviation Agency, Washington, DC , January 1964 (AD-600 387).*

[32] *J. F. Marcy and R. Johnson, "Flaming and Self-Extinguishing Characteristics of Aircraft Cabin Interior Materials," Report NO. NA-68-30 (DS-68-13), Federal Aviation Administration, National Aviation Facilities Experimental Center, Atlantic City, NJ 08405, July 1968 (AD 673 084).*

propagate following ignition; (c) the tendency for flash fire to erupt suddenly; (d) the tendency for flaming to become self-extinguishing upon removal of the ignition source; (e) the rate and total heat generated by the combustion process; (f) the measurement of smoke and combustion product concentration.

Laboratory-scale studies of the flame spread over solid and liquid fuels was the subject of an article by Nakakuki[33]. The portion of the work concerning solid fuels primarily dealt with horizontal flame spread over polymeric materials. A discussion of the mechanism of flame spread was presented and included the radiant heat from the flame to the fuel ahead of the flame, the conductive heat transfer through the gas phase, and the heat transfer to the fuel in the pyrolysis region.

Markstein and deRis[34], in their work concerning flame spread along edges, found that the rate of flame spread along the free upper edge of vertically suspended fabrics always exceeded the normal downward spread rate. They proposed a tentative interpretation of this in terms of convective transport of pyrolysis products toward the edge points.

Rowen and Lyons[35] measured the rate of burning and rate of heat release for plywood, hardboard, polyurethane, and polystyrene over a heat flux range of 2 - 6 watts/cm^2.

C. Heat Release (Fuel Contribution)

Heat release has been defined as the amount of heat produced by the combustion of a given weight or volume of material, and also has been referred to as fuel contribution[11]. Heat release is employed in assessing a fire hazard in that a material that generates little heat per unit weight or volume during combustion will contribute less to the total fire environment than a material that generates significantly larger amounts of heat per unit weight or volume. The measurement of heat release enables relative rankings of materials to be determined for hazard assessment.

Although the previously discussed ASTM E-84 25-foot tunnel test and the ASTM E-162 radiant panel test are primarily employed for determining surface flame spread, they can be used to provide a measure of heat release through the measurement of the temperature increase in the stack

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[33] *A. Nakakuki, "Flame Spread over Solid and Liquid Fuels," J. Fire & Flammability, 7, 19-40 (January 1976).*

[34] *G. H. Markstein and J. deRis, "Flame Spread Along Fuel Edges," J. Fire & Flammability, 6, 140-154 (April 1975).*

[35] *J. W. Rowen and J. W. Lyons, "The Importance of Externally Imposed Heat Flux on the Burning Behavior of Materials," J. Cell. Plast., 25-32, January-February 1978.*

gases. Two other methods are used more frequently, however. These are the Factory Mutual Calorimeter Test and the Ohio State University heat release rate apparatus.

The Factory Mutual Calorimeter method requires a test sample 1.4m x 1.5m (4.5 ft x 5,0 ft). A 1.2m x 1.2m area (4 ft x 4 ft) of the sample is exposed in the roof of a furnace whose dimensions are 5.3 meters long x 1.2 meters wide x 1.1 meters high (17.5 ft x 4.0 ft x 3.75 ft). The main fire exposure burners of the furnace are fueled with gasoline and the evaluation burners are fueled with propane. The test sample is burned using only the gasoline-fueled main fire exposure burners. The sample is replaced with a noncombustible cover material and the propane-fueled evaluation burners are adjusted to duplicate the flue temperature-time curve produced during the burning of the test sample. The heat added through the evaluation burner is considered to be equal to the heat released by the test sample.

The Ohio State University (OSU) heat release rate apparatus consists of a chamber 88.9 cm (35 in) high x 40.6 cm (16 in) wide x 20.3 cm (8 in) deep. A 39.4 cm (15.5 in) high pyramidal top section is connected to an outlet. An electrically heated ceramic radiant panel is located in the chamber. Dimensions of this panel are 35.0 cm x 46.0 cm (13.8 in x 18.1 in). The test sample must have an exposed surface area of 25.4 cm square (10 in square). The test sample is positioned 7.6 cm (3.0 in) from the radiant panel. The distance between the sample and radiant panel can be varied from 0 to about 18 cm (0 - 7 in). Calculations of heat release rate are made in terms of watts per unit of surface area exposed.

The employment of the Ohio State University release rate apparatus to measure the release rate of heat, smoke, and toxic gases was discussed in an article by Smith[36]. In this work a general mathematical equation was given from which release rates could be determined by monitoring the gases leaving the test chamber for heat, smoke, and toxic gas concentrations. This equation was

$$\text{(Concentration)(Air Flow Rate)} = \text{Release Rate.}$$

For heat release rate: concentration = $c_p\ (T - T_o)$; air flow rate = M; and rate of heat release = $c_p\ (T - T_o) \times M$. Here c_p = specific heat of air leaving the chamber; $(T - T_o)$ = temperature difference in the exit air, with and without the sample in the chamber; M = mass flow rate of air. Units of heat release rate are given in rate per unit of surface area since release rates are proportional to exposed surface area. A plot of the heat release as a function of time for a sample being tested

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[36] *E. E. Smith, "Application of the Ohio State University Release Rate Apparatus to Combustion Gas Studies," J. Fire & Flammability/Combustion Toxicology, 1, 95-103 (May 1974).*

was reported to provide a quantitative description of the ease of ignition of the sample, the rate of flame travel over its surface, and the rate and quantity of heat released over the conditions of the test.

Another article by Smith[37] discussed the work involved to develop a test apparatus and methods to measure experimentally the fire hazards of materials, such as ease of ignition, rate of burning, smoke emission, and toxic gas production. It was suggested that materials be evaluated in terms that affect the kinetics of release of heat, smoke, and toxic gases. These parameters include exposed surface area, surface properties, chemical composition, weight, and exposure conditions. It also was suggested that release rate data be employed to define fuel loading and for analyzing the initiation and propagation phases of a fire system.

Coulbert[38,39] discussed an attempt to determine if a method could be found by which the vast amount of experimental data might be applied to practical fire hazard situations involving enclosures. A set of five relative energy release criteria were defined. These criteria control the rate and the total energy released during the course of an enclosure fire. They are (1) flame spread rate, (2) fuel surface area limit, (3) ventilation limit, (4) enclosure volume, and (5) fuel load. Each of these were discussed in some detail. It was suggested that a heat release rate calorimeter with the capability to measure heat release rate, mass loss rate, toxic gases, and smoke production could provide data required for a wide variety of enclosures and fire loads.

D. Smoke

The emission of smoke is a major factor in the determination of the flammability characteristics of materials. Tests to measure smoke production usually involve the use of a photometric system to determine the amount of light absorbed or loss of visibility (obscuration) caused by the smoke emitted from a burning material. Smoke measurements are expressed in terms of specific optical density, defined as the optical density measured over unit path length within a chamber of unit volume produced from a specimen of unit surface area[40]. The amount of smoke produced is a function of several variables. Among these are the number and size of particles produced during burning, refractive index, the flow of air or other ventilation parameters, the rate of flame movement,

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[37] *E. E. Smith, "Measuring Rate of Heat, Smoke, and Toxic Gas Release," J. Fire Technology, 8,(3), 237-245 (August 1972).*

[38] *C. D. Coulbert, "Energy Release Criteria for Enclosure Fire Hazard Analysis - Part I," Fire Technology, 13,(3), 173-184 (August 1977).*

[39] *C. D. Coulbert, "Energy Release Criteria for Enclosure Fire Hazard Analysis - Part II," Fire Technology, 13,(4), 316-324 (November 1977).*

[40] *S. Steingiser, "A Philosophy of Fire Testing," J. Fire & Flammability, 3, 238-253 (July 1972).*

and the distance over which light must travel (length of light path).

Several methods are available for performing smoke tests. Among these are the ASTM D-2843 test, the National Bureau of Standards (NBS) smoke density test, and ASTM Methods D-757, E-162, and E-84. The Ohio State University release rate apparatus also can be employed to make smoke measurements[36].

The ASTM D-2843 test employs a cabinet that is frequently referred to as the Rohm and Haas XP2 smoke chamber. The cabinet is 76.2 cm (30 in) high, 30.5 cm (12 in) wide, and 30.5 cm (12.0 in) deep, and is completely enclosed except for 2.54 cm (1 in) high openings around the bottom. A propane-air flame from a Bernz-O-Matic TX-1 pencil tip burner is employed as the heat or ignition source. The flame is applied at an angle of 45° to the bottom of the specimen, the size of which can be either 2.54 cm x 2.54 cm x 0.635 cm (1 in x 1 in x 0.25 in) or 5.1 cm x 5.1 cm x 5.1 cm (2 in x 2 in x 2 in). Light absorption is measured by means of a horizontal photometer path located 50.8 cm (20 in) above the bottom of the test chamber.

The NBS smoke density chamber consists of a cabinet 91 cm (35.8 in) high x 91 cm (35.8 in) wide x 61 cm (24.0 in) deep. The cabinet is completely enclosed. The sample size required is 7.6 cm x 7.6 cm (3 in x 3 in). The test sample is supported vertically in a frame in such a manner that an area 6.5 cm x 6.5 cm (2.6 in x 2.6 in) is exposed to heat under either flaming or nonflaming (smoldering) conditions. The heat source is an adjustable electric furnace that will provide a heat flux of 2.5 watts/cm^2 (2.2 Btu/sec/ft^2) onto the surface of the test specimen. Light absorption is measured by means of a vertical photometer path over the full height of the test chamber.

Some of the differences between the XP2 chamber and the NBS chamber include (a) the size of the chamber, (b) sample size, (c) heat sources, and (d) the method of measuring light absorption. With respect to this last difference, a vertical photometer path would minimize any errors in the measurements due to smoke stratification. The NBS test also permits a material to be evaluated under either flaming or nonflaming conditions. In addition, the NBS chamber permits different heat flux levels to be used (up to 10 watts/cm^2), provides a weight monitoring capability, and allows variable ventilation conditions to be employed.

The ASTM E-84 25-foot tunnel test can be used to measure smoke density by means of a photometer at the same time surface flame spread and heat release are being measured. ASTM Method E-162 and Method D-757 provide data on smoke production through techniques that require smoke particles to be collected and weighed.

Several articles and reports have discussed the general, overall problem of smoke emission from burning materials. Some of these are reviewed here.

A discussion of some of the physical and chemical factors that affect the smoke produced from burning polymers was given by Hilado[41]. In this work both a Rohm and Haas XP2 and a National Bureau of Standards smoke density chamber were employed to evaluate the smoke emissions from several polymers. The reproducibility of smoke measurements was reported to be influenced by variations in temperature, stratification due to differences in density, and the agglomeration of smoke particles with time. The thickness and density of the polymer sample also were reported to greatly affect the amount of smoke produced. D_m values (maximum specific optical densities) from the XP2 chamber were 0.6 times the D_m values from the NBS chamber (for flaming exposure conditions) for material thicknesses ranging from 125 to 250 mils. The highest smoke densities obtained in these tests were for polyvinyl chloride (PVC), polystyrene, acrylonitrile-butadiene-styrene (ABS) resin, and polyester. Some materials were noted as producing more smoke under smoldering conditions than under flaming conditions, while for other materials the reverse was observed. Polyethylene, polypropylene, and styrene-acrylonitrile produced more smoke under smoldering (nonflaming) test conditions; PVC, polystyrene, ABS, polysulfone, polycarbonate, and polyester emitted more smoke under flaming conditions. In addition, the results indicated that while flame retardant additives were effective in reducing flame spread, they tended to increase the amount of smoke produced.

The formation of smoke during the combustion of polymeric materials was the subject of an article by Prado, et al[42]. Among the areas discussed in this work were (a) the general mechanisms of carbon particle formation, (b) the mechanism of polymer combustion, (c) the properties of smoke formed during the combustion of polymers, and (d) the parameters that influence the formation of soot. Included in the last area are the hydrocarbon/air ratio, the mixing intensity, the composition of the hydrocarbons in the gas phase, and inorganic additives. In this article it was noted that (a) smoke particles play an important role in the mechanism of fire spread, (b) smoke opacity is a function of the concentration and size distribution of the aggregates that make up the smoke, and (c) aromatic hydrocarbons form soot much more readily and in greater quantities than aliphatics. (38 references were given).

An article by Nelson[43] discussed the problems associated with evaluating the smoke formation from burning polymers that are attributed to sample thickness and sample flow characteristics. Specific optical density values were found to be very dependent on specimen thickness

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[41] *C. J. Hilado, "The Effect of Chemical and Physical Factors on Smoke Evolution from Polymers," J. Fire & Flammability, 1, 217-238 (July 1970).*

[42] *G. Prado, J. Jagoda, and J. Lahaye, "Smoke Formation by Combustion of Polymeric Materials," Fire Research, 1, 229-235 (1977/78).*

[43] *G. L. Nelson, "Smoke Evolution: Thermoplastics," J. Fire & Flammability, 5, 125-135 (April 1974).*

and, for meaningful values, the drip of thermoplastics during burning also must be considered. It was determined that several factors must be considered in order to reduce smoke. These were given as (a) high thermal stability, (b) propensity for char formation, (c) low aromatic content of volitile fuels, (d) high oxidation rate of those fuels, and (e) slow nucleation of soot particles. It was noted that results can be influenced by the presence of additives, flow property differences, the size and thickness of samples, and sample configuration.

The Task Group of Subcommittee IV, ASTM Committee E-5 on the Fire Tests of Materials and Construction, prepared a report[44] that reviewed the problem of smoke control in building fires. Areas discussed in this article included the nature of smoke, the development of smoke in building fires, the efforts directed toward the control of smoke through regulation and building design, current and proposed test methods for the measurement of smoke, and test criteria. Forty-two references were given.

A critical review of the various methods employed in the evaluation of the smoke-producing properties of materials was given by Tsuchiya and Sumi[45]. Among the methods reviewed by these authors were (a) the ASTM D-2843 test (Rohm and Haas XP2 smoke chamber test), (b) the NBS smoke density chamber test, (c) the Commonwealth Experimental Building Station test (similar to, but larger than the NBS chamber), (d) the Michigan Chemical Corporation apparatus of DiPietro and Stepniczka[3], and (e) the ASTM E-84 25-foot tunnel test. The authors concluded that these methods represent conditions limited by the test procedure and did not represent conditions actually encountered in real fire situations. Therefore, the concept of a smoke generation coefficient was introduced which the authors reported as providing a measure of smoke production of a material under varied conditions of temperature and oxygen concentration. The apparatus and method for determining the smoke generation coefficient for materials was given as well as a discussion of experimental results.

A large portion of a report by Einhorn, et al[46], was devoted to a discussion of the measurement of smoke and the parameters that influence the emission of smoke from urethane cellular plastics used in aircraft interiors. The smoke evolved was measured using a modified XP2 smoke

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[44] *C. H. Yuill, et al, "The Control of Smoke in Building Fires - A State-of-the-Art Review," Materials Research & Standards, 11, (4), 16-23 (1971).*

[45] *Y. Tsuchiya and K. Sumi, "Smoke-Producing Characteristics of Materials," J. Fire & Flammability, 5, 64-75 (January 1974).*

[46] *I. N. Einhorn, M. D. Kanakia, and J. D. Seader, "Physio-Chemical Study of Smoke Emission by Aircraft Interior Materials. Part II: Rigid- and Flexible-Urethane Foams," Report No. FAA-RD-73-60, II, Federal Aviation Administration, Systems Research and Development Service, Washington, DC 20591, July 1973 (AD-763 935).*

density chamber (ASTM D-2843). The time to reach 70% light obscuration was taken as an arbitrary criterion for comparing the smoke developed by the burning of various foam samples. The principal parameters that affect the development of smoke from urethane and isocyanurate polymers were reported to be the nature and functionality of the monomers, the degree of aromaticity in the polymer backbone, the molecular weight per cross-link density, and the type and concentration of additives that may be incorporated into the polymer system to retard combustion.

Among the most frequently employed test methods for evaluating the smoke-producing properties of materials is the Rohm and Haas XP2 smoke density chamber, which has been adopted as a standard in ASTM Method D-2843. Dunn[47] used this procedure to investigate the effectiveness of additives in polymeric materials to impart flame-retardancy. (See also previously reviewed articles[41,45,46]).

Brown and Dunn[48] conducted a rather extensive investigation of the smoke producing characteristics of several organic materials in which they employed a Rohm and Haas XP2 smoke density chamber. The amount of smoke produced was measured photometrically and the results were reported in terms of the maximum smoke generation, maximum rate of smoke generation, the period of time to reach an arbitrary "critical" smoke level, and the time period to reach maximum smoke generation. It was noted here that for a developing fire the rate of smoke production was considered to be the significant parameter, while for a fully developed fire the total amount of smoke produced was considered to be the important factor. From the results of this program the authors made the following conclusions. (1) Only limited reliance should be placed on small-scale tests as an indication of the behavior of a material in a large fire. (2) The use of a number of small-scale tests to evaluate materials only serves as an indication of the suitability of a material for a specific application. (3) The combustion of chlorinated polymers and rigid polyurethane foams produce large amounts of smoke. The addition of materials to reduce the flammability of these materials generally results in an increase in smoke production. (4) Epoxy-based adhesives generally produce more smoke than other types. (5) Solid-plastics, rubbers, textiles, and paints have smoke producing properties that are characteristic of their chemical composition, structure, and form.

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[47] *P. Dunn, "Organic Materials in Adverse Environments," Report No. 458, Department of Supply, Australian Defence Scientific Service, Defence Standards Laboratories, Maribyrong, Victoria, July 1971 (AD-889 159).*

[48] *J. R. Brown and P. Dunn, "The Combustion of Organic Polymeric Materials - Smoke Generation," Report No. 560, Department of Supply, Australian Defence Scientific Service, Defence Standards Laboratories, Maribyrong, Victoria, June 1973 (AD-914 236).*

Stueben and Imhof[49] determined the smoke density ratings of a series of aryl polyesters and polyethers using a Rohm and Haas XP2 smoke chamber. They concluded that certain correlations existed between polymer structure and smoke density. They also suggested that less emphasis be placed on numerical values and that materials be considered from the standpoint of generating low, medium, or high quantities of smoke.

Another extensively employed method for assessing the smoke-producing characteristics of materials is the National Bureau of Standards (NBS) smoke density chamber test which was described earlier. Gross, et al[50], used this method to evaluate the smoke-producing properties of 141 materials used as aircraft cabin furnishings. Smoke levels were reported in terms of specific optical density. Considerable variations were reported for the materials tested under similar conditions.

Lopez[51,52] has reported a study which was performed to determine the smoke emission characteristics of aircraft interior materials under various conditions of burning. Materials were tested in an NBS smoke density chamber under both flaming and nonflaming conditions at heat fluxes of 2.5 and 3.8 watts/cm^2 (2.2 and 3.3 Btu/ft^2-sec). Some of the materials also were tested in a mock-up under flaming and nonflaming conditions, in both vertical and horizontal orientations. Using maximum specific optical density as the criterion, the correlation between laboratory-scale and mock-up smoke tests was described as "fair." Additionally, the determination of the effects of smoke emissions on visual acuity was made and the predominant factor was found to be the irritating effects of the combustion gases, particularly hydrogen chloride and sulfur dioxide.

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[49] *K. C. Stueben and L. G. Imhof, "The Effect of Structure on the Smoke Density Rating of Aryl Polyesters and Polyethers," J. Fire & Flammability, 4, 8-14 (January 1973).*

[50] *D. Gross, J. J. Loftus, T. G. Lee, and V. E. Gray, "Smoke and Gases Produced by Burning Aircraft Interior Materials," Report No. NA-68-36 (DS-68-16), Federal Aviation Administration, National Aviation Facilities Experimental Center, Atlantic City, New Jersey 08405, June 1968 (AD-675 513).*

[51] *E. L. Lopez, "Smoke Emission from Burning Cabin Materials and the Effect on Visibility in Wide-Bodied Jet Transports," Report No. FAA-RD-73-127, Federal Aviation Administration, National Aviation Facilities Experimental Center, Atlantic City, New Jersey 08405, March 1974 (AD-776-963).*

[52] *E. L. Lopez, "Smoke Emission from Burning Cabin Materials and the Effect on Visibility in Wide-Bodied Jet Transports," J. Fire & Flammability, 6, 405-450 (October 1975).*

Sarkos[53] also has described a program in which materials used in aircraft interiors were evaluated for smoke emission by means of the NBS smoke density chamber test. Both flaming and nonflaming exposure conditions were used. Materials were compared on a peak smoke basis.

Seader and Chien[54] suggested the use of mass optical density to correlate and compare data obtained on the smoke-producing characteristics of materials as determined in an NBS smoke density chamber. Mass optical density was defined by the authors as $D_s m/A$, where D_s is the specific optical density, A is the exposed area of the sample under investigation, and m is the mass loss of the sample. The determination of mass optical density requires the simultaneous measurement of light obscuration and sample weight. The theoretical derivation and experimental evidence for employing mass optical density as a measure of smoke was presented. The authors reported mass optical density, compared to specific optical density, to be less dependent on the thickness and density of the sample provided the light transmittance is greater than 1%. In addition, they reported mass optical density to be independent of the surface area of a smoking polymer.

Another article by Seader and Chien[55] discussed the physical aspects of smoke development in an NBS smoke density chamber. A theory was developed to predict the degree of light extinction and a particulate optical density (POD) concept was introduced. The theory was reported to give consideration to light scattering, droplet agglomeration, droplet settling, multiple scattering, and polydispersion. Important parameters in the use of the theory were given as the airborn mass loss of the smoldering material and the fraction of that mass loss that is particulate matter. The experimental data required includes particle size distribution and properties as well as smoke concentration.

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[53] *C. P. Sarkos, "Measurement of Toxic Gases and Smoke from Aircraft Cabin Interior Materials Using the NBS Smoke Chamber and Colorimetric Tubes," Report No. FAA-RD-76-7, Federal Aviation Administration, National Aviation Facilities Experimental Center, Atlantic City, New Jersey 08405, March 1976 (AD-A023 413).*

[54] *J. D. Seader and W. P. Chien, "Mass Optical Density as a Correlating Parameter for the NBS Smoke Density Chamber," J. Fire & Flammability, 5, 151-163 (April 1974).*

[55] *J. D. Seader and W. P. Chien, "Physical Aspects of Smoke Development in an NBS Smoke-Density Chamber," J. Fire & Flammability, 6, 294-310 (July 1974).*

The smoke produced from three materials was measured in an NBS smoke density chamber[56] at energy flux levels ranging from 1.0 to 7.5 watts/cm^2. These materials were α-cellulose, Douglas fir, and a TDI-based flexible polyurethane. The results indicated more smoke was produced at a faster rate as the energy flux increased in the nonflaming region. In the transition from the nonflaming to the flaming region, both the total amount and rate of smoke production decreased while the percent mass loss was higher. It was reported that mass optical density appeared to be a more meaningful smoke index than specific optical density.

King[57] reported on some work in which selected materials were tested in an NBS smoke density chamber and correlations were made between optical density and mass density of smoke. Materials tested included red oak, rigid and plasticized polyvinyl chloride, acrylonitrile-butadiene-styrene resin, and polystyrene. Results indicated that the optical density and mass density relationship for smoke was a function of the composition of the material and specific burning conditions.

Jacobs[58] discussed the effects of dripping and sample thickness on smoke measurements made using an NBS smoke density chamber. The inclusion of an inert filler (silica, $Si0_2$) was found to inhibit the dripping of a sample and also produced an increase in the amount of measured smoke, which the author reported to be a better measure of the smoke producing capability of the material. The derivation of an empirical equation to predict smoke emission as a function of thickness also was discussed.

Maximum Specific Optical Densities (D_m) were determined for a variety of flame retarded and non-flame retarded polymers[59]. An NBS smoke density chamber was used and both flaming and nonflaming (smoldering) conditions were employed. The author recommended that materials be rated on their worst possible smoke density hazard (the higher maximum specific optical density for either flaming or smoldering conditions).

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[56] *W. P. Chien and J. D. Seader, "Smoke Development at Different Energy Flux Levels in an NBS Smoke Density Chamber," Fire Technology, 10, (3), 187-196 (August 1974).*

[57] *T. Y. King, "Empirical Relationships between Optical Density and Mass Density of Smoke," J. Fire & Flammability, 6, 222-227 (April 1975).*

[58] *M. I. Jacobs, "Factors Affecting the Measurement of Smoke Generation by Burning Polymers," J. Fire & Flammability, 6, 347-354 (July 1975).*

[59] *A. F. Grand, "Defining the Smoke Density Hazard of Plastics," J. Fire & Flammability, 7, 217-233 (April 1976).*

Parts and Thompson[60] reported on their work in which they employed an NBS smoke density chamber to evaluate the enhancement of the fire safety of two polymeric materials (molded polyvinyl chloride and neoprene foam). The means by which the fire performance of these materials was enhanced included (1) catalyzing char formation, (2) reducing the rate of volatile, combustible pyrolyzate formation with intumescent coatings or with ingredients that form insulating glass foams, and (3) catalyzing the oxidation of solid particulate smoke in the vapor phase during flaming combustion. It was reported that ferric and cupric acetylacetonate, used together with magnesium carbonate in plasticized polyvinyl chloride, reduced smoke optical density in laboratory tests by 42 to 68%, and without any deleterious effect on the ignitability of the base polymer.

An early effort to measure smoke properties described a modified NBS smoke density chamber (referred to as the Lawrence Livermore Laboratory (LLL) smoke chamber)[61]. This chamber was used to measure the smoke production and obscuration of certain woods and plastics using a heat flux of 2.5 watts/cm^2, both flaming and nonflaming exposures, a closed chamber with normal air content, and ventilation rates of 3, 6, 12 and 20 changes per hour.

A modified NBS smoke density chamber was used to determine the smoke opacity of wood, plastics, coatings, and combinationsof these[62]. Test conditions included pyrolysis and combustion, both with and without ventilation. A Materials Smoke Obscuration Index (MSOI) was proposed to rate materials. The MSOI was calculated from the product of the maximum smoke density and the average rate of smoke release divided by the critical time (the time required for the specific optical density to reach a value of 16). (MSOI = $D_m \times R/t_c$). Results of these tests indicated that wood and clean burning polymeric materials produced less dense smoke; with fire retardant additives or treatments these materials produced more dense smoke. Also, urethanes were reported to produce dense smoke in less than a minute (less than 15 seconds in a flaming exposure).

Gaskill[63] also has discussed the hazards of smoke and their measurement. The hazards mentioned included opacity, lachrymatory irritation,

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[60] *L. Parts and C.A. Thompson, "Flame- and Smoke-Retardant Polymer Systems," Quarterly Report, May-July 1976, Contract N00024-76-C-5336, Department of the Navy, Naval Sea Systems Command, Washington, DC 20362, September 1976 (AD-A030 094).*

[61] *J. R. Gaskill and C. R. Veith, "Smoke Opacity from Certain Woods and Plastics," Fire Technology, 4,(3), 185-195 (1968).*

[62] *J. R. Gaskill, "Smoke Development in Polymers During Pyrolysis or Combustion," J. Fire & Flammability, 1, 183-216 (July 1970).*

[63] *J. R. Gaskill, "Smoke Hazards and Their Measurement - A Researcher's Viewpoint, " J. Fire & Flammability, 4, 279-298 (October 1973).*

direct and indirect toxicity, heat, and synergistic effects. A description of the Lawrence Livermore Laboratory (LLL) smoke density chamber was presented. This chamber basically is the same as an NBS smoke density chamber but has an added feature of variable ventilation parameters.

In the work describe by Zinn, et al[64], samples of polyvinyl chloride and polypropylene were burned under non-flaming conditions at a radiant heating rate of 5 watts/cm^2. Among the parameters measured were smoke particle size distributions, total smoke particulate mass generated, smoke mean particle diameter, smoke optical density, and sample weight loss. Results indicated that the characteristics of smoke particulates and sample weight loss behavior were influenced by the presence, or absence, of different chemical additives for both polyvinyl chloride and polypropylene. In addition, a theoretical, one-dimensional model describing the smoldering decomposition of a polymeric material exposed to incident radiant heat flux was presented. Equations were developed to describe the solid phase decomposition, theoretical behavior of the solid-gas phase, and the transport of volatile, condensable thermal degradation products.

The density of smoke generated by burning polymers (polystyrene, polyester, and ABS) was measured by means of a smoke densitometer used in combination with an Oxygen Index Tester[3]. Smoke density (light obscuration) was measured by determining the light transmission through the particles. It was reported that the degree of light obscuration was dependent upon the size and number of smoke particles, the length of light path, the amount of chamber ventilation, the refractive index of the gases in the chamber, the ignition source, temperature, and the size and conditioning of the samples. During this work it was found that (a) flame retarded polymers generally produced denser smoke than untreated polymers, (b) as temperature increased the unretarded polymers produced much more smoke, and (c) as the flame retarded polymers developed a char formation the total amount of smoke generated was less than for untreated polymers.

Brauman, et al[65], described the development of a small-scale gravimetric collection technique that was employed to determine the effects of burning rate, oxygen concentration, thermal environment, sample geometry, and fire retardant additives on the quantities and

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[64] *B. T. Zinn, R. A. Cassanova, C. P. Bankston, R. F. Browner, E. A. Powell, J. U. Rhee, and K. Kailasanath, "Investigation of the Properties of the Combustion Products Generated by Building Fires," Report No. NBS-GCR-77-116, U.S. Department of Commerce, National Bureau of Standards, Washington, DC 20234, 1977 (PB-276 549).*

[65] *S. K. Brauman, N. Fishman, A. S. Brolly, and D. L. Chamberlain, "Smoke Generation from the Burning of Some Polymeric Materials," J. Fire & Flammability, 6, 41-57 (January 1976).*

composition of smoke produced from burning polymers (polypropylene, polystyrene, and a crosslinked polyester). The results of this program indicated that the amount of smoke produced from a burning polymer increased with the burning rate and also with an increase in oxygem concentration. It also was reported that the quantity of smoke produced from a particular polymer system will be highly dependent on the specific fire situation or test conditions.

An article by Bankston, et al[66], described the size distributions and concentrations of particles in smoke produced from the combustion of small samples of different materials under different environmental conditions. Materials investigated were wood, rigid urethane foam, and polyvinyl chloride. Tests were conducted under smoldering conditions at radiant heating levels of 3.2, 6.2 and 9.2 watts/cm^2. Results indicated that particle sizes increased with an increase in the radiant heating levels for smoldering conditions. In addition, the amount of smoke produced from these materials was greater at heating rates of 6.2 and 9.2 watts/cm^2 than at 3.2 watts/cm^2.

Four types of flammability testing apparatus were used to investigate the smoke, carbon monoxide, and carbon dioxide emitted from cellulosic materials treated with diammonium phosphate (DAP)[67]. The four systems or methods employed were (1) a 45° incline method, (2) an electric furnace method, (3) a large vertical furnace method, and (4) the limiting oxygen index (LOI) method. It was reported that as the concentration of retardant was increased the quantity of smoke and carbon monoxide increased or decreased as a function of the intensity of the heat source employed.

The development of a method to simultaneously measure sample weight loss and light transmission was described in an article by Chien, Seader, and Birky[68]. A smoke density chamber was modified to contain a force transducer and a weighing platform to continuously monitor sample weight. The authors suggested the appartus as being particularly suited to studying the response and smoking tendency of fire-retarded materials.

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[66] *C. P. Bankston, R. A. Cassanova, E. A. Powell, and B. T. Zinn, "Initial Data on the Physical Properties of Smoke Produced by Burning Materials under Different Conditions," J. Fire & Flammability, 7, 165-179 (Apr 1976).*

[67] *Y. Uehara and E. Yanai, "Smoke, CO, CO_2 from Cellulosic Materials Treated with DAP in a Fire Environment," J. Fire & Flammability, 4, 23-41 (January 1973).*

[68] *W. P. Chien, J. D. Seader, and M. M. Birky, "Monitoring Weight Loss in an NBS Smoke Density Chamber," Fire Technology, 9,(4), 285-298 (Nov.1973).*

The generation of smoke and toxic gases from enclosed fires, such as would likely be found on board ships, was studied by Cruz and Corlett[69]. These (smoke and gases) were measured as functions of the enclosure parameters, the degee of ventilation, and geometry. The results indicated that smoke production was significantly dependent upon enclosure parameters. A similar observation was noted for carbon monoxide generation.

A special cell and method was devised by Comeford and Birky[70] by which the smoke and HCL emitted during the pyrolysis of polyvinyl chloride could be simultaneously measured. Variables considered in this study included the addition of stabilizers, the rate of heating and the type of combustion (smoldering or flaming). The results of these tests indicated that the rates of evolution for smoke and HCL emitted from a variety of polyvinyl chloride formulations were functions of the rate of heating and the composition of the polymer.

An article by Schwarcz, Malone and Blinder[71] described the development of an equation which gave the variation in the quantity of smoke produced as a function of time. The equation was based on a kinetic model which required comparatively few assumptions and was reported to be applicable to experimental data obtained from any type of smoke measuring apparatus. Good agreement was reported between experimental results and calculated values when the equation was tested by burning polyvinyl chloride samples in an NBS smoke density chamber.

A general mathematical equation for smoke release rate was given by Smith in an article mentioned earlier[36]. The equation was

(Concentration)(Air Flow Rate) = (Release Rate).

Here, concentration = C_S, particles of smoke per volume; Air Flow Rate = V, volumetric flow rate of air; and Smoke Release Rate = C_S x V (particles per unit time).

A theory that related the specific optical density to particulate mass concentration, droplet size distribution, and droplet physical properties was developed[55]. These parameters have been measured by

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[69] *G. Cruz and R. C. Corlett, "Enclosed Fire Smoke and Toxic Gas Studies," Office of Naval Research Contract N00014-67-A-0103 T/O 29, Department of Mechanical Engineering, University of Washington, Seattle, Washington 98195, August 1974 (AD-785 090).*

[70] *J. J. Comeford and M. Birky, "A Method for the Measurement of Smoke and HCL Evolution from Poly(vinyl chloride)," Fire Technology, 8, (2), 85-90 (May 1972).*

[71] *J. M. Schwarcz, W. M. Malone, and S. Blinder, "Rate of Smoke Evolution from Burning Polymeric Materials," J. Fire & Flammability, 6, 554-567 (October 1975).*

Chien and Seader[72] and a comparison made between measured and predicted specific optical densities. In their work, alpha cellulose and Douglas fir were tested and the predicted specific optical densities were 181 for the cellulosic material and 594 for the Douglas fir. Measured specific optical densities were 185 and 640, respectively (a deviation of slightly over 2% and 7%).

An attempt to determine whether or not a useful correlation existed between smoke ratings obtained by small-scale tests and those obtained in full-scale tests was described by Christian and Waterman[73]. The results indicated that there were very limited correlation between the tests. It was suggested that perhaps the combination of results from two or more small-scale tests might correlate better with full-scale tests than either individual test.

Mickelson and Traicoff[74] designed a test chamber and method to investigate the smoke generating characteristics of a urethane polymer treated with a fire retardant. They were of the opinion that neither the NBS or the XP2 smoke density chamber provided data that correlated well with smoke produced in an actual fire.

A technique was described for estimating the temperatures at which smoke and fumes were emitted from materials used in aircraft[75]. In this work the problem was viewed by considering the conditions that could exist before a fire actually started. An ultraviolet-visible spectrophotometer was used to monitor the system for smoke by measuring changes in the transmission of light.

Robertson[76] conducted a study to determine if a correlation existed between two methods that assess the smoke-producing characteristics of materials in terms of specific optical density. The results of this study were generally inconclusive in that while there was some degree

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[72] *W. P. Chien and J. D. Seader, "Prediction of Specific Optical Density for Smoke Obscuration in an NBS Smoke Density Chamber," Fire Technology, 11, (3), 206-218 (August 1975).*

[73] *W. J. Christian and T. E. Waterman, "Ability of Small-Scale Tests to Predict Full-Scale Smoke Production," Fire Technology, 7, (4), 332-344 (November 1971).*

[74] *R. W. Mickelson and R. M. Traicoff, "Testing the Smoking Behavior of Fire-Retarded Materials," Fire Technology, 8, (4), 301-315 (November 1972).*

[75] *A. J. Christopher, E. J. P. Fear, and T. R. F. W. Fennell, "Emmision of Smoke and Fumes at Temperatures up to 500°C," Report No. Tech. Memo. MAT 183, Royal Aircraft Establishment, March 1974 (AD-923 783).*

[76] *A. F. Robertson, "Two Smoke Test Methods - A Comparison of Data," Fire Technology, 10, (4), 282-286 (November 1974).*

of agreement with respect to photometric measurements of smoke production, some materials produced significant differences in specific optical density. In another article Robertson discussed the problems involved in employing laboratory-scale smoke tests to predict the development of smoke in full-scale environments[77].

A comparison of the smoke emissions from different materials in both vertical and horizontal positions was made by Breden and Meisters[78]. They reported significant differences for thermoplastic materials because of a melting away from the incident heat flux in the vertical position.

Christopher[79] described the development of a system for assessing the smoke and fume emission characteristics of non-metallic materials. In this system a sample of material was heated from ambient temperature to 500°C (932°F), at heating rates between 1-20°C/min (34-68°F/min), in a stream of air. Results indicated that irritating fumes were frequently emitted at temperatures below those at which smoke was detected.

The engineering principles that are involved in the design of smoke detection systems using ionization type instruments were discussed in an article by Johnson[80]. Among the areas mentioned were (a) the theory of operation and the response of ionization detectors, (b) the placement of detectors, and (c) the protection of air ducts. The sensitivity of ionization chambers for use as smoke detectors was evaluated by determining the effect of resistance changes produced by aerosols[81].

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[77] *A. F. Robertson, "Estimating Smoke Production During Building Fires," Fire Technology, 11, (2), 80-94 (May 1975).*

[78] *L. Breden and M. Meisters, "The Effect of Sample Orientation in the Smoke Density Chamber," NBSIR-76-1030, Center for Fire Research, National Bureau of Standards, Washington, D.C. 20234, May 1976 (PB-263 633).*

[79] *A. J. Christopher, "Some Aspects of Smoke and Fume Evolution from Overheated Non-metallic Materials," in Aircraft Fire Safety, 45th Meeting of the AGARD Propulsion and Energetics Panel, held at the Plazzo Aeronautica, Rome, Italy, 7-11 April 1975, Report No. AGARD-CP-166, Document No. AD-A018 180, U.S. Dept. of Commerce, National Technical Information Service, 5285 Port Royal Road, Springfield, Virginia 22161, Oct. 1975.*

[80] *J. E. Johnson, "Engineering Early Warning Fire Detection," Fire Technology, 5, (1), 5-15 (February 1969).*

[81] *A. Scheidweiler, "The Ionization Chamber vs Smoke Dependent Resistance," Fire Technology, 12, (2), 113-123 (May 1976).*

E. Toxicity

There does not appear to be any widely accepted standard test methods for determining the toxicity of gases evolved from burning materials. A large part of the studies on toxicity to date have involved the use of commonly available analytical methods. These include infrared spectroscopy, mass spectrometry, gas chromatography, colorimetric methods, and combinations of these. Also, thermal analysis methods (TGA, DSC) can be employed to heat materials under controlled conditions and the evolved gases analyzed by means of the previously mentioned analytical systems.

The collection of gas samples can be a cause of significant errors in toxicity studies. Toxic gases will vary as a function of time and distance as well as containment[40]. Proper sampling techniques must therefore be employed in these investigations.

Toxicological studies of combustion gases usually involve a determination of the effects of these gases on laboratory animals. Tests to determine the effect of the inhalation of these gases as a function of concentration and exposure time are required. A detailed procedure for performing toxicological studies is the DIN 53 436 test method used in Germany and discussed in an article by Hilado[11].

An extensive and detailed discussion of the toxicity problems arising from the pyrolysis or combustion of polymeric materials was given by Autian[82]. A brief description of the mechanism of burning was presented along with a tabulation of a number of gases emitted from burning rubber insulation and polyvinyl chloride. A discussion also was given of the major constituents likely to be present in the gaseous decomposition products. These were (a) oxygen, or the lack of oxygen, (b) carbon monoxide, (c) carbon dioxide, (d) sulfur dioxide, (e) hydrogen sulfide, (f) aliphatic hydrocarbons, (g) aromatic hydrocarbons, (h) hydrogen cyanide, (i) hydrogen chloride and related compounds, (j) hydrogen fluoride and related compounds, (k) nitrogen compounds, and (l) epoxy compounds. Sections of this article presented a discussion of laboratory experiments to measure toxicity and emphasized the need to develop standard test procedures with which to measure toxicity. In addition, the author included an appendix in which he gave an introduction to toxicology in general. Among the areas discussed here were acute toxicity, lethality, primary irritants, sensitizing agents, behavior effects, subacute toxicity studies and chronic toxicity. Also discussed were factors that affect the toxicity of a chemical agent, such as the species, genetic effects, chemical structure, and physical state of the compound.

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[82] *J. Autian, "Toxicologic Aspects of Flammability and Combustion of Polymeric Materials," J. Fire & Flammability, 1, 239-268 (July 1970).*

Junod[83] has reported a literature review made on the hazards associated with plastics in fire situations. Among the areas discussed were (1) the behavior of plastic materials in fires, (2) the characteristics of the gases emitted from these materials under both pyrolysis and combustion conditions, (3) the effect of additives, (4) synergistic effects, (5) animal studies, and (6) the analytical methods employed to identify and measure the toxic species. Recommendations also were made for additional areas of research.

Few reports were found in this survey that dealt specifically with the toxicological problems caused by fires in rail passenger cars. One report that did, however, presented an assessment of the toxicological hazard resulting from a fire in the interior of a metrorail car of the Washington, D.C. subway system[84]. In this work, two full-scale tests on mock-ups were instrumented to measure the type and amount of combustion gases evolved and to determine their effect on test animals. Oxygen (O_2) depletion, carbon monoxide (CO), carbon dioxide (CO_2), hydrogen chloride (HCL), and hydrogen cyanide (HCN) were measured. Male Wistar rats were exposed to the gaseous combustion products and then examined for changes in their blood chemistry, gross pathology, and loss of function.

In these tests[84], CO and CO_2 were measured by non-dispersive infrared techniques. A polarographic oxygen cell was used for the measurement of oxygen. HCL was measured by collecting the combustion products in distilled water and using an ion-specific electrode to monitor the HCL level. Combustion products also were collected in a sodium hydroxide solution and the solution analyzed for cyanide to determine the HCN concentration. The overall toxicological hazard was assessed by correlating the gas measurements with the behavior of the animals and their blood chemistry. The blood chemistry analysis included carboxyhemoglobin (COHb) and cyanide determinations. It was concluded that a toxicological hazard definitely resulted from the combustion of polyurethane-type cushions.

An area in which a considerable amount of work has been done with respect to fire and toxicological hazards is that of aircraft cabin interiors. Numerous reports have been published of investigations made on the flammability characteristics of materials employed in furnishing cabin interiors (seat coverings, seat cushions, carpeting, side panels,

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[83] *T. L. Junod, "Gaseous Emissions and Toxic Hazards Associated with Plastics in Fire Situations - A Literature Review," Report No. NASA-TN-D-8338, National Aeronautics and Space Administration, Lewis Research Center, Cleveland, Ohio 44135, October 1976 (N77-10199).*

[84] *M. B. Birky, A. W. Coats, S. E. Alderson, J. E. Brown, M. Paabo, and B. Pitt, "Measurements and Observations of the Toxicological Hazard of Fire in a Metrorail Interior Mock-up," Report No. NBSIR-75-966, Center for Fire Research, Institute for Applied Technology, National Bureau of Standards, Washington, DC 20234, February 1976 (PB-250 768).*

overhead racks, etc). Many of these reports have been reviewed and the summaries of the toxicological aspects of some of these studies are presented here.

Colorimetric indicator tubes were employed to detect toxic combustion gases produced from 141 aircraft interior cabin materials in a fire environment[50]. Among the gases indicated as being present were carbon monoxide (CO), hydrogen chloride (HCL), hydrogen cyanide (HCN), hydrogen fluoride (HF), and sulfur dioxide (SO_2). A specific ion electrode was used to determine HCL concentrations greater than 500 ppm. Generally, HCL was produced from polyvinyl chloride and modacrylic materials, HF from polyvinyl fluoride, HCN from wool, urethanes, acrylonitile-butadiene-styrene, and modacrylics, SO_2 from polysulfone and rubber materials, and CO from all materials in varying amounts. The amount and rate of production of a given gas evolved during pyrolysis was indicated to be highly dependent upon temperature. It was reported that maximum levels of HCL were generally higher under flaming conditions than under smoldering conditions (higher temperature produces an increased rate of evolution). It was concluded that colorimetric tubes were adequate in providing an indication of the concentrations of toxic gases produced during the combustion of these materials. However, any attempt to relate measured concentrations to toxicological limits must take into consideration such parameters as the scaling of the areas and volumes involved, the integrated dosage where concentration varies with time, the synergistic effects of several components, and the effects of relative humidity, elevated temperatures, stratification, and adsorption on surfaces. Physiological factors also must be considered.

Five types of polyurethane seat cushion foams were exposed to a flaming ignition source in order to determine the combustion products as well as the effect of fire retardants[85]. It was reported that maximum concentrations of hydrogen cyanide (HCN) varied from 778 to 1603 ppm; carbon monoxide (CO from 420 to 664 ppm; carbon dioxide (CO_2) from 0.22 to 0.36 percent. Minimum oxygen concentrations varied from 15.2 to 16.4 percent. Treated samples reportedly produced a relatively slower build-up of toxic products during the first two minutes of the tests (5 minute total duration).

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[85] *R. W. Bricker, R. N. Stuckey, and J. F. Kuminecz, "Aircraft Seat Cushion Materials Tests," Report No. NASA-TM-X-74632, National Aeronautics and Space Administration, Lyndon B. Johnson Space Center, Houston, Texas, October 1975 (N77-21203).*

Einhorn, et al[86], reported on several analytical techniques used to investigate the thermochemistry of an aromatic polyamide fabric used in the interiors of commercial jet aircraft. It was intended to identify the products produced during pyrolysis, oxidative degradation, and flaming combustion. Elemental analysis and infrared spectra were used to characterize the polymer. Decomposition products, volatiles and residues, were identified by infrared analysis and a computerized gas chromatograph/mass spectrometer system. It was reported that (a) a thermally-resistant char was formed only in an inert environment, (b) the oxidation of the sample was complete by 1000°C (1832°F) in both air and oxygen, and (c) the rate of consumption was greater in oxygen than in air. Also, substantial differences were noted in the amounts of water, carbon monoxide, and carbon dioxide formed in the pyrolysis and oxidative degradation modes.

Spurgeon[87] has reported on a program in which tests were conducted on aircraft interior materials in order to provide data that would enable an appropriate laboratory method to be selected for generating and measuring toxic combustion gases. Two methods investigated for this purpose employed an NBS smoke density chamber and a microcombustion tube. Some qualitative advantages of the NBS smoke chamber were given as (1) the simultaneous acquisition of data on smoke density and toxic gases, (2) the rates of generation of gases can be determined, (3) the chamber can be used for animal exposure tests, and (4) test conditions more closely resemble those encountered in an actual fire situation. In this work, several sampling methods were evaluated to determine optimum sample recovery, including colorimetric detector tubes, bag sampling, impinger sampling, and syringe sampling, generally considered to be the best. The materials evaluated in these methods were limited to polyvinyl chloride, urethanes, wool, and Nomex fiber; and gas analysis was limited to carbon monoxide, hydrogen cyanide, and hydrogen chloride. The results indicated that neither method (NBS smoke chamber or microcombustion tube) was totally adequate in achieving the objective. However, the microcombustion tube was considered more suitable for ranking aircraft interior materials according to their relative toxicities than

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[86] *I. N. Einhorn, D. A. Chatfield, and R. W. Mickelson, "Analysis of the Products of Thermal Decomposition of an Aromatic Polyamide Fabric Used as an Aircraft Interior Material," in Aircraft Fire Safety, 45th Meeting of the AGARD Propulsion and Energetic Panel, held at the Palazzo Aeronautica, Rome, Italy, 7-11 April 1975, Report No. AGARD-CP-166, Document No. AD-A 018 180, U.S. Department of Commerce, National Technical Information Service, 5285 Port Royal Road, Springfield, Virginia 22161, October 1975.*

[87] *J. C. Spurgeon, "A Preliminary Comparison of Laboratory Methods for Assigning a Relative Toxicity Ranking to Aircraft Interior Materials," Report No. FAA-RD-75-37, Federal Aviation Administration, National Aviation Facilities Experimental Center, Atlantic City, New Jersey 08405, October 1975 (AD-A018 148).*

the NBS smoke chamber. The relative toxicity of the materials as determined in this work was polyvinyl chloride > wool > Nomex fabric > urethane foam. In addition, some limited animal toxicity tests were conducted and the correlation of animal toxicity data with toxic gas concentrations was investigated. The time-to-incapacitation values were reported to be useful in ranking materials according to toxicity.

Sarkos[53] employed an NBS smoke density chamber and colorimetric detector tubes to measure toxic gas emissions from aircraft cabin materials. Colorimetric detector tubes are small glass tubes packed with a chemical that reacts and changes color when a gas mixture containing a specific component passes through it. The length of the color change is related to the concentration of the specific component and the flow rate and volume of the gas mixture. A calibration scale provided by the manufacturer is used to relate the length of color change to concentration. While colorimetric detector tubes are simple to use, provide rapid analyses, and are comparatively inexpensive, they also are relatively imprecise and can be influenced by the presence of other gases.

The number of toxic gases, as well as the nature and quantities, that are produced by a burning polymer were reported to be highly dependent upon the conditions under which combustion occurred and the physical and chemical properties of the material. Gases measured in this work[53] were selected on the basis of being the most likely to be present and the most often mentioned in the literature. These included carbon monoxide (CO), hydrogen chloride (HCl), hydrogen cyanide (HCN), hydrogen fluoride (HF), nitrogen oxides (NO_x), ammonia (NH_3), sulfur dioxide (SO_2), hydrogen sulfide (H_2S), toluene diisocyanate (TDI) (for urethane foams), and aldehydes. The data indicated that the reproducibility of gas measurements taken from the geometric center of the NBS smoke chamber was dependent upon the test material, the gas measured, and the methodology for gas sampling and analysis. The measurement of HCl exhibited poor reproducibility by virtue of its highly reactive nature. The concentration of CO was reportedly very reproducible.

Another investigation was performed in which the relative amount of toxic gases produced during the pyrolysis of 75 typical aircraft cabin materials was determined[88]. The thermal decomposition of 250 mg samples was accomplished in a combustion tube at a temperature of 600°C (1112°F) and an airflow of 2 liters/min. Samples were conditioned for a minimum of 24 hours at 50% relative humidity and 21°C (70°F) prior to testing. Combustion products were collected in liquid-filled fritted bubblers. Hydrogen cyanide, hydrogen sulfide, hydrogen chloride, hydrogen bromide,

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[88] *J. C. Spurgeon, L. C. Speitel, and R. E. Feher, "Thermal Decomposition Products of Aircraft Interior Materials," Report No. FAA-RD-77-20, Federal Aviation Administration, National Aviation Facilities Experimental Center, Atlantic City, New Jersey 08405, April 1977 (AD-A039 511).*

and formaldehyde were determined by differential pulse polarography; nitrogen dioxide and sulfur dioxide were measured by visible spectrophotometry; hydrogen fluoride was measured by potentiometric titration; and carbon monoxide by nondispersive infrared analysis. The most reproducible measurements were reported to be for carbon monoxide. The quantities of nitrogen dioxide, sulfur dioxide, and formaldehyde were influenced to a greater degree by the combustion process and its random nature. Tests also were conducted to determine the effects of experimental parameters on gas yields. These included sample weight (250 mg and 750 mg), percent of oxygen (0, 10.5, and 21%), the rate of airflow (1 to 3 ℓ/min), and temperature (400, 600 and 800°C). The main shortcomings of laboratory test methods were said to be a lack of adequate reproducibility for gas analysis and they do not simulate the conditions encountered in a real fire.

In addition to the work conducted on aircraft cabin materials, other areas of interest reported were concerned with the toxicological aspects of materials used in manned space vehicles or underwater vessels. A compilation of papers given at a conference dealing with the fire safety of materials used in spacecraft was reviewed[89]. Although there was no specific category or session devoted to toxicity, Harris[90] presented a paper in which he discussed a program to evaluate toxicological hazards of spacecraft materials. The program consisted of (1) routine testing to determine offgassing characteristics of spacecraft materials, (2) the analysis of space vehicle atmospheres during both manned and unmanned tests, (3) the verification of results to determine that materials added to spacecraft interiors did not contribute to the contamination of the cabin atmosphere, and (4) the provision of methods for determining acceptability in the materials selection phase of the overall program. The major portion of this paper dealt with toxicity testing using animals and the design of specialized tests.

Demas and Hatfield[91] reported on their work to determine the amount and nature of the volatile products produced during the outgassing or thermal degradation of wire insulation materials employed in nuclear

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[89] *P. H. Bolger (Chairman), Conference on Materials for Improved Fire Safety, held at the Manned Spacecraft Center, Houston, Texas, May 6-7, 1970, Report No. NASA-SP-5096, Technology Utilization Office, National Aeronautics and Space Administration, Washington, DC, 1971 (N72-16409).*

[90] *E. S. Harris, "Toxicology of Spacecraft Materials," pp. 207-210 in Conference on Materials for Improved Fire Safety, NASA-SP 5096, Technology Utilization Office, National Aeronautics and Space Administration, Washington, D.C., 1971 (N72-16409).*

[91] *P. Demas and N. Hatfield, "Emission of Volatiles from Electrical Insulation Materials Used in Nuclear Submarines," Report 8-903, Materials Department, Naval Ship Research and Development Center, Bethesda, Maryland 20034, February 1972 (AD-891 923L).*

submarines. The areas of work discussed were the development of an experimental apparatus, trapping procedures, and analytical techniques to determine these volatiles. Materials were studied at temperatures ranging from ambient to pyrolytic. Organic constituents in the volatile effluents were determined by hydrogen flame gas chromatography. Mass spectrometry techniques were employed to determine nitrogen oxides, ammonia, sulfur dioxide, hydrogen sulfide, hydrogen chloride, and carbon dioxide. Carbon monoxide was measured either by catalytic conversion to methane and gas chromatography or by infrared absorptive methods. Wet chemical methods were used to measure hydrogen cyanide. In addition, thermogravimetric analysis (TGA) was performed on each material.

In a similar vein, Williams and Carhart[92] discussed a program to evaluate materials with respect to their potential to pollute the atmosphere of submersibles. The effluents given off by the materials were determined over a temperature range of 70 to 400°C (158 to 752°F).

The gases formed during the thermal decomposition of cellophane were determined by Robles[93] at temperatures near 246°C (475°F). Among the compounds identified in the vapors were carbon dioxide, nitrogen dioxide, nitrous oxide, carbonyl sulfide, sulfur dioxide, methanol, formaldehyde, and acrolein. No gaseous decomposition products were determined from samples of styrofoam heated under similar conditions.

A detailed analysis of the combustion products of plastics was done by Boettner, Ball and Weiss[94] to identify any products of incomplete combustion which would be acutely toxic in an accidental fire. Samples weighing 1-3 grams were heated at a rate of 5 to 50°C/min (41 to 122°F/min) in a measured flow of air or air + oxygen. The materials generated large quantities of gaseous and condensed products without being completely combusted to carbon dioxide and water. Major combustion products (0.1 to 15%) were identified by infrared spectroscopy. Minor combustion products were identified by mass spectrometry as well as gas chromatography.

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[92] *F. W. Williams and H. W. Carhart, "Evaluation of Materials for Manned Vessels to Assure Habitable Atmospheres," NRL Memorandum Report 3091, Naval Research Laboratory, Washington, D.C. 20375, August 1975 (AD-A014 410).*

[93] *E. G. Robles, Jr., "Thermal Decomposition Products of Cellophane," Report No. 68M-16, Project No. C68-7, U.S. Air Force Experimental Health Laboratory, McClellan Air Force Base, CA 95652, April 1968 (AD-752 515).*

[94] *E. A. Boettner, G. L. Ball, and B. Weiss, "Combustion Products from the Incineration of Plastics," Report No. EPA-670/2-73-049, U.S. Environmental Protection Agency, National Environmental Research Center, Office of Research and Development, Cincinnati, Ohio 45268, 1973 (PB-222 001).*

Results indicated that the hazard from the combustion products of plastics depended upon the primary structure of the polymer, the additives employed in formulating the plastic, and the conditions under which the combustion took place. Three categories of polymers were considered. These were (1) those consisting of carbon, hydrogen, and oxygen, (2) those containing nitrogen, and (3) those containing halogen or sulfur heteroatoms.

Those materials composed of carbon, hydrogen, and oxygen produce carbon dioxide and water when carried to complete combustion. The incomplete combustion of these type materials produces carbon monoxide as the major toxic compound. Also emitted are gaseous and condensed hydrocarbon products.

The complete combustion of polymers containing nitrogen produce molecular nitrogen, small quantities of nitrogen oxides, carbon dioxide, and water. Incomplete combustion results in hydrogen cyanide, cyanogen, nitriles, ammonia, and hydrocarbon gases. It was noted that nitrogen-containing combustion compounds were more sensitive to changes in combustion conditions. Generally, more ammonia and cyanide will form the more incomplete the combustion.

In addition to carbon dioxide and water, plastics containing halogen or sulfur will produce gases such as hydrogen chloride, hydrogen fluoride, and sulfur dioxide upon complete combustion. Incomplete combustion produces organic halogen or sulfur compounds that contribute to toxicity problems.

Hagen[95] determined the combustion gases from three plastic materials over a pyrolysis temperature range of 530-580°C (986-1076°F). The materials examined were (a) a polycarbonate foil, (b) a hard polyurethane foam, and (c) a soft polyurethane foam prepared from an isomeric mixture of 2,4- and 2,6-toluene diisocyanate and a linear polyester of adipic acid and diethylene glycol. Among the combustion products identified were carbon monoxide (CO), carbon dioxide (CO_2), hydrocarbons, formaldehyde, acetaldehyde, acetone, o-cresol, p-alkylphenol, and phenol from the polycarbonate foil; CO, CO_2, hydrogen cyanide (HCN), aromatic amines, formaldehyde, acetaldehyde, acetone, propionaldehyde, and m-cresol from the hard polyurethane foam; CO, CO_2, HCN, aromatic amines, formaldehyde, acetaldehyde, acetone, propionaldehyde, and isocyanate from the soft polyurethane foam. It was reported that the main danger of poisoning from the combustion gases of polyurethanes was due to the presence of very toxic isocyanates.

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[95] *E. Hagen, "The Composition of Combustion Gases of Polyurethane Foams and Polycarbonate," Report No. FTD-HT-23-1474-68, Foreign Technology Division, Wright-Patterson Air Force Base, Ohio 45433, August 1969 (AD-863 434).*

An investigation of the toxic gases evolved during the thermal degradation of a flexible urethane foam, polyethylene, pigmented polystyrene, and some fluorocarbon film was reported by Schmitt[96]. The instrumentation employed was a Setchkin ignition test apparatus along with a quadrupole mass spectrometer. In addition, colorimetric detection tubes and a thermogravimetric analyzer were employed. Hydrogen cyanide was reported to be present in the gaseous combustion products evolved from the urethane foam while hydrogen fluoride and hydrogen chloride were reported to be present in the degradation products from the fluorohalocarbon film.

Four types of polyurethane foams were evaluated under burning and pyrolysis conditions to determine their flammability and toxic-gas production characteristics[97]. An assessment was made of the ability of these foams to self-extinguish flame and smoldering after removal of an electrical ignition source, a flaming ignition source, or a flameless heat source. During these tests it was noted that (1) a non-flammable foam became flammable with increased carbon content, (2) foams exposed to similar temperatures produced widely differing amounts of toxic products after the ignition source was removed, the rate of toxic gas production being dependent upon the extent of smoldering, and (3) hydrogen chloride loosely bound on water or soot particles may be a more severe toxicological hazard than gas-phase hydrogen chloride if either form gains access to the respiratory tract.

The toxicity of the pyrolysis products from ten polymeric materials was determined by the use of two different experimental methods[98]. The methods were those employed at the Materials Science Toxicology Laboratories of the University of Tennessee (MSTL/UT) and at the NASA Johnson Space Center (NASA/JSC). Details of these procedures, along with their differences, were discussed. It was noted that relative quantities of such products of combustion as carbon monoxide, carbon dioxide, hydrogen cyanide, hydrogen chloride, hydrogen fluoride, and sulfur dioxide were functions of the materials themselves and the conditions under which the pyrolysis or combustion occurred. These conditions were heating rate, maximum temperature, and the abundance or lack of oxygen during the thermal decomposition. The results indicated that

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[96] *C. R. Schmitt, "Thermal Degradation Characteristics of Various Polymeric Materials," J. Fire & Flammability, 3, 303-315 (October 1972).*

[97] *P. A. Tatum and F. W. Williams, "Flammability and Toxic-Gas Production from Urethane Foams Used in Anechoic Chambers," NRL Report 7793, Naval Research Laboratory, Washington, D.C. 20375, September 1974 (AD-923 436L).*

[98] *W. H. Lawrence, R. R. Raje, A. R. Singh, and J. Autian, "Toxicity of Pyrolysis Products: Influence of Experimental Conditions, The MSTL/UT and NASA/JSC Procedures," J. Combustion Toxicology, 5, 39-53 (Feb. 1978).*

there was little correlation between the two methods employed in this work (when compared according to actual sample weights required to attain the specific end point). A better correlation was achieved when relative rankings were made according to LC_{50} values (lethal concentration values). A series of standard materials was proposed to allow comparisons between test methods and test laboratories.

The relative toxicity was determined for the pyrolysis gases emitted from samples of polyester urethane flexible foams[99]. Toxicity tests were performed by exposing Swiss albino mice to the gases evolved from the pyrolysis of 1.0 g of foam at a heating rate of 40°C/min (104°F/min) from 200 to 800°C (392-1472°F) without forced air flow. Results indicated that polyester urethane foams were comparable to polyether urethane foams with respect to toxicity.

In some work done to evaluate the effect of fire retardants on the toxicity of pyrolysis gases, it was reported that once a material such as polyurethane flexible foam attained a certain level of ignition resistance by the incorporation of a fire retardant, the addition of more fire retardant did not significantly alter the toxicity of the pyrolysis gases[100].

Hilado[101] reported on a program whose primary objective was to determine the sensitivity of relative toxicity to heating rate. Differences in heating rates from 40 to 60°C/min (104 to 140°F/min) were reported to have no substantial influence on the relative toxicity ranking of the foams and fabrics tested. Fabrics were ranked in the decreasing order of toxicity and were given as wool, cotton, Nomex, and polybenzimidazole (PBI). Rankings were made with respect to time to death (t_D) and time to incapacitation (t_I). Sixty-six references also were given.

The parameters that need to be considered in the development of a laboratory screening test to characterize materials with respect to the inhalation toxicity of their pyrolysis products were discussed by Terrill, Montgomery, and Reinhardt[102]. Included in these parameters were

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[99] *C. J. Hilado and E. M. Olcomendy, "Relative Toxicity and Flash-Fire Propensity of the Pyrolysis Gases from Polyester Urethane Flexible Foams," J. Consumer Product Flammability, 5, 163-167 (September 1978).*

[100] *C. J. Hilado, J. E. Schneider, and R. M. Murphy, "Effect of Fire Retardant on Relative Toxicity of Pyrolysis Gases from Polyurethane Foams," J. Fire Retardant Chemistry, 5, 83-85 (May 1978).*

[101] *C. J. Hilado, "Relative Toxicity of Pyrolysis Products from Some Foams and Fabrics," J. Combustion Toxicology, 3, 32-60 (February 1976).*

[102] *J. B. Terrill, R. R. Montgomery, and C. F. Reinhardt, "Devising a Screening Test for Toxic Fire Gases," Fire Technology, 13, (2), 95-104 (May 1977).*

(1) animal selection, (2) animal exposure, (3) animal observations, (4) selection and sensitivity of analytical methods, (5) configuration of test sample, (6) mode of sample decomposition, (7) system configurations, and (8) likely end use conditions. Since toxicity test results are known to depend on the test procedure employed, the authors suggested that a series of test and test conditions would be more beneficial than a single test in evaluating a material with respect to its toxicity.

Along these same lines, another source[103] concluded that currently employed screening tests were not acceptable for evaluating the toxicities of pyrolysis/combustion products. Guidelines were discussed for developing the needed tests as well as recommendations for additional research.

Hilado and Cumming[104] discussed the variations in the results from different test methods employed in determining the toxicity of pyrolysis gases. Materials evaluated in this work were polycarbonate, polyethylene, polystyrene, and acrylonitrile-butadiene-styrene (ABS) polymer. The test methods compared included the University of San Francisco (USF) Method B (a heating rate of 40°C/min from 200 to 800°C without forced air flow) and the Civil Aeromedical Institute of the Federal Aviation Administration (CAMI) Method (pyrolysis of a 0.75 g sample at 600°C with the air recirculated). Additional methods used in the comparison were USF Methods F, G, and H (a fixed temperature of 800°C with no forced air flow, air flow of 16 ml/sec, and air flow of 48 ml/sec, respectively) and USF Methods E, I, and J (a fixed temperature of 600°C with no forced air flow, air flow of 16 ml/sec, and air flow of 48 ml/sec, respectively). The results indicated that relative toxicity rankings were dependent upon the test conditions, and the criterion of toxicity employed (incapacitation or death). Differences were noted between increasing-temperature and fixed-temperature programs, between 600°C and 800°C limit temperatures, and between no forced air flow and forced air flow conditions.

In some similar work[105] the relative toxicity rankings of polycarbonate, polyethylene, polystyrene, and ABS resin were determined by use of the USF/NASA and FAA/CAMI methods. The results indicated that

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[103] *Advisory Center on Toxicology, "Fire Toxicology: Methods for Evaluation of Toxicity of Pyrolysis and Combustion Products," National Academy of Sciences, National Research Council, Washington, D.C., August 1977 (AD-A043 899).*

[104] *C. J. Hilado and H. J. Cumming, "The Effect of Test Conditions on the Relative Toxicity of the Pyrolysis Products from Some Plastics," Fire Technology, 13, (4), 325-328 (November 1977).*

[105] *C. J. Hilado, H. J. Cumming, A. M. Machado, J. E. Schneider, C. R. Crone, D. C. Sanders, B. R. Endecott, and J. K. Abbott, "Comparison of Animal Responses to the Combustion Products Generated by Two Test Procedures, the USF/NASA Methodology and the FAA/CAMI System," J. Combustion Toxicology, 4, 325-359 (August 1977).*

the rankings were dependent upon test conditions and upon the criterion selected for animal response (time to incapacitation or time to death). Other differences were observed between the increasing-temperature or fixed-temperature programs, between the maximum temperature limits of 600°C and 800°C, and between the ventilation parameters used (no forced air flow, single pass air flow, or continuous recirculation). None of the test conditions of the USF/NASA method (seven sets of conditions) produced the same relative toxicity rankings as the FAA/CAMI method, which were, in decreasing order of toxicity, polyethylene, polycarbonate, ABS, polystyrene.

The relative toxicity of seventy samples of cushioning and upholstery materials was determined by means of the USF/NASA toxicity screening tests[106]. The test was reported to be able to differentiate between these materials on the basis of time to incapacitation (t_i) and time to death (t_d). Briefly, in this method a 1.0 g sample of material was pyrolyzed at a heating rate of 40°C/min to an upper limit of 800°C. During this time four Swiss albino male mice were exposed for 30 minutes in a 4.2-liter chamber. Materials were ranked on the basis of t_i or t_d. In this test method a rising temperature was to simulate a developing fire while a fixed temperature of 800°C was to simulate a fully developed fire.

Thirty-nine samples of polyurethane foams, both flexible and rigid, were evaluated for their relative toxicities by means of the appropriate USF screening test. Results showed that a very wide range in performance existed among these foams[107].

Some additional work in which the USF/NASA screening tests were employed included the determination of the relative toxicity of 14 building materials[108]. In this work, various samples of cellulosic board products and roofing felts were examined and no potential differences were reported for the relative toxicity ratings of these materials. Also, several samples of upholstery fabrics were evaluated by means of this test[109].

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[106] *C. J. Hilado and A. Furst, "Relative Toxicity of Pyrolysis Products of Some Materials Used in Home Furnishings," J. Combustion Toxicology, 3, 425-464 (November 1976).*

[107] *C. J. Hilado, H. J. Cumming, and A. N. Solis, "Relative Toxicity and Flash Fire Propensity of the Pyrolysis Gases from Polyurethane Foams," J. Cell. Plast., 408-415 (Nov./Dec. 1977).*

[108] *C. J. Hilado, H. J. Cumming, and L. A. Gall, "Relative Toxicity of Pyrolysis Products of Some Building Materials," J. Combustion Toxicology, 4, 304-313 (August 1977).*

[109] *C. J. Hilado, M. T. Lopez, and G. H. Damant, "Relative Toxicity of Pyrolysis Products from Some Upholstery Fabrics," J. Coated Fabrics, 6, 155-175 (January 1977).*

Some modifications to the USF/NASA toxicity screening test were made to determine if these would influence the relative toxicity rankings as determined by this method[110]. These changes included (1) an increase in the upper pyrolysis temperature limit (2) a reduction in the distance between the sample and test animals, and (3) an increase in the animal chamber volume. The results indicated that while some differences were noted, they did not reverse or change the order of rankings.

The relative toxicity of the pyrolysis products of polycarbonate (bisphenol A) and wool were determined by means of the USF/NASA screening method[111]. The results indicated the possibility of a different mechanism of intoxication for wool as compared to bisphenol A polycarbonate. In some other work[112], bisphenol A polycarbonate was selected as a reference material for use in the USF relative screening test method because of its availability and stability over long periods of time.

Hilado and Cumming[113] have reported the relative toxicity for about 270 materials measured under 10 sets of test conditions (USF screening test). These conditions included (a) increasing temperature over the range 200-600°C at a rate of 40°C/min with no forced air flow; (b) over a temperature range of 200-800°C at a rate of 40°C/min with no forced air flow and an air flow of 16 and 48 ml/sec; (c) at a fixed temperature of 600°C with no forced air flow and an air flow of 16 and 48 ml/sec; (d) at a fixed temperature of 800°C with no forced air flow and an air flow of 16 and 48 ml/sec. The results indicated a wide range of performance and it was suggested that materials be compared under conditions resembling those of intended usage.

A determination of the relative toxicity of several upholstery fabrics examined the effects of fabric parameters such as type, weight, and weight of backcoating, as well as the effects of variations in the test conditions[114]. The relative toxicity, in decreasing order and based on

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[110] *C. J. Hilado, L. A. LaBossiere, H. A. Leon, D. A. Kourtides, J. A. Parker, and M. S. Hsu, "The Sensitivity of Relative Toxicity Rankings by the USF/NASA Test Method to Some Test Variables," J. Combustion Toxicology, 3, 211-236 (August 1976).*

[111] *C. J. Hilado, H. J. Cumming, and S. C. Packham, "The Use of a Behavioral Response System in the USF/NASA Toxicity Screening Test Method," J. Combustion Toxicology, 4, 283-292 (August 1977).*

[112] *C. J. Hilado, H. J. Cumming, and J. B. Williams, "Bisphenol A Polycarbonate as a Reference Material," J. Combustion Toxicology, 4, 367-375 (August 1977).*

[113] *C. J. Hilado and H. J. Cumming, "A Compilation of Relative Toxicity Data," J. Consumer Product Flammability, 4, 244-266 (September 1977).*

[114] *C. J. Hilado and H. J. Cumming, "Relative Toxicity of Pyrolysis Products from Upholstery Fabrics: Effects of Fabric Variables and Test Conditions," J. Combustion Toxicology, 4, 393-414 (August 1977).*

time to death, was reported to be wool, silk, polyester, leather, cotton, rayon, nylon, and polyolefin. For those fabrics containing wool, the toxicity appeared to decrease with a decrease in the amount of wool present. While no significant effects were attributed to fabric weight, fabric weave, and backcoating, the relative toxicity rankings were influenced by temperature, heating rate, and air flow.

A paper by Herpol[115] discussed the toxicological aspects of a program in which seven materials were exposed to three different combustion conditions. The materials included plasticized polyvinyl chloride, polyethylene sheet, rigid polyisocyanurate foam, and four types of wood. The temperatures at which experiments were conducted were 400, 600, and 800°C (752, 1112, and 1472°F). As a result of this work the following observations were noted. (a) There are many materials involved in a real fire situation in which the combustion conditions are constantly changing. Prediction of the behavior of a material from a laboratory test therefore is very difficult, if not near impossible. A laboratory test is valid for one material under a specific set of conditions. (b) Symptoms associated with a lack of oxygen appear when the oxygen concentration of inhaled air decreases to 12-15%. (c) The toxicities of inhaled hydrogen cyanide (HCN) and carbon monoxide (CO) are purely additive (when studied using rats). (d) For most materials the greatest quantity of CO generated takes place at approximately 600°C (1112°F).

Twelve materials were exposed to flaming combustion conditions in an NBS smoke chamber and to oxidative pyrolysis conditions at 600°C (1112°F) in a combustion tube furnace[116]. Hydrogen cyanide (HCN), hydrogen sulfide (H_2S), hydrogen chloride (HCl), hydrogen bromide (HBr), and formaldehyde were determined by differential pulse polarography, nitrogen dioxide (NO_2) and sulfur dioxide (SO_2) by visible spectrophotometry, and hydrogen fluoride (HF) by an ion-selective electrode. A nondispersive infrared analyzer was employed to determine carbon monoxide (CO) directly. The yields of gases were compared on a mg/g basis for each method (NBS chamber vs combustion tube). CO, formaldehyde, NO_2, and SO_2 were reported to be dependent on exposure conditions, while HCl, HCN, and H_2S were not.

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[115] *C. Herpol, "Biological Evaluation of the Toxicity of Products of Pyrolysis and Combustion of Materials," Fire & Materials, 1, 29-35(1976).*

[116] *L. C. Speitel, R. E. Feher, and J. C. Spurgeon, "A Preliminary Comparison of Thermal Decomposition Products of Aircraft Interior Materials Using the National Bureau of Standards Smoke Chamber and the Combustion Tube Furnace," Report No. FAA-NA-77-22, Federal Aviation Administration, National Aviation Facilities Experimental Center, Atlantic City, New Jersey 08405, March 1978 (AD-A054 811).*

An investigation was conducted in which a quantitative analysis was made of the amounts of hydrogen cyanide (HCN), carbon monoxide (CO), and carbon dioxide (CO_2) emitted during the combustion of nitrogen - containing organic materials[117]. An assessment also was made of the relative importance of these products in forming a dangerous atmosphere. The materials evaluated included an acrylic fiber, nylon, wool, an urea-formaldehyde foam, and a rigid urethane foam. Toxicity index values of combustion products were calculated from the experimental results and dangerous concentration levels given in the literature. These levels were given, for a 30-minute exposure, as 135 ppm for HCN, 4000 ppm for CO, and 70,000-100,000 ppm for CO_2. The results led the authors to report that the toxicity due to HCN could be 55 times as great as that due to CO for acrylic fiber, 5 times as great for nylon, 8 times as great for wool, 26 times as great for urea-formaldehyde, and twice as great for rigid urethane foam.

The toxicity of polyfluoroalkoxyphosphazene and polyaryloxy-phosphazene was studied by Sebata, Magill and Alarie[118] at the University of Pittsburgh. They used two terms to evaluate toxicity hazard. The first, nominal exposure concentration (N.C.), was expressed as total weight loss in milligrams divided by total air flow in liters (mg/ℓ), and was used to compare materials on an identical weight loss basis. The other, concentration factor (C.F.), was expressed as the weight of the sample loaded (in mg) divided by the air flow through the chamber for one minute (in liters), and was used to compare the materials on an identical weight loading basis. The results indicated that the thermal decomposition products from polyfluoroalkoxyphosphazene were more toxic than those from polyaryloxyphosphazene on a same sample weight basis. A much higher carbon monoxide concentration was produced from the fluoro-polymer.

Lipska[119] presented a summary on the pyrolysis and oxidation of cellulosic and synthetic materials which discussed the thermal degradation of polymers, the analysis of decomposition products, theories on

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[117] *K. Sumi and Y. Tsuchiya, "Combustion Products of Polymeric Materials Containing Nitrogen in Their Chemical Structure," pp 152-159 of Flammability of Cellular Plastics, Volume 8, Fire and Flammability Series, Technomic Publishing Co., Inc., 265 W. State Street, Westport, Connecticut 06880, 1974.*

[118] *K. Sebata, J. H. Magill, and Y. Alarie, "Thermal Stability and Toxicity of Polymers: Polyphosphazenes," Report No. SETEC-MME-77-109, Metallurgical and Materials Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania 15261, November 1977 (AD-A046 778).*

[119] *A. E. Lipska, "The Pyrolysis of Cellulosic and Synthetic Materials in a Fire Environment," Report No. USNRDL-TR-1113, U.S. Naval Radiological Defense Laboratory, San Francisco, California 94135, December 1966 (AD-645 858).*

the mechanism of pyrolysis, fire retardants, and the hazards produced from the thermal degradation of these type materials. While primarily devoted to various aspects of the thermal decomposition of wood, toxic combustion products from some common materials were given. These were hydrogen sulfide from leather, hydrogen cyanide from silk and wool, hydrogen chloride and nitrogen oxides from plastics, and acrolein from wood and some paints. In addition the ways in which toxic combustion gases can cause injuries were given. These were (1) by interferring with normal vision and causing a burning sensation in the respiratory tract, (2) by producing deleterious effects which could result in fatalities, and (3) by stimulating respiration which produces an increase in the inhalation of toxic combustion products.

A limited review of the literature was presented by Melvin[120] that included the early history and data on deaths, injuries, and costs due to the pyrolysis and combustion of resins, plastics, and natural materials. Some experimental data was given on the flame propagation rates and pyrolysis products of five synthetic and natural fiber carpet materials. Also included was a discussion of the factors that affect the flammability of textiles. Among these were: (a) the porosity of the fabric (a porous fabric facilitates the ignition of a fabric and allows oxygen to reach the combustion site); (b) the area/volume ratio of a fabric (as this ratio increases the ease of ignition increases); (c) the position or location of a fabric (vertical orientation is more hazardous than a horizontal orientation). In addition, it was pointed out that a knowledge of the composition of a plastic makes it possible to predict approximations of the decomposition products. As an example, materials that contain chlorine produce hydrogen chloride, the amount being approximately proportional to the chloride content, while nitrogen-containing materials produce hydrogen cyanide and ammonia. Common materials also produce toxic decomposition products (wood gives off formaldehyde and acetic acid when burned; wool, silk, and leather produce hydrogen cyanide).

More studies on toxicity have been carried out by Hilado and his co-workers, including investigations on home fabric materials[121],

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[120] *W. W. Melvin, Jr., "Chemical and Physical Properties and Thermal Decomposition Products of Certain Natural Products and Synthetic Materials," Report No. EHL(K)-72-14, USAF Environmental Health Laboratory, Kelly Air Force Base, Texas 78241, May 1972 (AD-751 899).*

[121] *C. J. Hilado and M. T. Lopez, "Procedures for Screening Materials for Potential Fire Toxicity and Data on Some Materials Found in the Home," J. Consumer Product Flammability, 4, 40-59 (March 1977).*

upholstery materials[122], and polymers[123]. In the work done to evaluate the potential toxicity of home fabric materials[121] several parameters were studied including the effect of air flow, the effect of flame retardants, and the effect of fabric dye and type. These studies included the use of animals subjected to a 30-minute exposure.

Seven different test conditions were employed to evaluate the toxicity of several upholstery materials[122]. Test results showed that the relative toxicity of these materials were influenced by temperature, heating rate, and air flow. Those tests in which air flow was employed displayed a greater degree of variation than those tests in which the pyrolysis products were allowed to accumulate without any air flow.

The relative toxicity of polyethylene, polystyrene, polymethyl methacrylate, polyaryl sulfone, polyether sulfone, polyphenyl sulfone, and polyphenylene sulfide was determined by means of a screening test (USF method)[123]. Polyphenyl sulfone displayed the least toxicity among the polymers containing sulfur.

Measurements were made on the concentrations of oxygen, carbon monoxide, carbon dioxide, and other toxic gases emitted from beds and upholstered chairs[124]. Various material combinations and ignition sources were used, as well as both smoldering and flaming conditions. Gas analyses were made by means of infrared spectroscopy and a paramagnetic oxygen analyzer. Where particular gases were expected to be formed, colorimetric detector tubes were used. Gases measured in this manner were hydrogen cyanide (HCN), hydrogen chloride ($HC\ell$), hydrogen sulfide (H_2S), sulfur dioxide (SO_2), oxides of nitrogen (NO_x), phosgene ($CO\ C\ell_2$), bromine (Br), chlorine chlorine dioxide ($C\ell\ C\ell\ O_2$), ammonia (NH_3), and organic amines. The additive or synergistic effects of these gases acting with other gases was demonstrated using mice.

Some additional information concerning toxicity included the following:

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[122] *C. J. Hilado and H. J. Cumming, "The Effect of Test Conditions on the Relative Toxicity of the Pyrolysis Products from Some Upholstery Fabrics," J. Coated Fabrics, 7, 133-156 (October 1977).*

[123] *C. J. Hilado, J. A. Soriano, K. L. Kosola, D. A. Kourtides, and J. A. Parker," Toxicity of Pyrolysis Gases from Synthetic Polymers," NASA-TM-78458, National Aeronautics and Space Administration, Ames Research Center, Moffett Field, California, December 1977 (N78-18127).*

[124] *C. A. Hafer and C. H. Yuill, "Characterization of Bedding and Upholstery Fires," Final Report NBS-GCR-70-1, NBS Contract CST-792-5-69, SwRI Project No. 3-2610, for Fabric Flammability Section, National Bureau of Standards, Washington, D.C., March 1970 (PB-192 365).*

a. The pyrolysis of polyethylene in an atmosphere containing oxygen was reported to produce aldehydes, alcohols, carbon monoxide, and carbon dioxide prior to ignition[14];

b. McGill, et al[125], described a technique whereby the qualitative and quantitative analysis of volatiles from the degradation of polymeric materials could be made;

c. The relative toxicity was determined for pyrolysis gases from six elastomers[126]. Both the rising temperature and fixed temperature methods gave the same order of ranking and acrylonitrile rubber displayed the greatest toxicity;

d. Dose-respone curves were generated for the decomposition products from Douglas fir, polyvinyl chloride, flexible polyurethane, teflon, and fiber-glass-reinforced polyester[127];

e. Stone and his co-workers[128] studied the absorption of hydrogen chloride on soot aerosol formed during the burning of mixed samples of polyvinyl chloride and polyethylene;

f. The thermal degradation of polyvinyl chloride was investigated at 190°C (374°F) in pure nitrogen and nitrogen containing 10, 20, and 40% hydrogen chloride (by volume)[129]. The rate of dehydrochlorination and the molecular enlargement were reported to increase with the hydrogen chloride content.

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[125] *W. J. McGill, L. Payne, and J. Fourie, "A Technique for the Analysis of Trace Amounts of Volatile Products from Polymer Degradations," J. Appl. Poly. Sci., 22, 2669-2675 (1978).*

[126] *C. J. Hilado, K. L. Kosola, A. N. Solis, D. A. Kourtides, and J. A. Parker, "Toxicity of Pyrolysis Gases from Elastomers," NASA-TM-78461, National Aeronautics and Space Administration, Ames Research Center, Moffett Field, California, December 1977 (N78-16096).*

[127] *Y. Alarie and S. C. Barrow, "Toxicity of Plastic Combustion Products. Toxicological Methodologies to Assess the Relative Hazards of Thermal Decomposition Products from Polymeric Materials," NBS-5-9005, Graduate School of Public Health, University of Pittsburgh, Pittsburgh, PA, February 1977 (PB-267 233).*

[128] *J. P. Stone, R. N. Hazlett, J. E. Johnson, and H. W. Carhart, "The Transport of Hydrogen Chloride by Soot from Burning Polyvinyl Chloride," J. Fire & Flammability, 4, 42-51 (January 1973).*

[129] *T. Hjertberg and E. M. Sorvik, "On the Influence of HCL on the Thermal Degradation of Polyvinyl Chloride," J. Appl. Poly. Sci., 22, 2415-2426 (1978).*

A general mathematical equation was given by Smith[36] for the toxic gas release rate as determined by the Ohio State University (OSU) release rate apparatus. This equation was

(Concentration)(Air Flow Rate) = Release Rate.

Here the concentration = C_t, the concentration of toxic gas in weight per unit volume; the Air Flow Rate = V, the volumetric flow rate of air; and the Release Rate = C_t x V, the weight of toxic gas per unit time.

A detailed description was given by Crane, et al[130], of a small-scale, laboratory test system in which small animals were employed to determine the relative toxic hazard presented from combustion products evolved from the burning of non-metallic materials. Seventy-five materials were tested to evaluate the system and the concept of "inhalation dose" was discussed. In this work, a combustion tube furnace was used as the heat source and a decomposition temperature of 600°C (1112°F) was selected as being typical of an environment in a real fire. Concentrations of carbon monoxide, hydrogen cyanide, oxygen, and carbon dioxide were measured. Materials were ranked (1) on the basis of times-to-incapacitation and times-to-death of the animals, (2) on the basis of equal material weights loaded into the furnace, (3) on the basis of the loss of equal weight of material during pyrolysis, and (4) on the basis of animal response times corrected for differences in animal weights and sample weights. In the appendices of this report were given (a) the description and operation of the animal exposure chamber, (b) a description of the materials tested and their physical properties, (c) the tabular animal response times, and (d) the dose-inhalation relationships in inhalation toxicology.

Five-minute lethal concentrations (LC_{50}) values were determined for hydrogen chloride, hydrogen fluoride, hydrogen cyanide, and nitrogen dioxide gases, both individually and in combination with carbon monoxide, by means of animal exposure experiments[131]. In these tests, male Wistar rats were exposed to the four pyrolysis gases combined with carbon monoxide for 5 minute durations. Results were presented in terms of symptomatology, mortality response, and pathology. The results indicated

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[130] *C. R. Crane, D. C. Sanders, B. R. Endecott, J. K. Abbott, and P. W. Smith, "Inhalation Toxicology: I. Design of a Small-Animal Test System; II. Determination of the Relative Toxic Hazards of 75 Aircraft Cabin Materials," Report No. FAA-AM-77-9, Office of Aviation Medicine, Federal Aviation Administration, 800 Independence Avenue, S.W., Washington, D.C. 20591, March 1977 (AD-A043 646).*

[131] *L. C. DiPasquale and H. V. Davis, "The Acute Toxicity of Brief Exposures to Hydrogen Fluoride, Hydrogen Chloride, Nitrogen Dioxide, and Hydrogen Cyanide Singly and in Combination with Carbon Monoxide," Report AMRL-TR-71-120, Aerospace Medical Research Laboratory, Aerospace Medical Division, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio 45433, December 1971 (AD-751 442).*

the carbon monoxide concentrations which are not hazardous to life did not intensify or increase the toxicity of HCℓ, HF, HCN, or NO_2.

Toxicity data for various natural and synthetic materials under simulated fire conditions was given by Hilado, et al[132]. Test animals (mice) were exposed to the pyrolysis gases generated by these materials and the times required for the animals to reach specified behavior levels were noted. These behavioral levels included (a) time to the first sign of incapacitation, (b) time to staggering, (c) time to convulsions, (d) time to collapse, and (e) time to death. The materials evaluated in this work included 9 types of woods, 11 synthetic polymers, 6 elastomers, and 25 polymers. Results indicated that there were few synthetic materials more toxic than natural materials such as wood, cotton, wool, and silk.

Apparent lethal concentrations (ALC_{50}) were determined for 17 samples of polymeric materials[133]. ALC_{50} was defined as the concentration of gaseous pyrolysis products in the atmosphere being inhaled, based on the weight of original sample, evolved under a specific set of test conditions, which will produce death in 50 percent of the test animals within 30 minutes of the onset of exposure. ALC_{50} values were found to range from 24 mg/ℓ to 110 mg/ℓ. Modified phenolic resins were reported to have less toxicity than the epoxy resins evaluated.

A series of articles by Hilado and Cumming has described more work on toxicity studies. In the first of these[134], work was done in which the concentration of carbon monoxide at the time of death of the last animal was employed to assess the importance of carbon monoxide as a toxicant. Also, experiments were conducted in which different lots of animals were exposed to selected toxicants from samples of surgical cotton, and polycarbonate and to pure carbon monoxide[135]. Results indicated that bisphenal A polycarbonate was a more suitable reference material than pure carbon monoxide. In addition, these authors[136] presented a review of available LC_{50} data on the toxic gases produced in fires. This review indicated

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[132] *C. J. Hilado, H. J. Cumming, and C. J. Casey, "Toxicity of Pyrolysis Gases from Natural and Synthetic Materials," Fire Technology, 14, (2), 136-146 (May 1978).*

[133] *C. J. Hilado, H. J. Cumming, J. E. Schneider, D. A. Kourtides, and J. A. Parker, "ALC_{50} Values for Some Polymeric Materials," J. Combustion Toxicology, 5, 5-10 (February 1978).*

[134] *C. J. Hilado and H. J. Cumming, "Studies with the USF/NASA Toxicity Screening Test Method: Carbon Monoxide and Carbon Dioxide Concentrations," J. Combustion Toxicology, 4, 376-384 (August 1977).*

[135] *C. J. Hilado and H. J. Cumming, "Variation in Animal Response to Different Toxicants," J. Combustion Toxicology, 4, 389-392 (August 1977).*

[136] *C. J. Hilado and H. J. Cumming, "A Review of Available LC_{50} Data," J. Combustion Toxicology, 4, 415-434 (August 1977).*

hydrogen cyanide and nitrogen dioxide (HCN and NO_2) to be the most toxic gases. It also was noted, for animal exposures, that mice were more susceptible than rats to hydrogen chloride and hydrogen fluoride, and less susceptible than rats to nitrogen dioxide.

III. FIRE ENDURANCE; FULL-SCALE TESTING

The assessment of fire endurance is primarily concerned with the response of complete systems instead of components or individual materials. There appears to be wide agreement that the performance of individual materials does not necessarily indicate the performance of the total system. Hence, there is a need for full-scale testing of complete, assembled systems before an assessment of ultimate performance can be made.

Some tests given for determining fire endurance are:

a. ASTM E-119 test standard for building construction and materials;

b. ASTM E-152 test for door assemblies;

c. ASTM E-163 test for window assemblies;

d. Union Carbide tests for thermal insulation;

e. Factory Mutual heat damage test;

f. UL 181 test for air ducts;

g. Bureau of Mines flame penetration test;

h. NASA Ames T-3 thermal test facility.

For specific details of these methods the reader is referred to the test methods themselves.

Most of the full-scale tests reported over the past several years have been performed on aircraft interiors. Examples of these type full-scale tests have been reported by Marcy[137,138] and by Stuckey and his colleagues[139,140].

The first of these[137] was a study made to determine the combustion characteristics of aircraft cabin interior materials in order to establish the relative fire hazards inherent in aircraft. While the flammability, smoke, and toxic gas characteristics of the materials were measured by laboratory tests, tests also were conducted in the interior of an actual aircraft fuselage at different locations to determine the relative ease with which the materials would ignite and burn. The results of this program indicated that (a) large concentrations of hydrogen chloride, hydrocyanic acid, unsaturated hydrocarbons, and halogenated hydrocarbons were evolved from a modacrylic type fabric, (b) exposure to flame (and temperature) rather than carbon monoxide inhalation was the primary danger to life, and (c) smoke was the most severe factor in the early stages of a fire. A study to determine the increase in the flammability of a material as a result of preheating, which would be typical in the late stages of a large-scale fire, also was suggested.

The other report by Marcy[138] was of a study made of the burning characteristics of aircraft interior materials ignited in cabin mockup enclosures. The purpose of the program was to test plastic and synthetic interior materials for flammability, smoke, and toxic gas characteristics to establish criteria that would ultimately produce improved airworthiness standards. The work was concerned with large-scale tests on selected materials considered to be the most critical with respect to fire safety, seat upholstery fabric and foam padding. It was an attempt to evaluate the effects of different ignition modes, under various

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[137] *J. F. Marcy, "A Study of Air Transport Passenger Cabin Fires and Materials," Report No. FAA-ADS-44, Federal Aviation Administration, National Aviation Facilities Experimental Center, Atlantic City, New Jersey 08405, December 1965 (AD-654 542).*

[138] *J. F. Marcy, "Air Transport Cabin Mockup Fire Experiments," Report No. FAA-RD-70-81, Federal Aviation Administration, National Aviation Facilities Experimental Center, Atlantic City, New Jersey 08405, December 1970 (AD-717 855).*

[139] *R. N. Stuckey, D. E. Supkis, and L. J. Price, "Full-Scale Aircraft Cabin Flammability Tests of Improved Fire-Resistant Materials," Report No. NASA-TM-X-58141, National Aeronautics and Space Administration, Johnson Space Center, Houston, Texas 77058, June 1974 (N74-28433).*

[140] *R. N. Stuckey, R. W. Bricker, J. F. Kumminecz, and D. E. Supkis, "Full-Scale Aircraft Cabin Flammability Tests of Improved Fire-Resistant Materials -- Test Series II," Report No. NASA-TM-X-58172, National Aeronautics and Space Administration, Johnson Space Center, Houston, Texas 77058, April 1976 (N76-23181).*

physical and environmental conditions in the cabin, on fire growth and extinguishment, and to relate the results to laboratory-scale tests.

In this program[138] tests were conducted in compartments approximately 1.8m x 1.8m x 5.2m long (6 ft x 6 ft x 17 ft long). Temperatures of the fuel load, interior surfaces, and air were continuously monitored by chromel-alumel thermocouples. One radiometer measured total heat flux on the end wall opposite the fire. Smoke density was measured over a 0.3-meter (1-foot) optical path using a photocell system. Oxygen concentrations were obtained from a paramagnetic type of detector. An infrared detector was used to measure carbon monoxide and carbon dioxide levels. Colorimetric detector tubes were employed to determine other toxic gases. Ignition sources included both open flaming (propane-fed Bunsen burner) and incandescent types (calrod heater). A halogenated gas (bromotrifluoromethane) was employed as an extinguishing material. This gas was reported to be effective in preventing a buildup of smoke as well as putting out a fire, but prolonged exposure to an incandescent heat source could result in pyrolysis into toxic gases. It also was noted that dense smoke developed in the early stages of the cabin fires, before the air temperature or carbon monoxide level increased to harmful proportions.

The report by Stuckey, Supkis, and Price[139] described three full-scale aircraft flammability tests. These were conducted with the overall objective being to evaluate the effectiveness of new fire-resistant materials by comparing their burning characteristics with those of materials used previously. Pre-1968 materials were used in Test 1, which primarily was to compare results with previous tests and to provide baseline data for subsequent tests. In Test 2, newer, improved fire-resistant materials were evaluated and results compared with the first test. Test 3 was essentially a duplication of Test 2, but a smokeless fuel ignition source was used which enabled a better determination of the smoke level produced to be made. The specific objectives of this program were three-fold. These were (1) to define the degree of propagation and the magnitude of fires originating in an aircraft cabin, (2) to identify the gaseous combustion products resulting from these fires, and (3) to determine the degree to which visibility was reduced within the cabin because of smoke.

These tests[139] were conducted in 4.6-meter (15-foot) long sections of a Boeing 737 fuselage. These sections were furnished as passenger cabins of an aircraft (containing sidewalls, windows, ceiling panels, hatracks, and seats). The ignition source for Tests 1 and 2 was JP-4 fuel (0.95 liter (1 quart) in a 30.5 cm (1-foot) square pan; burning time of approximately 5 minutes). The ignition source for Test 3 was 1.18 liters(1.25 quarts) of a smokeless fuel (50/50, acetone/methanol). Air flow for all tests was 5.7 m^3/min (200 ft^3/min). Appropriate instrumentation was provided to measure temperatures (chromel-alumel thermocouples), smoke density (photocell system), heat flux levels (3 asymptotic calorimeters), and toxic gases. Two systems were employed

in the detection of gaseous combustion products, one for hydrolyzable gases and one for nonhydrolyzable gases. Samples were taken every 30 seconds. Infrared spectroscopy methods were used to determine carbon dioxide, carbon monoxide, methane, ethylene, Freon 11, and Freon 113; mass spectrometry was used to determine oxygen and carbon dioxide; gas chromatography was used to determine ethane and propane. Specific ion electrodes were used to determine concentrations of hydrolyzable chlorides, fluorides, and cyanides. In addition, color and infrared movies were taken during the tests, still photos were taken before and after the tests, and black and white and infrared television cameras were used to monitor the tests.

Test results from this program[139] indicated the following:

a. The Pre-1968 materials produced a substantial propagation of a fire, a rapid decrease in visibility, a flash fire, considerable quantities of gaseous combustion products, and high temperatures.

b. Newer materials did not permit a fire to propagate and produced much less smoke, lower amounts of toxic combustion gases, and lower temperatures. Also, no flash fire was produced from these materials.

c. Test 3, using a smokeless fuel, indicated that the type of ignition fuel influenced the results of the tests. In this test there was a greater decrease in temperatures, smoke, and toxic gas production, as well as less damage (no flash fire) than in Test 2. The variations were attributed to differences in thermal input and smoke production of the fuels used.

As in numerous other reports, the need for full-scale tests was stressed. Materials that have acceptable flammability characteristics, as determined by laboratory tests, may experience synergistic reactions to geometric or environmental conditions when used in the final configuration.

In a later report by Stuckey, et al[140], two full-scale tests were conducted to evaluate the effectiveness of new fire-resistant materials for aircraft interiors. Details of these tests are essentially the same as those that were given previously[139]. In one test, using JP-4 fuel as the ignition source, visibility was lost after about 140 seconds from the time of ignition. The peak cabin temperature was 482°C (900°F), with the average temperature being 149°C (300°F). The maximum heat flux, at standing head level, was slightly less than 2.84 Kw/m^2 after 150 seconds. In the other test, using smokeless fuel, the peak temperature was 760°C (1400°F) at a seat armrest, and 575°C (1067°F) near the ceiling. Visibility was lost after 255 seconds from the time of ignition. The radiant heat flux averaged approximately 6.81 Kw/m^2.

The results of these two tests[140] indicated that the newer materials did not ignite, but rather decomposed. They did not support combustion.

However, these materials did produce quantities of hydrogen cyanide that were considere to be objectionable.

A few reports were found in the literature on bus fires, one an accidental fire that occurred during a road test[141], and another on a program to evaluate the fire hazard of busses used by the Washington, D.C. Metropolitan Transit Authority (WMTA)[142]. The objectives of this latter work[142] were (1) to determine the minimum amount of heat from an ignition source that would be required to start a fire in a bus interior, and (2) to determine the path or the mechanism by which a fire is most likely to intensify and spread once it has been initiated.

In this work[142] a series of small-scale tests were performed in addition to three full-scale tests. The laboratory tests included the Flooring Radiant Panel Test, ASTM E-162 Method, the NFPA-258 Smoke Density Chamber Test, and the NBS upholstery test. The full-scale tests were conducted on an actual bus. From the results of these tests it was concluded that the seats were the most probable source of hazard, provided they could be ignited. It was indicated that an accidental ignition from a dropped cigarette or match was not likely, but a deliberate ignition from a match was possible if the flame was applied at a proper location. Ignition of a seat was achieved readily from such sources as paper trash on the seat, newspaper under the seat, or a flammable fluid (lighter fluid) poured onto the seat. It was determined that the development and spread of a fire was primarily through the involvement of the seat cushion material. Also, dense smoke, which considerably reduced visibility, filled the bus interior between 1-2 minutes after the urethane foam padding in the seat assembly was ignited. As a result, it was recommended that either the padding be removed or it be protected by some type of barrier material in order to provide an improved margin of safety for passengers.

Of particular interest to this program was a report that described a program to assess the potential fire hazard in the interior of rail cars, specifically the subway cars of the Washington Metropolitan Area Transit Authority (WMATA)[143]. It was reported that small-scale laboratory

[141] *J. H. Reed, F. H. McAdams, L. M. Thayer, I. A. Burgess, and W. R. Haley, "Special Investigation -- UMTA Prototype Bus Fire, Near Phoenix, Arizona, May 13, 1975," Report No. NTSB-HAR-75-8, National Transportation Safety Board, Bureau of Surface Transportation Safety, Washington, D.C. 20594, December 1975 (PB-248 776).*

[142] *E. Braun, "Report of Fire Tests on an AM General Metro Bus," Report No. NBSIR-75-718, Center for Fire Research, Institute for Applied Technology, National Bureau of Standards, Washington, D.C. 20234, June 1975 (COM-75-10750).*

[143] *E. Braun, "A Fire Hazard Evaluation of the Interior of WMATA Metrorail Cars," Report No. NBSIR-75-971, Center for Fire Research, Institute of Applied Technology, National Bureau of Standards, Washington, D.C. 20234, December 1975 (PB-249 776).*

tests were inadequate in assessing the fire hazard and therefore a series of full-scale tests on interior mock-ups were conducted. The results of the full-scale tests indicated that the fire hazard potential was primarily from the seat padding and covering, and also from the plastic wall linings. More specifically, the hazard was from the spread of flame and the development of smoke and heat.

In this program[143] the subassemblies from Metrorail cars that were tested included interior walls, carpet with pad, and seat cushions. These were evaluated using an NFPA 258T smoke density chamber, the FAR-28.853 vertical test, the ASTM E-162 radiant panel method, and two special tests developed at the National Bureau of Standards, the Flooring Radiant Panel Test and the upholstery test for seat cushions. In addition, the integrity of the floor assembly of a completed Metrorail car was evaluated to determine if smoke could pass into the interior compartment of a car from an exterior fire.

The NFPA Smoke Density Chamber Method was used to measure the smoke generated from solid specimens exposed to a radiant flux level of 2.5 watts/cm^2 by the attenuation of a vertical beam of light passing through the chamber. Standard FAR-28.853, which is used by the FAA, prescribed a vertical test in which a 3.9-cm (1.5-in) flame, applied to the bottom edge of a specimen, provided data on flame time, burn length, and flaming time of dripping materials. The Radiant Panel Test measured flame spread and heat release from a sample under varying heat fluxes ranging from 0.3 to 4.0 watts/cm^2. The NBS Flooring Radiant Panel Test exposed a sample to a radiant energy gradient that varied along a 1-meter length from 1.1 watts/c m^2 to 0.1 watts/cm^2 and indicated the critical radiant flux necessary to support continued flame progagation. The upholstery test developed by the NSB was used to determine the ignitability of upholstered furniture when exposed to a lighted cigarette.

Seven full-scale tests were conducted on mock-ups of Metrorail car interiors[143]. The mock-ups consisted of floor, wall, and ceiling sections and three seat assemblies. The evaluation was made in terms of vertical and horizontal flame spread, the increase in temperature, and the density of the smoke. General criteria were (1) that there be no significant fire spread from the point of ignition, and (2) that the level of smoke permit the escape from a burning car in a reasonable time. Ignition sources employed in this program included a paper trash bag containing one full sheet of newspaper, one pound of loosely stacked newspaper, and two pounds of loosely stacked newspaper.

An analysis of the data from these full-scale tests[143] indicated (a) the maximum average temperature ranged from 55°C to 288°C (131°F to 550°F), (b) tests of urethane cushions produced average temperatures near the ceiling of 138°C to 288°C (280°F to 550°F), (c) neoprene seat assemblies had lower average gas temperatures, the average being 92°C (198°F), and (d) maximum heat flux readings were 0.51 watts/cm^2. Perhaps the most significant finding was the full-scale tests showed that

the materials failed to perform in their end-use configuration as predicted by small-scale tests.

Two of the seven full-scale tests on the mock-ups also were used to evaluate the toxicological hazards from a fire in a Metrorail car[143]. In this portion of the work, the oxygen depletion was measured, as were the levels of carbon monoxide, carbon dioxide, hydrogen chloride, and hydrogen cyanide. Male Wistar rats were exposed to the combustion products and then examined for changes in blood chemistry, gross pathology, and loss of function. More specific details of these toxicity tests were discussed earlier[84].

The results from a series of tests conducted on rail car assembly mock-ups were reported in an article by Nelson, et al[144]. In this work, various materials were evaluated with respect to usage area and included glazing panels, seat cushion materials, seat back panels, and wall panels. The ignition source, to simulate trash fires, was 50 sheets of newspaper placed on an outboard seat and ignited with a match. Results of this series showed that a fire in which a single urethane seat assembly was involved was adequate to produce flashover conditions in a moderately sized compartment in approximately 6 minutes.

A. Flash Fires

During the course of this survey the phenomenon of flash fire, or flashover, within compartments or enclosures, such as aircraft cabins or similar vehicle interiors, was mentioned frequently. A flash fire has been defined as a flame front that propagates through a fuel-air mixture as a result of the energy release from the combustion of that fuel[145]. Some of the work in which this phenomenon was discussed is reviewed briefly in this section.

Marcy[137], in his work to evaluate the combustion characteristics of aircraft cabin interior materials, reported that a flash fire could develop from a relatively small fire and was usually accompanied by a rapid increase in flame propagation, smoke density, temperatures, air pressure, carbon monoxide, and oxygen deficiency. He reported that there was a relativley small amount of heat liberated during a flash fire. It also was reported that most areas damaged were above the window level (of an aircraft cabin), and the rate of flame spread was calculated to be approximately 21 meters/minute (68 feet/minute).

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[144] *G. L. Nelson, A. L. Bridgman , W. J. J. O'Connell, and J. B. Williams, "Material Performance in Transportation Vehicle Interiors," J. Fire & Flammability, 8, 262-278 (July 1977).*

[145] *J. E. Brown and J. J. Comeford, "A Technique for the Measurement of Flash Fire Potential of Polymeric Materials," Report No. NBSIR-75-757, Center for Fire Research, Institute for Applied Technology, National Bureau of Standards, Washington, D.C. 20234, Dec. 1975 (PB-248 914).*

A report by Paabo and Comeford[146] discussed a program to develop a laboratory model for assessing the flash fire potential of materials and to obtain data on the composition of gases that produce flash fires. It had been noted previously that a flash fire appeared to involve gas phase combustion reactions from the thermal decomposition products of solid organic materials within an enclosure. Propagation of flame in the gas phase was reported to be dependent on the composition of the combustibles and the ratio of the combustibles to air. Other parameters of importance were heating rate, the source of ignition, and the type of heating.

In this work[146] a flash fire cell was constructed from a Pyrex cylinder 50 cm (19.7 in) long x 5 cm (1.97 in) in diameter, a total volume of approximately 1 liter. A sample holder was connected to the main body of the cell and means were provided to obtain gas samples. The ignition source was a 10 KV ac arc, approximately 1 cm in length (0.4 in), between copper or platimum electrodes. Weighed samples were heated by a Bunsen burner or electric furnace. Pyrolysis temperatures ranged from 250°C (482°F) to 500°C (932°F). Combustion products were analyzed by means of gas chromatographic techniques and infrared spectroscopy.

The results of these experiments[146] showed that a complex mixture of gases and smoke was produced during the thermal decomposition of polyurethanes in air. The analysis of these gases and smoke was performed as a means of determining the possible causes of flashover. Low temperature decomposition products were reported to be hydrogen, carbon monoxide, and hydrocarbons through propylene. Additional work was to be performed to better define the role of smoke in flash fires.

A program to investigate and evaluate the parameters which may contribute to the production of flash fires resulting from the degradation of polymeric materials in an enclosed environment was reported by Brown and Comeford[145]. A flash fire cell was constructed of a Pyrex cylinder 50 cm long and 5 cm in diameter having a volume of approximately 1 liter (similar to that described above). The heat source was a regulated electric furnace and the ignition source was a 10 KV ac arc 5 to 10mm (0.2-0.4 in) long between platinum electrodes. The cell also contained a continuous polarographic oxygen analyzer. The occurrence of a flash fire was detected by the abrupt change in the curve of oxygen concentration. The magnitude of the change seemed to be related to the intensity of the flash fire.

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[146] *M. Paabo and J. J. Comeford, "A Study of the Decomposition Products of Polyurethane Foam Related to Aircraft Cabin Flash Fires," Report No. FAA-RD-73-46, Federal Aviation Administration, National Aviation Facilities Experimental Center, Atlantic City, New Jersey 08405, July 1973 (AD-763 327).*

It was determined that there were two probable major stages in the total combustible-pyrolyzate evolved during the thermal degradation of polyurethane foams. The first stage contained essentially all of the readily condensable pyrolysis products. The postulated mechanism for this stage, a degradation of the urethane group below 380°C (716°F), consisted of (a) primary aromatic amine and carbon dioxide with a residue derived from polyether, (b) secondary amines with carbon dioxide, and (c) aromatic diisocyanate with residue of polyether-polyol. The second stage, which occurred above 380°C (716°F), contained the majority of the combustible products (primarily low molecular weight combustibles). In this stage the residues of polyetherpolyol and derivatives of polyethers produced alkanes, alkenes, and carbonyl compounds.

The results from this work[145] indicated that flash fires occurred when the oxygen volume fraction was diluted to approximately 17% by the pyrolysis products. The products of the second stage primarily were responsible for the flame front in the flash fires. Also, flash fires were produced in the test apparatus when sample to volume ratio was at a minimum of 0.2 g/ℓ and the pyrolysis temperature was more than 380°C (716°F).

Manka, Pierce, and Huggett[147] reported on a program whose purpose was to develop a method to evaluate the flash fire potential of aircraft cabin materials. Twenty-four materials were studied in an attempt to obtain a better understanding of the phenomena associated with a flash fire.

A cell was constructed of Pyrex glass pipe with an ID of 5 cm (1.97 in). The volume of the cell was 1.7 liters (0.06 ft^3). Mixing of the pyrolyzate with air was achieved by means of a magnetic stirrer. Chromel-alumel thermocouples were positioned in the cell to determine the passage of a combustion wave and to allow an estimate of flame speed to be made. Gas samples could be removed with a gas tight syringe through rubber sampling systems. A 10,000-volt spark was used to ignite the pyrolyzate-air mixture. Weight samples (1 gram) were pyrolyzed at a temperature of 500°C (932°F), usually sufficient to achieve complete pyrolysis of most organic materials. Samples usually experienced a heating rate of approximately 200-250°C (392-482°F) per minute, which is similar to the rate encountered in fire environments. The ignition source was triggered at regular intervals (spark duration of 1 second), and continued until flash fire or complete pyrolysis occurred. Sample weights were adjusted (increased or decreased) depending on the results. If a flash fire was produced, the sample weight was decreased; if no

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[147] *M. J. Manka, H. Pierce, and C. Huggett, "Studies of the Flash Fire Potential of Aircraft Cabin Interior Materials," Report No. FAA-RD-77-47, Department of Transportation, Federal Aviation Administration, Systems Research and Development Service, Washington, D.C. 20590, December 1977 (AD-A048 475).*

flash fire occurred, sample weight was doubled. Thus, the minimum sample weight that would produce a flash fire could be determined.

A minimum energy concept was proposed[147] for characterizing the flash fire of the mixture of gaseous products formed during the pyrolysis of organic materials. This concept stated that a flash fire was possible when the potential combustion energy content of the pyrolyzate-air mixture exceeded 425 cal/liter. Results showed that polyvinyl chloride foam and polycarbonate samples yielded flashable mixtures. Poly (phenylene oxide) and polyether polyurethane samples produced the most easily flashed mixtures.

Hilado and co-workers have done a considerable amount of work to determine the potential or tendency of several materials to produce flash fires. Some of these programs have been reviewed and are summarized below.

A laboratory screening test was developed to assess the flash fire propensity of materials[148]. Eighty-six materials were tested at 800°C (1472°F) and their relative propensities determined in terms of the time to produce a fire and the height of the fire. Materials reported to be the least prone to flash fires were polyvinyl chloride, polyphenylene oxide and sulfide, and polyether and polyaryl sulfone. The largest flash fires were reported from wood, polyolefin fabrics and plastics, nylon fabrics and plastics, and polyurethane flexible foam. The polyolefins were reported to take the longest time to produce flash fires.

Thirty-three samples of cushioning materials also were evaluated with respect to their tendency to produce flash fires[149]. The results indicated that the production of flash fires could be reduced by chemical formulation. Fire retardants were reported to be sometimes effective in reducing flash fires.

In conjunction with a toxicity study mentioned earlier[107], it was noted that chemical formulation could reduce flash fire propensity but improvement was not necessarily reached by the addition of fire retardants. In addition, it was reported that flash fires from the pyrolysis of flexible polyurethane foams appeared more likely at 800°C (1472°F) than at 500°C (932°F).

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[148] *C. J. Hilado and H. J. Cumming, "Screening Materials for Flash-Fire Propensity," Modern Plastics, 56-59 (November 1977).*

[149] *C. J. Hilado, H. J. Cumming, and A. N. Solis, "Flash Fire Tests on Cushioning Materials," J. Consumer Product Flammability, 4, 359-379 (December 1977).*

In some other work[150], eighteen materials were evaluated with respect to their flash fire propensity using the USF flash fire screening test. Nylon and polypropylene took the longest time to produce a flash fire; polypropylene produced the largest. It also was noted that fabrics with backcoating produced smaller flash fires than materials without backcoating.

Screening tests were conducted on samples of rigid foam plastic insulation in order to determine their flash fire propensity[151]. Samples included five types of polyurethane (3 low density, 2 high density), two urethane-modified isocyanurate types, polymethylacrylimide, polybismaleimide, a modified polyimide, polystyrene, and polyvinyl chloride. Test results showed flash fire heights ranging from 0-20.3 cm (0-8 in); times to flash fire ranged from 44 to 203 seconds; weight loss ranged from 62 to 100 percent. Under the specific test conditions employed in this work, these materials were considered to have little or no propensity toward flash fire.

The flash fire propensity of the pyrolysis gases from samples of polyester urethane flexible foams was determined. In these tests[99], 0.10 g of foam was pyrolyzed at 800°C (1472°F) without forced air flow and any combustible gases were allowed to mix with air in a vertical combustion tube and be ignited by the hot surface of the pyrolysis tube. Results indicated that polyester urethane foams were less susceptible to flash fires than polyether urethane foams.

B. Modeling Fire Environments

Since it is generally agreed that materials do not behave in actual, full-scale fire environments as suggested by small-scale, laboratory tests, and since full-scale tests are both time consuming and expensive to conduct, any method with which accurate predictions of material behavior in real fire situations could be made would be extremely advantageous. Several reports discussed efforts that were directed toward the development of models that would enable such predictions to be made. Some of these are summarized below.

Fang[152] reported a study to obtain an improved understanding of the burning behavior of incidental fires, such as those starting in a

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[150] *C. J. Hilado and H. J. Cumming, "Flash Fire Propensity of Some Upholstery Fabrics With and Without Backcoating," J. Coated Fabrics, 7, 240-249 (January 1978).*

[151] *C. J. Hilado and R. M. Murphy, "Flash Fire Propensity of Rigid Foam Insulation," J. Thermal Insulation, 1, 283-286 (April 1978).*

[152] *J. B. Fang, "Analysis of the Behavior of a Freely Burning Fire in a Quiescent Atmosphere," Report No. NBSIR-73-115, Center of Building Technology, Institute for Applied Technology, National Bureau of Standards, Washington, D.C. 20234, February 1973 (PB-226 907).*

wastebasket or a piece of furniture, and to provide a basis for predicting heat transfer rates from the flame to nearby surroundings. Parameters considered included the rate of fuel burning, the heat of combustion of the volatiles, and the geometry and size of the fuel source. A mathematical model described the physical and geometric properties of a turbulent buoyant diffusion flame over a free burning fire for both axisymmetric and two dimensional cases. The simulation of the flame consisted of a combustion zone near its source and a buoyant plume above. Analytical solutions were presented that illustrated the effects of fuel mass-flow rate, physical properties of the fuel and ambient air, and the size and shape of the burning area on the general characteristics of a buoyant flame.

Smith[153] discussed a fire system model that may be employed to evaluate the fire hazards produced by the combustion of various materials. The model was based on the release rate data for heat, smoke, and gases generated by the materials and can be used to calculate the hazard levels of temperature, and smoke and gas concentrations as a function of time. It was noted that when release rates are employed, the exposed surface area, rather than the weight of material, is of prime consideration since release rates are proportional to exposed surface area and not weight.

Smith[154] also has discussed the evaluation of fire performance tests and their relation to real fires. The evaluation was made in terms of conceptual design, significance, and theoretical limitations. Performance tests were divided into two types, those that measure performance of materials in simulated fire conditions and those that predict the performance of materials by employing basic combustibility data. It was concluded that release rate values can be used to rate and specify materials as a function of location in the fire system and nature of occupancy.

Measurements were made by Durbetaki, et al[155], to provide data on thermophysical properties, combustion processes, and ignition times. Modeling analyses were performed for single and pairs of thermally thin materials under radiative heating and single thermally thick materials under convective heating.

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[153] *E. E. Smith, "Model for Evaluating Fire Hazard," J. Fire & Flammability, 5, 179-189 (July 1974).*

[154] *E. E. Smith, "Relation of Performance Tests to Actual Fire," Fire Technology, 13, (1), 40-44 (February 1977).*

[155] *P. Durbetaki, W. C. Tincher, L. S. Lloyd, C. D. Lowry, and W. J. Tingle, "Prediction of Fire Hazard from Fabrics and Building Materials," Center for Fire Research, National Bureau of Standards, Washington, D.C. 20234, February 1977 (PB-272 977).*

An extensive fire modeling program reported in the literature was the Dayton Aircraft Cabin Fire Model (DACFIR). This work was performed by the University of Dayton Research Institute for the Federal Aviation Administration (FAA) and has been described in detail in a series of reports that are summarized below[156-159].

The first report[156] detailed the development of a basic mathematical model and computer simulation program to describe a fire in the cabin of a wide-body commercial aircraft. The model and simulation program were developed in an attempt to be able to predict the levels of smoke and toxic gases produced from burning interior materials in a full-scale cabin fire from laboratory test data on the same materials.

The mathematical model[156] employed a technique whereby the distribution of burning or smoldering areas on combustible materials can be approximated by dividing the material surface into square area elements. The performance of the material during the combustion process was modeled by permitting the surface area elements to exist in one of seven distinct states, four primary ones designated as virgin (original condition), smoldering, burning (flaming), or charred, and three intermediate states, which define the transition between the four primary states. By defining the rate at which the flame propagates and the times of transition in going from one of the primary states to another, it was possible to predict parameters such as the release of heat, smoke, and toxic gases, as well as ignition, spread rate, and the ultimate extinction of the fire. Other factors considered in this model include laboratory test data on the materials, the ignition source, and the geometry of the section of the cabin in which the fire originated.

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[156] *J. B. Reeves and C. D. MacArthur, "Dayton Aircraft Cabin Fire Model, Volume I - Basic Mathematical Model," Report No. FAA-RD-76-120, I, Department of Transportation, Federal Aviation Administration, Systems Research and Development Service, Washington, D.C. 20590, June 1976 (AD-A033 682).*

[157] *J. B. Reeves, "Dayton Aircraft Cabin Fire Model, Volume II - Laboratory Test Program," Report No. FAA-RD-76-120, II, Department of Transportation, Federal Aviation Administration, Systems Research and Development Service, Washington, D.C. 20590, June 1976 (AD-A033 683).*

[158] *P. M. Kahut, "Dayton Aircraft Cabin Fire Model, Volume III - Computer Program User's Guide," Report No. FAA-RD-76-120, III, Department of Transportation, Federal Aviation Administration, Systems Research and Development Service, Washington, D.C. 20590, June 1976 (AD-A033 989).*

[159] *C. D. MacArthur and J. F. Myers, "Dayton Aircraft Cabin Fire Model Validation - Phase I," Report No. FAA-RD-78-57, Department of Transportation, Federal Aviation Administration, Systems Research and Development Service, Washington, D.C. 20590, March 1978 (AD-A058 547).*

Included in the laboratory test data were measurements of the flame spread rates, ignition times, heat flux at the beginning of smoldering, smoldering times, and burning times for individual materials.

It was noted[156] that the rate at which a fire developed depended upon the type of material from which these surfaces were constructed, the orientation of the surfaces, and upon the thermal conditions in the cabin. The material characteristics considered important were the rate of flame spread, ignition time, and burning time. Consideration must be given to the variations of these parameters as a function of incident heat flux.

Emission rates of smoke, gases, and heat were taken as functions of the thermal and chemical properties of the material undergoing combustion as well as the size of the fire and the amount of oxygen available. The model was developed using rates from laboratory tests and it was assumed that the rates for a given material depended only upon the externally applied heat flux to which the material was subjected. Two emission rates were considered, one for a smoldering condition and the other for a flaming condition. Smoldering was assumed to be an endothermic reaction with no heat being released into the cabin atmosphere[156].

It was difficult to model the distribution of smoke, toxic gases, and heat in the cabin because of the turbulent character of the flow, the complications of enclosure geometry, and the fuel combustion behavior. The model assumed the division of the atmosphere in the cabin into two separate horizontal zones. The upper zone contained combustion products and heated air, the lower contained cool and uncontaminated air. The amount of mixing was considered to depend upon such factors as the temperature and density difference between the zones, the degree of turbulence in each zone, the extent of ventilation, and the time scale. Some of the other variables in the model included the depth of the upper zone, the average surface temperature of the materials in contact with the gas in each zone, and the concentrations of smoke and toxic gases in the upper zone.

In order to compute the average surface temperature of a material, three thermal-physical properties are required. These are material density, specific heat, and thermal conductivity.

Parameters that must be considered, and that will vary as a function of applied heat flux, were the following:

1. Flame spread rate in a horizontal, vertical upward, and vertical downward direction;

2. Time to flame;

3. Time to char from the flaming state;

4. Heat release rate;

5. Rate of smoke release;

6. Release rate in the flaming state of hydrogen cyanide (HCN), hydrogen chloride (HCℓ), hydrogen fluoride (HF), carbon monoxide (CO), and sulfur dioxide (SO_2).

The second report in the series[157] described the laboratory tests and results which were performed to support the development of the Dayton Aircraft Cabin Fire Model (DACFIR Model). Discussed in the report[157] were test procedures, test results, an analysis of the test data, and the development of a set of material properties as input data for the simulation program. The objectives of the test program were to define the combustion properties of representative wide-body aircraft cabin materials at varying levels of applied radiant heat flux, and to provide specific input data so that the performance of the DACFIR model could be evaluated using this representative data.

Eighteen materials commonly used in cabin interiors were tested. These materials were grouped into usage categories typical in wide-body aircraft, and were tested in a vertical or horizontal position, or both, depending on usage.

A combustion analyzer apparatus, developed at Ohio State University (OSU), was used to measure the rates of flame spread, the rates of heat release, and the rates of smoke evolution as functions of heat flux incident upon the materials tested. The heat flux level ranged from 1.4 W/cm^2 to 6.0 W/cm^2. A National Bureau of Standards smoke chamber was used to measure the increase in smoke density in the chamber due to smoke accumulation from a burning sample. A "burnthrough" apparatus, developed by the Boeing Company, was used to measure the effect on material surfaces at the high heat flux levels which are common in actual fires. This apparatus also was used to measure the time for a material to cease smoldering after the external heat flux was removed.

Toxic gases were measured by means of colorimetric tubes. Samples of materials were burned in the NBS smoke chamber at heat fluxes of 2.5, 5.0, and 7.5 W/cm^2. Among the gases measured were carbon monoxide (CO), sulfur dioxide (SO_2), hydrogen chloride (HCℓ), hydrogen fluoride (HF), and hydrogen cyanide (HCN). Results were expressed in parts per million (ppm). A total of nine gases can be accomodated by the model.

Experimental data was collected for the materials in both a flaming and a smoldering state. Parameters measured for the materials in a flaming state were flame spread rate, smoke release rate per unit area, heat release rate per unit area, toxic gas release rate per unit area, time of flame, and the time to become charred from flaming combustion. All these were determined as a function of heat flux. Parameters measured for the materials in a smoldering state were the heat flux at

which smoldering was induced in a few seconds (~ 20), smoke release rate per unit area, toxic gas release rate per unit area, the time to begin smoldering, and the time to become charred from smoldering.

Appendices at the end of the report[157] present detailed, specific information of (a) test data, (b) flammability properties or representative materials, (c) smoke emission and optical density data, and (d) toxic gas emission data from the NBS chamber.

The third report in the series[158] was intended to serve as a guide to be used for the computer simulation program of the DACFIR model. Included as a part of this guide were instructions for the preparation of input data, a sample of input and output, the basic definitions regarding the mathematical model and the simulation program, and a brief description of the structure of the program. The input to the model consists of (1) a description of the aircraft cabin geometry and the ventilation conditions, (2) a description of material properties as measured by the laboratory tests, and (3) a description of the initial fire conditions. Also contained in the report are program statistical data and information concerning the availability of the program code. This report was not intended to be a complete reference source for the computer programmer.

Results have been presented[159] from an evaluation of the Dayton Aircraft Fire Model (DACFIR) by comparison to seven full-scale cabin mock-up fire tests. A description of the laboratory program to provide flammability, smoke, and gas generation data on the materials used in the full-scale tests also was presented.

Laboratory tests were made using a combustion analyzer developed at Ohio State University. The data obtained included (1) the rate of surface flame spread in the horizontal, vertical upward and vertical downward directions, (2) the time to ignition (time to flame) when exposed to a small pilot flame, (3) the time to burn (time from ignition to charred state), (4) heat release rate, (5) total heat release, (6) smoke release rate, and (7) the total smoke released. The heat fluxes employed during these tests were 1.5, 2.5, 3.5, and 4.5 or 5.0 W/cm^2.

As a result of these tests some refinements were made to the mathematical model. These were (1) generalizations in the description of the cabin geometry so that cabins of various widths could be included, (2) improvements in the modeling of thermal radiation, (3) a computation of oxygen consumption, and (4) the method for treating forced ventilation. Work on this program is continuing.

A recent report by the Rice Center[160] presents some preliminary data to support a generalized technique by which the relative acceptability of materials for use in vehicle interiors might be determined. In this approach, data from several tests are combined and a rating of the relative flammability of a material is determined from an overall fire hazard point of view.

In this work[160] the concept of rating materials was based on an "acceptability factor." The data from five tests, selected to reflect fundamental material behavior, were collected. These five tests were:

1. Limiting Oxygen Index (LOI). This test was used to provide an indication of the relative capability of a material to support combustion, as well as a measure of its ease of ignition.

2. Maximum Specific Optical Density (Dm). This test reflects the smoke producing property of a material.

3. Thermal Gravimetric Analysis (TGA). This test provided an indication of the thermal stability of a material by measuring percent weight loss as a function of temperature.

4. A measure of the vertical flame spread with a forced draft was used to rate the fire spreading potential of a material.

5. Evolved gases were measured by employing mass spectrometry and an infrared matrix isolation technique.
This established the presence of significant species but did not determine their toxicological significance.

The acceptability factor (AF) was generated by defining scales with an upper and lower limit for each test, normalizing the data, and adding the factors to obtain a single number. By comparing acceptability factors, an appropriate material could be selected. For materials with similar acceptability factors, the value of a specific test could be used as the basis for selection. At the time of publication full-scale tests were required in order to verify this approach.

IV. FLAMMABILITY - GENERAL

Several articles were reviewed that dealt with relatively large scale flammability programs, and as such, they were concerned with several parameters or material properties instead of a single characteristic. Some of these articles have been summarized below.

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[160] *Rice Center, "Flammability Studies of Materials Used in Transportation Vehicles," Report No. DOT-05-60149, Department of Transportation, Office of the Secretary, Office of University Research, Washington, DC 20590, October 1977.*

Among the earliest efforts to characterize the flammability properties of materials used in vehicle interiors was that reported in 1969[161]. The primary objective of the program was to determine the flammability characteristics for those materials used in the interiors of automobiles and school buses. The types of materials tested included upholstery cover materials (cloth and vinyl), cushioning materials, seat components, headliner materials, floor coverings, and door panels.

In this work[161] it was decided that the rate of flame spread would be the most important parameter in evaluating the fire hazard in the interiors of these type vehicles. This decision was reached by assuming that ignition in the vehicle interior would be accidental, and that evacuation of the vehicle would take place while burning was localized, thus minimizing the probability of injury. Thus, more than 200 materials were tested to determine experimentally their relative rates of flame spread.

Briefly, the test method employed during the course of this work[161] was as follows. Samples of the materials to be tested were preconditioned prior to actual testing in an environment of 70 ± 2°F (21.1 ± 1.1°C) and 65 ± 5% humidity. Samples were secured and supported during the test by a rectangular framework positioned horizontally in the test chamber, which in this case was a laboratory hood. The ignition source was a flame from a Bunsen burner. The rate of flame spread was determined by observing the flame front on the surface of the test sample, and by measuring the time required for the flame front to pass between two measured and marked points on the sample. Reasons for designing the test in this manner are discussed in detail in the report, but are not included here.

Results of the tests indicated that heavier or multilayered components had a tendency to self-extinguish, or had low flame spread rates (< 4 in/min; < 10.2 cm/min), while single sheet materials (upholstery covers and headliner materials) were the most rapid burning. Vinyl-covered fabrics had higher flame spread rates, as much as 10 in/min (25.4 cm/min) in some cases, and produced more smoke than the cloths. It also was noted that items of ABS (acrylonitrile - butadiene-styrene) resins produced heavy, black, sooty smoke, and materials such as polyethylene, polypropylene, and nylon melted but did not produce any observable smoke.

Additionally in this work[161], some of the flammability test methods of that time were reviewed and the salient features of each were summarized. This illustrated the differences between the various test methods. Among these were differences in sample size, the geometric

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[161] *A. Goldsmith, "Flammability Characteristics of Vehicle Interior Materials," Final Technical Report, Project J6152, Engineering Mechanics Division, IIT Research Institute, 10 W. 35th Street, Chicago, Illinois 60616, May 1969 (PB-189 653).*

configuration of the samples during testing, the type and severity of fire conditions, and ventilation parameters. All these and more make it difficult for the results of the tests to be compared with any confidence or validity. From the comparison of the then current test methods it was concluded that the differences between the laboratory-scale type tests that have the most significant influence on the results were the orientation of the test sample and the amount of time the sample was exposed to the ignition flame.

According to the author other recommendations or suggestions that ought to be considered in evaluating flammability hazards are the following. (1) Flame spread rate is not a complete indication of the hazard presented by a material. (2) The major defect of any laboratory-scale flammability test is the inability to correlate the data to a full-scale environment. (3) Consideration should be extended to the measurement of the heat flux from a burning object to an adjacent object, as well as to the rate of flame spread and the rate of heat release. (4) In full-scale tests, measurements should be made of the gaseous decomposition products (toxic gases) as a function of time and also as a function of the heat flux to an interior object.

A report prepared for the National Aeronautics and Space Administration (NASA) described a fire safety program developed in conjunction with the Apollo space program[162]. While this program specifically dealt with the fire safety problems associated with space capsules, there were several areas or topics of a general nature discussed in the report that could be applied to any fire safety program. Among these subjects were the establishment of realistic criteria to govern flame spread, off-gassing during combustion, and the effect of fire on vital components and equipment; design considerations, such as the selection of materials or components and the positioning of the components; test requirements, including screening and full-scale tests. Among the recommended types of tests are those that provide data on flame propagation rate, flash point, fire point, and qualitative and quantitative information on the gases evolved from the materials. The report also discussed other aspects of fire safety design such as potential sources of ignition, flammable nonmetallic materials, environmental considerations, fire detection, fire extinguishment, and fire survival.

Material testing in this program[162] was reported to consist of three phases. These were (1) screening tests on individual materials, (2) testing of assembled components, and (3) full-scale testing of the final design with all components. Screening tests were performed on nonmetallic materials to determine their flammability properties and

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[162] *General Electric Company, "Systematic Control of Nonmetallic Materials for Improved Fire Safety," Report No. NASA-SP-5109, Technology Utilization Office, National Aeronautics and Space Administration, Washington, D.C., 1972.*

evaluate their toxic gas production. The flammability tests included a drip-ignition test, upward and downward propagation tests, and a flash-point and firepoint test. In addition to carbon monoxide determination, it was suggested that other potentially toxic products which should be considered in toxic gas analysis are hydrogen cyanide, benzene, xylene, methyl ethyl ketone, chloroform, butanol, dichloromethane, 1,4 - dioxane, formaldehyde, trichloroethylene, hydrogen chloride, ammonia, hydrogen fluoride, carbonyl fluoride, and silicon tetrafluoride.

Full-Scale tests were said to be required in order to accomplish the following objectives:

1. To determine whether or not a fire will propagate;

2. To determine the degree of flame propagation;

3. To determine the magnitude of the fire; and

4. To identify the nature of the propagation paths.

Some previously mentioned work by Einhorn, et al[46], was performed to determine the flammability characteristics and thermal degradation of urethane cellular plastics used in aircraft interiors. Urethane polymers were prepared and studies were made on them to determine the effect of the chemical structure of isocyanates and polyols on performance during exposure to fire environments. Also, reactive and non-reactive fire retardants were incorporated into a series of foams. Flammability characteristics evaluated included the ease of ignition, fire propagation, fire endurance, smoke emission, and oxygen index.

In this report[46] the FAA regulations governing the flammability of aircraft interior materials were reviewed. Briefly, these were as follows. In 1947 the maximum burn rate permitted for these materials was 4 inches/minute (10.2 cm/min) as tested in a horizontal position. A 1966 revision required that certain materials be self-extinguishing in the vertical position within an 8-inch (20.3-cm) char length. In May 1972 the allowable char and/or burn limit was reduced to 6 inches (15.2 cm) for some materials and set at 8 inches (20.3 cm) for upholstery fabrics.

Also the authors[46] listed the hazards to life support for a typical aircraft fire. These were, in decreasing order of importance (authors opinions): (a) flame propagation, (b) smoke development, (c) attack by superheated air or gases (maximum survivable temperature), (d) asphyxiation caused by rapid depletion of available oxygen, and (e) toxicity hazards of combustion products. Another factor mentioned was the combined effect of these.

Parker, et al[163], described an approach by which polymers could be selected that would increase and improve fire safety in aircraft. The flammability and thermal protection characteristics of a polymer were associated with the molecular structure and the thermochemical properties. It was demonstrated that improved fire safety could be attained by using polymers with desired thermochemical properties.

Other aspects of the problem also were discussed. Included were the following: (a) fire threat versus fire hardening; (b) the development of a fire resistant materials technology base; (c) heat rejection mechanisms of char-forming polymers; (d) the thermodynamic analysis of one-dimensional char-forming pyrolysis; (e) the prediction of char yields of polymers from molecular structure; (f) the application of polycyclic aromatic polymers as base materials for fire protection; (g) the application of high char-yield polymers for the design and construction of aircraft modules.

A large portion of the article[163] was concerned with char-forming polymers. Some of the more pertinent points brought out with respect to these materials are given below.

1. Char-forming materials are generally cross-linked polycyclic aromatic polymers. Examples of high char-yield organic polymers are aromatic heterocyclics, polyimides, and polyquinoxalines.

2. The use of fire suppressant additives and fluoropolymers to reduce flammability may increase toxic gas and smoke production. Char-forming polymers can reduce flammability and also reduce toxicity and smoke production.

3. The anaerobic determination of char-yield is a definite, reproducible thermochemical property which can be obtained by thermogravimetric analysis at modest heating rates to 800°C (1472°F) in pure nitrogen.

4. Isocyanurates at 40% or more char-yield give the best combination of fire isolation properties and flammability characteristics.

In the work by Fang[164], various types of upholstered chairs and wood cribs were burned within the confines of a ventilated compartment.

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[163] *J. A. Parker, D. A. Kourtides, R. H. Fish, and W. J. Gilwee, Jr., "Fire Dynamics of Modern Aircraft from a Materials Point of View," Report No. AGARD-CO-166, Document No. AD-A018 180, U.S. Department of Commerce, National Technical Information Service, 5285 Port Royal Road, Springfield, Virginia 22161, October 1975.*

[164] *J. B. Fang, "Measurements of the Behavior of Incidental Fires in a Compartment," Report No. NBSIR-76-679, Center for Fire Research, Institute for Applied Technology, National Bureau of Standards, Washington, D.C. 20234, March 1975 (COM-75-10419).*

The main concern or objective of this work was to characterize the fire environment resulting from incidental fires of medium intensity. This was accomplished by measuring the levels and ranges of temperature rise, the incident heat flux, the duration of burning, the rate of heat release, and the rate of smoke production associated with these fires. The burning of a standardized wood crib array was reported to generate a reproducible fire which adequately represented the basic features of incidental fires of moderate intensity.

In the experiments conducted during the course of this program[164], upholstered chairs of various types, obtained from a used furniture outlet, were placed into a test compartment whose dimensions were 2.9 m x 3.2 m x 2.4 m high (9.5 ft x 10.5 ft x 7.9 ft high). Commercial radiometers and heat flux meters were placed at preselected locations within the compartment. Direct measurement of the rate of weight loss was accomplished by means of four strain-gauge type load cells located at the corners of a 0.94 m x 1.60 m (3.1 ft x 5.2 ft) platform. Temperatures at selected locations were monitored by chromel-alumel thermocouples of 0.5mm (0.02 in) diameter. Smoke levels were measured by means of a photometric system using the principle of light attenuation. Data from the thermocouples, radiometers, and heat flux meters were recorded on a high speed digital acquisition system, as well as punched on paper tape. The outputs of smoke meters and load cells were monitored by strip chart recorders. Ignition sources employed throughout included methamine "timed burning" tablets for chairs and ethyl alcohol in a steel pan for wood crib tests.

Specific data were obtained and summarized on the duration of burning, the maximum rate of weight loss, temperature of the hot gases, rates of heat transfer to the surroundings, the smoke generation at the peak of the fire, and the maximum distance at which specimen indicators were affected. Examples of some of the findings reported included:

a. Generally, it was determined that the hazard due to high temperatures within the compartment preceded the hazard due to smoke production and accumulation. Temperatures ranged from 45°C to 420°C with a mean of 180°C (113°F to 788°F, mean 356°F); levels of incident heat flux ranged from 0.5 W/cm^2 to 5.5 W/cm^2 with a mean of 2.2 W/cm^2. These temperatures and heat flux levels are capable of causing the spontaneous ignition of any combustible materials that may be nearby.

b. The rate at which smoke was produced was extremely variable and was dependent upon the nature of the fuel in addition to the size and intensity of the fire. Chair cushions made of a latex foam generated the greatest amount of smoke, compared to cushions of urethane foam or cotton.

c. The primary means of energy transport was radiation. This comprised approximately 75-85% of the total energy.

d. The maximum rate of heat output and the total amount of heat energy released per unit of projected area by the test fires were estimated to be of the order of 120 kw and 2.7 x 10^4 J/cm^2 for fires in a waste receptacle, 320 kw and 15.0 x 10^4 J/cm^2 for large wood crib fires, 130 kw and 5.8 x 10^4 J/cm^2 for small wood crib fires, and 870 kw and 16.0 x 10^4 J/cm^2 for furniture fires of medium or moderate intensity.

e. The peak heat flux level varied widely in the immediate vicinity of the test fire. It ranged from approximately 0.9 W/cm^2 for cotton padded chairs to 8.5 W/cm^2 for those chairs padded with plastic foam.

A survey by Damant[10] presented some of the flammability characteristics of flexible polyurethane foam. The smoldering tendencies and flaming characteristics of 37 samples of materials were determined under a variety of ignition sources. These included (1) conventional foams, to which no flame retardants were added, (2) flame retarded foams, to which chemicals were added to improve their fire resistance characteristics, and (3) high-resiliency foams, which were inherently flame retardant by virtue of their manufacturing process.

In this work[10] the results of the vertical and horizontal flame tests indicated that the orientation or geometry of the test specimens significantly influenced the burn characteristics of the materials. The most severe cases were those in which the sample was in a vertical position. All conventional urethanes were totally consumed in the vertical flame tests, the high-resiliency urethanes demonstrated good flame resistance characteristics, and the flame retarded materials produced varied results. In the horizontal flame tests the conventional urethanes also were totally consumed. Burn rates were nearly proportional to nominal density, ranging from 35.3 cm/min (13.9 in/min) for low density foams to 11.4 cm/min (4.5 in/min) for the high density materials. A comparison of the test data showed that the burn rates of materials in the vertical orientation were greater than horizontally positioned samples by a factor of 2.9-7.8. The overall average burn rate was higher by a factor of 5.1. The length of flame char in vertical flame tests was greater than flame char lengths in horizontal tests by a factor of 1.6.

An article by Factor[165] presented a detailed discussion of the theory of polymer burning and the theory of polymer flame retardance. Major areas included in the article were (a) a model (candle-like) of polymer burning, (b) the theory of flame retardance, both vapor phase and condensed phase flame inhibition, and (c) the mechanism of smoke formation. Some of the major points presented in these areas included:

a. Polymers generally burn in a manner similar to candles (candle-like model). In this model, external heat causes the polymer to

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[165] *A. Factor, "The Chemistry of Polymer Burning and Flame Retardance," J. Chem. Educ., 51, (7), 453-456 (July 1974).*

decompose in the condensed phase, producing volatile fuel gases which react with oxygen in the vapor phase as a flame which in turn produces more heat. Surface oxidation is thought to play a significant role in the mechanism by which fuel gases are produced during the burning of most polymers.

b. Flame retardance in plastics is generally achieved by the incorporation of compounds containing flame retarding elements into the base or starting polymer. In the vapor phase inhibition of flame, a material that lowers the concentration of chain carrying free radicals or increases their rate of termination will successfully prevent flame spread. Two modes of solid (condensed) phase flame inhibition were mentioned, cooling and formation of a char barrier. Several cooling modes were given, including the filler effect, dripping, and the use of endothermically decomposing materials in the pyrolysis zone of the burning polymer. The formation of a char serves to insulate the unreacted substrate from the heat and to contain volatile fuels and keep them from feeding the flame.

c. Results of probe studies indicate that smoke was produced by the reactions of radicals involving the formation and condensation of acetylene. It was noted that flame retardants acting in the vapor phase were determined to increase the production of smoke. This increase in smoke emission was attributed to the likelihood that these type retardants decreased the rate of early smoke-consuming hydroxyl radical reactions. Also, typical gases emitted from burning plastics included carbon monoxide, carbon dioxide, organic acids, aldehydes, halogen acids, hydrogen cyanide, hydrogen sulfide, and sulfur dioxide.

While on the subject of flame retardance, some review articles should be mentioned as a starting point for a reader desiring to pursue this topic in more detail. Among these is the article by Kasem and Rouette[166]. In this paper a critical review of the flammability and flame retardancy of commonly used fabrics was given. The following topics was discussed: (a) the flammability characteristics of fabrics (factors affecting fabric flammability, mechanism of burning of fabric, measurement of fabric flammability); (b) the technology of flame retardancy (development of flame retardancy, techniques of fabric flame retardation, synergism in flame retardancy); (c) the mechanism of flame retardancy (the function of some flame retardants, pyrolysis and flame retardancy, synergism in flame retardancy, dehydration theory of flame retardancy); (d) glow retardancy. Sixty-six references were given.

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[166] *M. A. Kasem and H. K. Rouette, "Flammability and Flame Retardancy of Fabrics: A Review," J. Fire & Flammability, 3, 316-329 (October 1972).*

A review of the state-of-the-art of antimony-halogen synergism was given by Pitts[167]. This in depth presentation included the types of compounds used, their current utility, and a discussion of the probable mechanisms involved in the flame retardancy effect. Results on the relative flame retardancies of the oxides and oxyhalides of antimony, arsenic, and bismuth were given.

Wald[168], in a review of existing and proposed flammability regulations and test methods applicable to carpets and rugs, discussed various areas of fire retardancy. Among these were the modification of polymers used in preparing the rug fibers, treating the backing material with additives, and the topical finishing approach.

Another area that should be mentioned in this review is that of employing analytical instruments and techniques to determine the flammability characteristics of materials, particularly thermal methods of analysis such as differential thermal analysis (DTA), thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC). These methods can be of value in the preliminary studies of materials, either to determine those that warrant further investigation, or to eliminate those that do not. As a brief example of the type of information and data generated by these methods the following summaries are given.

In a previously mentioned report by Gross, et al[50], the thermal decomposition of some aircraft cabin materials was evaluated by thermogravimetric analysis (TGA), differential thermogravimetric analysis (DTGA), and differential scanning colorimetry (DSC). TGA provided data in terms of weight as a function of temperature, DTGA gave data on the rate of weight loss as a function of temperature, and DSC gave data on exothermic and endothermic reactions as a function of temperature.

The thermal degradation of flame-retarded and unretarded polymers was investigated by thermogravimetric analysis and comparative differential scanning calorimetry techniques[3]. Among the polymers studied were polystyrene, polyester, and acrylonitrile-butadiene-styrene (ABS). The temperature at which physical or chemical changes occurred were obtained from the DSC curves, which are distinct for each material. The results indicated that the major weight loss for the flame retarded polymers occurred at higher temperatures than for the untreated polymers. In addition, an increase in the quantity of flame retardant produced initial decomposition at a lower temperature, but a greater amount of char was obtained.

[167] *J. J. Pitts, "Antimony-Halogen Synergistic Reactions in Fire Retardants," pp. 37-70, Flammability of Cellular Plastics, Vol. 8, Fire and Flammability Series, Technomic Publishing Co., Inc., 265 W. State St., Westport, Conn. 06880, 1974.*

[168] *W. Wald, "Carpets and Rugs: Potential for Fire Retardant Chemical Treatments," J. Fire & Flammability/Consumer Product Flammability, 2, 314-319 (December 1975).*

The objective of some work reported by Jackson[169] was to develop a combined mass spectroscopy-thermogravimetric system which would enable the gases evolved from the thermal decomposition of polymers to be identified. Among the decomposition products identified in this manner were carbon dioxide, water, toluene, benzene, ammonia, carbon monoxide, and several hydrocarbons.

Also, DTA was employed to determine the temperature at which chemical and physical changes occurred in a 200 mg sample of plastic materials heated at 5-10°C/min (41-50°F/min) and TGA to determine the weight change of these materials as a function of temperature[94]. In a paper dealing with the thermal stability of polyphosphazenes[118], thermogravimetric and differential thermogravimetric analyses were made at different heating rates in air and nitrogen atmospheres. A non-isothermal procedure used in monitoring the weight change as a function of temperature proved to be the most useful in this work. A non-isothermal TGA technique provided data from which the activation energies of the chemical degradation process could be determined.

V. FLAMMABILITY-MISCELLANEOUS

In the previous sections of this report several articles have been reviewed that were concerned with specific aspects of the overall problem of flammability (flame spread, smoke, toxicity, etc.). Summaries of these reports were presented in order to familiarize the reader with some of the details and potential problem areas associated with these topics.

In this section, the mention of additional articles dealing with flammability is made for the purpose of providing still more sources of information to the interested reader. Most of the articles are of a general nature, or deal with several phases of flammability.

Two of the more applicable articles with respect to this program were by Litant[170] and by Wiggins[171]. In the first of these[170], various fire safety problems associated with ground mass transportation were discussed. It was reported that a large majority of the fires originating in passenger compartments were the result of arson, seat cushions being a prime target. The most widely employed types of seat cushion materials were given as polyurethane, latex, or neoprene foams, the last being the

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[169] *A. G. Jackson, "Thermal Degradation of Polymers Using Mass Spectroscopy-Thermogravimetric Analysis Techniques," Report No. AFML-TR-71-60, Part II, Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio 45433, April 1972 (AD-900 861L).*

[170] *I. Litant, "Fire Safety Problems in Ground Mass Transportation," J. Fire & Flammability, 8, 255-261 (July 1977).*

[171] *J. H. Wiggins, "A National Program for Fire Safety in Transportation," Fire Research, 1, 209-221 (1977/78).*

most resistant to flame spread. Neoprene foam, although emitting dense black smoke and hydrogen chloride gas, has a reported flame spread index of less than 10, as determined by the ASTM E-162 Radiant Panel Test. By comparison, polyurethane foams have flame spread index values of more than 300, many being significantly greater than 300.

The article by Wiggins[171] presented some general outlines for a national program to provide fire safety in transportation. It was reported that the rules regarding the flammability of materials employed in the passenger compartments of transportation vehicles were to be concerned with aspects of safety, environment, ecology, energy, effectiveness and economy. A discussion of the rule making process in all government agencies as well as the Department of Transportation was given. The article also presented an historical perspective on fire losses, a discussion of scientific risk management, and a discussion on technology assessment integrated with scientific risk management. In addition, some recommendations were given. Among these were (1) the establishment of a high quality data bank along with an upgrading of fire-accident data, (2) the designation of a central organization or authority to coordinate research efforts between different organizations, and (3) the monitoring of laws, regulations, policies, etc., to eliminate conflicts and insure compliance.

Two additional reports presented statistical data on aircraft accidents involving fires. While this data is not directly applicable to rail passenger cars, other information contained in these reports was of interest. In the first of these[172] the principal causes of the hazardous environment associated with fires were given and included (1) thermal conditions, such as radiant heat, hot gases, hot air, and flame; (2) products of combustion, such as carbon monoxide and carbon dioxide; (3) products of pyrolysis, examples of which are hydrogen chloride, chlorine gas, hydrogen fluoride, bromine, ammonia, and hydrogen cyanide. Of these, thermal conditions were reported to be the limiting factors in escape and survival time. In addition to statistical data the other report[173] traced the development of regulations concerned with the flammability of aircraft materials.

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[172] *G. V. Lucha, M. A. Robertson, and F. A. Schooley, "An Analysis of Aircraft Accidents Involving Fires," Report No. NASA-CR-137690, National Aeronautics and Space Administration, Ames Research Center, Moffett Field, California 94035, May 1975 (N76-16051).*

[173] *National Transportation Safety Board, "Special Study -- U.S. Air Carrier Accidents Involving Fire, 1965 Through 1974, and Factors Affecting Survivability," Report No. NTSB-AAS-77-1, Bureau of Technology, National Transportation Safety Board, Washington, D.C. 20594, February 1977 (PB-267 [illegible]).*

Robertson[174] proposed a method by which the parameters or factors that influence the life safety hazard resulting from fires could be classified. These hazard components were (1) the lack of oxygen (oxygen deficiency), (2) toxic combustion products, (3) smoke, (4) hot gases, and (5) exposure to flames. It was suggested that the quantity of combustible materials effluent during a fire might be used to measure potential fire gas hazard.

An article by Castle[175] presented data illustrating the differences in fire environments and discussed the function of various parameters in fire protective materials which provide protection against these environments. Included in the article are the definition and measurement of fire environments (temperature of combusting gases, radiant heat flux, convective heat flux); heat flux data and fire tests (ASTM E-119 tests, pool fires, pit fires, and subscale tests); test selection; material behavior in various fire environments; and the types of fire protection materials.

Harmathy[176] discussed the conventional concept of fire resistance and introduced a newer concept. The fire resistance of compartment boundaries is usually considered a measure of their capability to prevent the spread of a fire. In these tests, materials are exposed to a fire on only one side. In reality, these materials may become exposed to fire on both sides, in which case the standard tests (such as ASTM E-119) would not provide an accurate measure of fire resistance. A discussion of the calculations required for assessing the performance of some key building components in fires was presented.

A critical evaluation of the rules contained in FAR 25-853, 25-855, and 25-1191 with Appendix F was discussed by Godfried[177]. Four test methods specified by the FAR were described. These included a fire proof test, a fire resistance test, a vertical test,and a horizontal test. It was demonstrated that the application, test requirements, and test methods criteria could on occassion provide questionable fire safety. Among the

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[174] *A. F. Robertson, "Effluent Fire Product - A Crude Approach to Fire Gas Hazard Assessment," Fire Technology, 10, (2), 115-128 (May 1974).*

[175] *G. K. Castle, "The Nature of Various Fire Environments and the Application of Modern Material Approaches for Fire Protection of Exterior Structure Steel in Them," J. Fire & Flammability, 5, 203-222 (July 1974).*

[176] *T. Z. Harmathy, "Fire Resistance Versus Flame Spread Resistance," Fire Technology, 12, (4), 290-302 (November 1976).*

[177] *L. M. Godfried, "Critical Evaluation of Todays Fireproof Testing of Aerospace Materials," in Aircraft Fire Safety, 45th Meeting of the AGARD Propulsion and Energetics Panel held at the Palazzo Aeronautica, Rome, Italy, 7-11 April 1975, AGARD-CP-166, Document No. AD-A018 180, U.S. Dept. of Commerce, National Technical Information Service, 5285 Port Royal Road, Springfield, Virginia 22161, October 1975.*

parameters discussed as being contributing factors to the variations in test data were the differences in the methods employed in conditioning samples prior to testing, differences in the thickness of the samples, different ignition points on the samples, differences in specified flame temperatures and ignition times, and a lack of consideration to the effects of material combinations on the fire.

Some additional information concerning the flammability of plastics or polymers included the following:

a. A literature survey on the development and evaluation of flame-proof, self-extinguishing, and fire-retardant polymers[178]. Of particular interest was the mechanism involved in flame-retarding, the effects of smoke on visibility, and the toxic hazards of gaseous combustion products. It was indicated that no single factor served to characterize the flammability of materials. Absorptivity, emissivity, specific heat, thermal conductivity, polymer degradation temperature, convective cooling rate, and sample geometry preclude the use of ignition time as an objective measure of flammability. Also, no one test seemed likely to be developed that could measure the flammability of all materials used under all conditions.

b. A description of the procedures used for characterizing and evaluating structural plastics was given by Jurevic[179]. Included in the section on thermal properties were methods to determine flammability (ASTM D-635 and Method 2021 of Federal Test Method Standard No. 406), thermal conductivity (ASTM C-177), and thermal expansion (ASTM D-696). Details of each test were given.

c. A literature survey by Hilado[180] covered the fire behavior of plastics. Among the areas discussed in the review were (a) combustion and fire spread, (b) fire retardants, (c) smoke and toxicity, and (d) flammability regulations. Eighty-four references were given.

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[178] *A. D. Delman, "Advances in the State-of-the-Art of Flame-Resistant Polymer Development," Lab Project 940-31, Progress Rept. 7, SF 020-03-06, Task 1000, Physical Sciences Division, U.S. Naval Applied Science Laboratory, Brooklyn, New York 11251, August 1968 (AD-838 689L).*

[179] *W. G. Jurevic, "Structural Plastics Applications Handbook. Supplement I. Test Methods," Report No. AFML-TR-67-332, Supplement I, Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio 45433, June 1969 (AD-858 389).*

[180] *C. J. Hilado, "An overview of the Fire Behavior of Polymers," Fire Technology, 9, (3), 198-208 (August 1973).*

d. Hertz[181] reported on some work to develop and optimize lightweight, laminated plastic systems that were non-burning and generated little smoke and were to be used in a space shuttle environment. Panels were tested for flammability, optical smoke density, and off-gassing. Polyimides were determined to be significantly more flame resistant than phenolics, epoxies, or polyesters.

e. An article by Barry and Newman[182] discussed the flammability, thermal effects, and the toxicity of gases from the pyrolysis of synthetic polymeric materials. The authors stressed the need for research on synergistic interactions, and reported that the prospect of using computers for toxicity analysis was excellent. They also suggested that programs might be developed to predict potential synergistic by-products produced from interactions between combustion products.

f. Nonmetallic polymers were investigated for potential use in aircraft interiors. The flame resistant characteristics and toxicity data of these materials were measured[183].

g. Junod[83] reviewed the literature and presented a discussion of (a) hazards of plastics in fire environments, (b) gases emitted, (c) the factors that influence these emissions, (d) the characteristics of toxic gases, and (e) the results of laboratory studies.

h. The thermochemical and flammability properties of some typical thermoplastic materials were determined and reported by Kourtides, et al[184]. Among these properties were (a) glass transition and melting temperatures, (b) changes in enthalpy (by differential scanning calorimetry), (c) thermogravimetric analysis in anaerobic and oxidative environments, (d) oxygen index, (e) smoke emission, (f) relative toxicity of pyrolysis products, and (g) some selected physical properties.

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[181] *J. Hertz, "Development of Lightweight Reinforced Plastic Laminates for Spacecraft Interior Applications," Report No. MA-456T, General Dynamics Corp., Convair Division, 5001 Kearny Villa Road, San Diego, California 92138, December 1975 (N76-18238).*

[182] *T. J. Barry and B. Newman, "Some Problems of Synthetic Polymers at Elevated Temperatures," Fire Technology, 12, (3), 186-192 (August 1976).*

[183] *G. Haley, B. Silverman, and Y. Tajima, "Development of Fire Resistant, Nontoxic Aircraft Interior Materials," NASA-CR-137920, National Aeronautics and Space Administration, Ames Research Center, Moffett Field, California 94035, September 1976 (N77-14205).*

[184] *D. A. Kourtides, J. A. Parker, and C. J. Hilado, "Thermoplastic Polymers for Improved Fire Safety," NASA-TM-X-73185, National Aeronautics and Space Administration, Ames Research Center, Moffett Field, California November 1976 (N77-14206).*

i. Improved aircraft interior materials were reported to have been developed by the modification of polymer structure, process parameters, and mechanical configurations[185].

j. Molded polyvinyl chloride and neoprene foam were modified in order to improve their fire safety characteristics. Fire- and smoke-retardant additives were incorporated into the polymer systems of both materials. In addition, intumescent coatings were used with the polyvinyl chloride system[186].

k. A data base of residential fire accidents was developed by Slater[187] to aid in the assessment of fire hazards associated with burning plastics. Case histories were compiled based on criteria that (1) an identifiable plastic product had a significant part in the fire, and (2) the sequence of events could be at least partially reconstructed.

ℓ. Burn, smoke emission, and toxicity tests were conducted to determine the fire resistivity of nonmetallic materials considered for use in aircraft seats[188].

m. More recently Kourtides and Parker[189] have studied the thermochemical and flammability characteristics of some typical thermoplastic materials in use or considered for use in aircraft interiors. Among these characteristics were (a) thermal mechanical properties (glass transition temperature, melting point), (b) changes in polymer enthalpy by differential scanning calorimetry, (c) thermogravimetric analysis in an oxygen-free and an oxidative environment, (d) oxygen index, (e) smoke emission, and (f) the relative toxicity of the volatile products of pyrolysis. Materials were given a relative ranking for flammability,

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[185] *J. Gagliani, U. A. K. Sorathia, and A. L. Wilcoxson, "Development of Fire-Resistant, Low Smoke Generating, Thermally Stable End Items for Aircraft and Spacecraft," NASA-CR-151472, National Aeronautics and Space Administration, Lyndon B. Johnson Space Center, Houston, Texas 77058, June 1977 (N77-28301).*

[186] *L. Parts, R. D. Myers, C. A. Thompson, and N. F. May, "Flame- and Smoke-Retardant Polymer Systems," MRC-DA-722, Monsanto Research Corp., Dayton Laboratory, Dayton, Ohio 45407, February 1978 (AD-A049 923).*

[187] *J. A. Slater, "Development of a Data Base for Assessing Plastics Fire Hazards," Report No.NBSIR-78-1422, Center for Fire Research, National Bureau of Standards, Washington, D.C. 20234, April 1978 (PB-280 027).*

[188] *L. L. Fewell, E. L. Trabold, and H. H. Spieth, "Fire Resistivity and Toxicity Studies of Candidate Aircraft Passenger Seat Materials," J. Fire & Flammability, 9, 377-402 (July 1978).*

[189] *D. A. Kourtides and J. A. Parker, "Assessment of Relative Flammability and Thermochemical Properties of Some Thermoplastic Materials," Polymer Eng. & Sci., 18, (11), 855-860 (August 1978).*

smoke generation, and toxicity. It was noted that flammability characteristics of polymers varied with sample thickness, the variation being more significant in the oxygen index determinations than in the smoke evaluation tests. Toxicity studies were made using albino mice. Parameters measured included time to incapacitation (T_i) and time to death (T_d), the choice of which as the criterion affects the relative rankings. On the basis of T_d, polyphenylene oxide and chlorinated polyvinyl chloride homo polymer were the least toxic. On the basis of T_i, however, these were among the most toxic.

Another area in which a considerable amount of flammability assessment work was performed was that of seat materials. This included work on various types of foams and upholstery fabrics, as well as textiles in general. Some of this reported work included:

a. The formulation, screening, optimization and characterization of open-cell, fire-resistant, low-smoke emitting, thermally stable, resilient polyimide foams suitable for seat cushions in commercial aircraft and spacecraft. Polyimide resins were reported to undergo intumescent behavior during combustion without producing detectable amounts of smoke or toxic by-products[190].

b. The study by McCarter[191] on the smoldering behavior of various flexible polyurethane foams. Comparisons of smoldering behavior were made on the basis of oxygen index values, density, permeability, and charring tendencies of the foams. It was reported that foams based on conventional polyols exhibited distinctly different combustion behavior than foams based on grafted polyols, as well as foams containing fire retardants. This study indicated a significant correlation between the smoldering and charring tendencies of polyurethane foams. In addition, the tendency of a foam to smolder was reported to be strongly influenced by the nature of the crosslinks in the foam.

c. Damant, in a previously mentioned report[10], surveyed the flammability characteristics of a flexible polyurethane foam used as an upholstery filling material using both smoldering and flaming conditions. Heat sources used to study smoldering conditions included cigarettes, smoldering strips of fabric, and combinations of these. For flaming conditions, methenamine tablets were used as well as flames in a vertical, horizontal, and 45° sample orientation.

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[190] *J. Gagliani, "Fire Resistant Resilient Foams," Report No. NASA-CR-147496, National Aeronautics and Space Administration, Johnson Space Center, Houston, Texas 77058, February 1976 (N76-18278).*

[191] *R. J. McCarter, "Smoldering of Flexible Polyurethane Foam," J. Consumer Product Flammability, 3, 128-140 (June 1976).*

d. The flammability of polyurethane foams and their use with protective coatings as a means to reduce the probability of fire involvement was studied by Smith[192]. Results of tests indicated that a coating composed of portland cement, lime, sand, and water retarded and delayed the flame spread and the fuel contribution of foamed polyurethane.

e. The effects of heat transfer, fuel load, sample geometry, and other scaling parameters encountered in full-scale fires involving foams were evaluated by Tatum, et al[193].

f. Damant[194] reported on an evaluation of the flammability characteristics of commonly used upholstery materials exposed to both flaming and non-flaming (smoldering) conditions. In some other work[195] the smoldering characteristics of fabrics employed as covering materials on upholstered furniture were studied with particular emphasis placed on the fabric/fill interface exposed to a lighted cigarette. Some of the parameters investigated were the effects of substrate, and the effects of fabric variables such as fiber content, weight, backcoating, direction, weave, and construction. Twenty-nine general conclusions were given along with 30 references.

g. A screening test to determine the smolder susceptibility of seat fabrics was described by Hilado and his colleagues[196]. The test consisted of placing a lighted cigarette in a crevice between two cushions filled with polyurethane flexible foams. Results indicated that 100% cotton and 100% rayon fabrics had the greatest degree of susceptibility to smoldering, based upon smolder time and weight loss. Smolder time was reported to be the most reproducible response. Poor reproducibility was obtained on the basis of weight loss, char weight, and burn length.

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[192] *A. Smith, "Fire/Flammability Test of Polyurethane Foams and Protective Coatings," Technical Report M-129, Constructive Engineering Research Laboratory, P. O. Box 4005, Champaign, Illinois 61820, July 1976 (AD-A028 386).*

[193] *P. A. Tatum, P. D. Marshall, and F. W. Williams, "Modified Smoldering Test of Urethane Foams Used in Anechoic Chambers," NRL Report 8093, Naval Research Laboratory, Washington, DC 20375, March 1977 (AD-A038 439).*

[194] *G. H. Damant, "A Survey of Upholstery Fabrics and Their Flammability Characteristics," J. Fire & Flammability/Consumer Product Flammability, 2, 5-57 (March 1975).*

[195] *G. H. Damant and M. A. Young, "Smoldering Characteristics of Fabrics Used as Upholstered Furniture Coverings," J. Consumer Product Flammability, 4, 359-379 (December 1977).*

[196] *C. J. Hilado, D. L. Brandt, and G. H. Damant, "Smoldering Tests on Furniture and Aircraft Seat Fabrics," J. Consumer Product Flammability, 5, 123-134 (September 1978).*

h. Benisek and Phillips[197] described an attempt to evaluate the burning behavior, along with the smoke and carbon monoxide emission, of several upholstery fabrics. Evaluations were conducted on individual materials and on composites (upholstery fabrics plus foam cushioning). The results indicated that the burning behavior and toxic gas emission of composite upholstery samples could not be predicted from the tests conducted on the individual materials. It was noted that all flammability parameters were inter-dependent.

i. Simcock[198] described a procedure to measure the resistance to flammability of textiles in both a horizontal and vertical orientation.

j. Stanton[199] reported on an evaluation of fabrics based upon heat transmission from direct flame contact as well as for flammability. Some characteristics determined to affect fabric heat transfer included fiber thermal stability, thickness, weave or knit pattern, air permeability, and bulk density.

k. Freeston, et al[200], determined the flammability characteristics of a series of fabrics in air and also in oxygen-rich environments. Among the parameters measured were ignition temperature, the time for ignition at various temperatures, burning rates, and the limiting oxygen index. In addition, measurements were made to determine heat transfer through the fabrics.

ℓ. Ernst[201] described test methods used to evaluate the thermal response of materials exposed to varying degrees of thermal environments.

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[197] *L. Benisek and W. A. Phillips, "The Importance and Relevance of Burning Behavior, Smoke, and CO Emission from Upholstered Seating," J. Consumer Product Flammability, 5, 96-110 (June 1978).*

[198] *C. M. Simcock, "Methods of Assessing the Flame-Resistance of Textiles and of Clothing Assemblies," Report No. UK-9, Stores and Clothing Research and Development Establishment, Army Department, Ministry of Defence, United Kingdom, 1969 (AD-843 266).*

[199] *R. M. Stanton, "Heat Transfer and Flammability of Fibrous Materials," Technical Report AFML-TR-70-238, Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio 45433, February 1971 (AD-881 723).*

[200] *W. D. Freeston, Jr., J. S. Panto, L. Barish, and M. M. Schoppee, "The Mechanical,Flammability, and Dyeability Properties of High Temperature, Organic Fibers," Report No. AFML-TR-70-267, Part II, Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio 45433, May 1971 (AD-888 789L).*

[201] *E. D. Ernst, "Laboratory Test Techniques for Evaluating The Thermal Protection of Materials When Exposed to Various Heat Sources," Report No. AFML-TR-74-118, Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio 45433, March 1974 (AD-784-923).*

m. Stamm[202] discussed new standards and methods for determining the flammability of textiles.

n. Damant[203] has given a rather detailed summary of work performed by the California Bureau of Home Furnishings on furniture composites.

A considerable amount of work also has been done in which the flammability of materials employed in manned space vehicles and naval vessels (both surface and underwater types) was determined. A compilation of the papers given at a conference dealing with the fire safety of materials used in spacecraft was reviewed[89]. The categories of papers presented were (1) flammability requirements and test techniques, (2) materials development, (3) configuration control and materials applications, and (4) special tests. Examples of the types of work reported are:

a. A paper by Johnston and Pippen[204] that described nine tests employed to screen materials for use in the Apollo space program;

b. Component flammability testing to determine the flammability characteristics of a variety of different shapes, sizes, and configurations that made up a functional assembly system[205];

c. The use of a low-density, polyurethane-based foam to suppress a fire and to protect structural components[206].

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[202] *G. Stamm, "Current Status of Testing Textiles for Flammability and Combustibility, Part 2," Report No. FTD-HC-23-1538-74, Translation Division, Foreign Technology Division, Wright-Patterson Air Force Base, Ohio 45433, April 1974 (AD-918 702L).*

[203] *G. H. Damant, "Flammability Aspects of Upholstered Furniture," J. Consumer Product Flammability, 3, 21-61 (March 1976).*

[204] *R. L. Johnston and D. L. Pippen, "Development of Materials Screening Test for Oxygen-Enriched Environments," pp. 23-27 in Conference on Materials for Improved Fire Safety, NASA-SP-5096, Technology Utilization Office, National Aeronautics and Space Administration, Washington, D.C. 20546, 1971 (N72-16409).*

[205] *G. R. Primeaux, "Flammability Testing of Components," pp. 29-33 in Conference on Materials for Improved Fire Safety, NASA-SP-5096, Technology Utilization Office, National Aeronautics and Space Administration, Washington, D.C., 1971 (N72-16409).*

[206] *R. H. Fish, "The Performance of Lightweight Plastic Foams Developed for Fire Safety," pp. 103-110 in Conference on Materials for Improved Fire Safety, NASA-SP-5096, Technology Utilization Office, National Aeronautics and Space Administration, Washington, DC 20546, 1971 (N72-16409).*

Alger, et al[207], reported a study made of fire characteristics as a function of typical conditions found on board Navy ships. Burning rates, fuel consumption, heating patterns, and the measurement of oxygen, carbon dioxide, and carbon monoxide at the time of extinguishment were discussed. Results of the tests indicated that (a) flaming combustion stopped when the oxygen concentration fell within a 10-15% range, while smoldering combustion continued to about 6% oxygen; (b) time to self-extinguishment was inversely proportional to the burning rate which in turn was controlled by the type of fuel and geometry; (c) oxygen depletion did not cause the burning rate to decrease dramatically until just before extinguishment.

A study whose purpose was (1) to determine the influence of sample orientation, ambient-gas composition, and pressure on the burning rate of a combustible material, and (2) to use small-scale tests to make a preliminary evaluation of fire-resistant materials such as textiles, elastomers, and insulating materials was reported by Cook, Meierer and Shields[208]. It was reported that the flammability hazard of a material was the greatest when the orientation was such that flame propagation was in a vertical direction. In addition, the burning rates of similar materials were reported to be more accurately measured with the test samples at a angle of 45° (the fastest and therefore most hazardous orientation being 90°).

The objective of a program reported by Johnson and Stahly[209] was to develop PN $C\ell_2$ polymers or derivatives that would impart fire-retardance to four types of resins. These were polyester, epoxy, polyurethane, and phenolic. The fire retardancy, as well as smoke and toxicity properties, also were determined.

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[207] *R. S. Alger, S. J. Wiersma, R. G. McKee, W. H. Johnson, F. I. Laughridge, and L. L. Wiltshire, "Ship Fire Characteristics: Part I -- Sealed Compartments," Report No. NSWC/WOL/TR-125, Research & Technology Department, Naval Surface Weapons Center, White Oak Laboratory, White Oak, Silver Spring, Maryland 20910, November 1976 (AD-A044 543).*

[208] *G. A. Cook, R. E. Meierer, and B. M. Shields, "Screening of Flame-Resistant Materials and Comparison of Helium with Nitrogen for Use in Diving Atmospheres," Contract No. N00014-66-C0149, Office of Naval Research, U.S. Navy, Washington, D.C. 20375 , March 1967 (AD-651 583).*

[209] *R. D. Johnson and E. E. Stahly, "Development of Flame-Retardant Plastic Systems for Shipboard Application," RES 70-38, Project No. S4643, Task No. 13983, Contract No. N00024-69-C-5431, Naval Ship System Command, Department of the Navy, Naval Ship Engineering Center, Code 6101E, Center Bldg., Prince Georges Center, Hyattsville, Maryland 20782, July 1970 (AD-873 707L).*

Supkis[210] discussed a program to evaluate selected fire-retardant materials for possible application to commercial aircraft. Emphasis was placed on the results of flammability screening tests conducted on the materials, including limiting oxygen index, smoke generation, and thermogravimetric analysis (TGA). The last test (TGA), which measured weight loss as a function of increasing temperature, provided a thermal degradation profile of a material. A TGA criterion of 204°C (400°F) was based on studies that indicated humans cannot survive more than several seconds when exposed to a temperature of 204°C (400°F).

In a related area, the response of gas and smoke detectors was evaluated with an aim toward developing improved on-board fire protection for aircraft[211]. The detectors evaluated included photoelectric, ionization, and gas sensor types. Results indicated that both ionization and photoelectric detectors were nearly equal in detecting pyrolysis products from synthetic polymers, and only ionization detectors were sensitive to the combustion products from simple cellulosic materials.

The characteristics of fires within enclosures were reviewed in an article by Martin, Renner, and Jones[212]. Included were (a) basic fire behavior in enclosures, (b) experimental work with model-room fires, and (c) empirical studies of ventilation-controlled or well-ventilated enclosure fires. It was pointed out that ventilation was a very important parameter in determining the behavior of an enclosed fire. Under most circumstances, ventilation will determine the maximum burning rate.

VI. ADDED FLAMMABILITY INFORMATION

In addition to the work mentioned in the previous sections, several reports were received at a time later than that considered convenient for inclusion in the appropriate categories of this report. Most of these were concerned with the measurement of smoke or the toxicity of combustion products. These are summarized briefly below.

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[210] *D. E. Supkis, "Refurbishment of NASA Aircraft with Fire-Retardant Materials," Report No. NASA-TM-X-58165, National Aeronautics and Space Administration, Lyndon B. Johnson Space Center, Houston, Texas 77058, October 1975 (N76-13040).*

[211] *S. J. Wiersma and R. G. McKee, "Fire Detector Response in Aircraft Applications," Aviation, 12-18 (August/September 1978).*

[212] *S. B. Martin, R. H. Renner, and R. E. Jones, "Application of Fire Fundamentals to Modes of Macroscale Phenomena from Nuclear Weapon Bursts," USNRDL-TR-67-114, U.S. Naval Radiological Defense Laboratory, San Francisco, California 94135, July 1967 (AD-659 982).*

A series of papers was presented at an ASTM symposium on the subject of the measurement and control of smoke in building fires[213]. Among the areas discussed were (a) the use of a tunnel test to classify smoke evolved during surface burning, (b) an evaluation of the XP2 smoke density chamber, (c) a method to measure visibility in smoke and (d) the development of a laboratory test to measure smoke photometrically.

Mickelson and Einhorn[214] reported that some of the primary parameters that influence the development of smoke in polymers are the nature and functionality of the monomers, the degree of aromaticity in the polymer backbone, the molecular weight per crosslink density, and the additives that may be incorporated into the polymer system to retard combustion. The effect of additives on the smoking tendency of urethane foams also was discussed.

A report describing an interlaboratory evaluation of the NBS smoke density chamber method to measure the smoke evolved from burning samples was given by Lee[215]. The median coefficient of variation of reproducibility was reported to be 7.2% for non-flaming conditions and 13% under flaming conditions.

Chien and Seader[216] discussed their work involving the measurement of smoke in a modified NBS smoke density chamber using natural and synthetic polymeric materials. Included were discussions on the theoretical aspects of the optical-transmission method and the physical aspects of smoke development.

A report on the measurement of smoke from various materials in both vertical and horizontal positions was given by Breden and Meisters[217].

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[213] *American Society for Testing Materials, "Symposium on Fire Test Methods-Restraint and Smoke 1966," ASTM Special Technical Publication No. 422, American Society for Testing Materials, 1916 Race St., Philadelphia, Pa. 19102, 1967.*

[214] *R. W. Mickelson and I. N. Einhorn, "The Effect of Additives on the Smoking Tendency of Urethane Foams," Division of Organic Coatings and Plastic Chemistry Preprints, Vol. 28, No. 1, April 1968.*

[215] *T. G. Lee, "Interlaboratory Evaluation of Smoke Density Chamber," Report No. NBS-TN-708, National Bureau of Standards, Department of Commerce, Washington, D.C. 20234, December 1971 (COM-72-50062).*

[216] *W. P. Chien and J. D. Seader, "Smoke Measurement in a Modified NBS Smoke-Density Chamber," Report No. NSF-RA-E-75-140, Research Applied to National Needs, National Science Foundation, Washington, D.C. 20550, April 1975 (PB-259 339).*

[217] *L. Breden and M. Meisters, "The Effect of Sample Orientation in the Smoke Density Chamber," Report No. NBSIR-76-1030, Center for Fire Research, Institute for Applied Technology, National Bureau of Standards, Washington, D.C. 20234, May 1976 (PB-263 633).*

The physiological and toxicological effects of smoke were studied using cellulosics, urethanes, polyvinyl chlorides, and Douglas fir[218]. Some additional studies also were reported using both natural and synthetic materials[219].

Birky[220] reviewed the hazards presented by the combustion products from fires. Statistics quoted indicated that 70-80% of fire fatalities were caused by smoke inhalation. Also discussed in this report were (a) the methodology for assessing smoke and toxicological hazards in a fire, (b) the analysis of combustion products, (c) the biological assessment of toxicity, (d) the mechanisms and models involved in toxicity studies, and (e) an evaluation of building codes and standards. Ninety-seven references were given as well as a tabulated summary and comparison of various methods employed to evaluate the toxicity of combustion products.

At a symposium, eighteen papers were presented[221] in four categories concerning the effects of combustion products on humans. These categories were (a) problems caused by the smoke evolved during fires, (b) casualties from smoke and fire, (c) physiological and toxicological aspects of fire exposure, and (d) the development and characterization of smoke.

The Committee on Fire Toxicology of the National Research Council[222] reviewed current methods for evaluating the toxicity of pyrolysis and

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[218] *I. N. Einhorn, M. M. Birky, M. L. Grunnet, S. C. Packham, J. H. Petajan, and J. D. Seader, "The Physiological and Toxicological Aspects of Smoke Produced During the Combustion of Polymeric Materials," Report No. NSF-RA-E-73-196, National Science Foundation, Research Applied to National Needs, 1800 G. Street, N.W., Washington, DC 20550, Sept. 1973 (PB-244 876).*

[219] *I. N. Einhorn, S. C. Packham, N. L. Grunnet, and J. H. Petajan, "The Physiological and Toxicological Consequences of Smoke Produced During the Combustion of Polymeric Materials," Report No. NSF-RA-E-75-141, Research Applied to National Needs (RANN), National Science Foundation, Washington, D.C. 20550, May 1975 (PB-259 301).*

[220] *M. Birky, "Hazard Characteristics of Combustion Products in Fires: The State-of-the-Art Review," Report No. NBSIR 77-1234, Center for Fire Research, Institute for Applied Technology, National Bureau of Standards, Washington, D.C. 20234, May 1977 (PB-267 828).*

[221] *Committee on Fire Research, "Physiological and Toxicological Aspects of Combustion Products: International Symposium," Report No. ISBN-0-309-02521-4, National Academy of Sciences, 2101 Constitution Avenue, Washington, D.C. 20418, July 1976 (PB-279 460).*

[222] *Committee on Fire Toxicology, "FIRE TOXICOLOGY: Methods for Evaluation of Toxicity of Pyrolysis and Combustion Products, Report No. 2," Report No. NAS/ACT/P-843-2, Advisory Center on Toxicology, National Research Council, 2101 Constitution Avenue, N.W., Washington, D.C. 20418, August 1977 (AD-A043 899).*

combustion products. Among the conclusions were that the screening tests currently available were not acceptable in that all have at least one shortcoming. The Committee made several recommendations for developing adequate toxicity assessment methods. These included (a) the evaluation of materials under both pyrolysis and flaming conditions, (b) small animals (rats or mice) should be used as the test model, (c) incapacitation should be considered the most important end point, (d) a minimum set of parameters should be monitored in the test chamber during animal exposures, and (e) the relative toxicity of materials should be determined by comparison with reference materials rather than attempting absolute determinations.

Among the additional material reviewed was a report by Lee and Huggett[223] on an interlaboratory evaluation of the ASTM E-84 tunnel test method. Data were collected and analyzed on flame spread, smoke, and fuel contribution. There was reported to be a between-laboratory coefficient of variation in flame spread classification of 7-29% for carpets and 18-43% for other materials that were tested. The between-laboratory coefficient of variation for smoke developed was reported to be 34-85%, while the coefficient of variation for fuel contribution was reported to be 22-117%. Causes for these variations were discussed.

Also, Hastie and McBee[224] studied the mechanism for phosphorus controlled flame retardancy in thermoplastics by means of a combination of mass spectrometric and optical spectroscopic techniques; and it was reported that two important parameters in the fire behavior of urethane foam were the type of upholstery material used to cover the foam and the rate of burning[225].

Wang[226] studied the pyrolysis of polymers at heating rates similar to those encountered during the preignition of such type materials. He developed a pyrolysis-gas chromatographic technique that provided good control of temperature, heating rate, heating time, and atmosphere.

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[224] *J. W. Hastie and C. L. McBee, "Mechanistic Studies of Triphenylphosphine Oxide-Poly(Ethyleneterephthalate) and Related Flame Retardant Systems," NBSIR-75-741, Institute for Materials Research, National Bureau of Standards, Washington, D.C. 20234, August 1975 (COM-75-11136)*

[225] *Anonymous, "Testing Plastics for Fire Behavior: Smoke Hazards Get More Attention," Modern Plastics, 47-49 (May 1976).*

[226] *R. C. Wang, "Rapid Pyrolysis of Untreated and Flame Retardant Treated Polymers," University Microfilms International, 300 N. Zeeb Road, Ann Arbor, Michigan 48106, 1978.*

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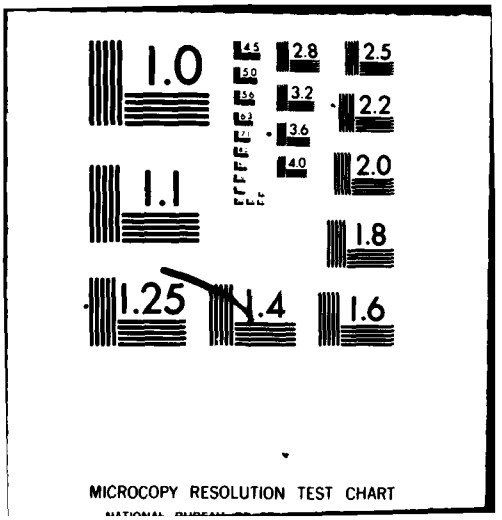
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VII. SUMMARY

A review of the literature was conducted to provide information on the flammability characteristics of materials employed in the interiors of rail passenger cars. While few articles or reports were found that dealt specifically with these type vehicles, a considerable number of articles were found that were concerned with the flammability properties of materials used in the interiors of commercial aircraft and buses (seat cushions and covers, carpeting, wall and ceiling coverings, etc.). Also, several reports described work concerned with the flammability of upholstered furniture materials. All these, in addition to articles of a general nature, were included in this review because of the general similarities involved (i.e., seating arrangement; general geometry considerations; the materials used in aircraft, buses, or furniture are used, or could be used, in rail passenger cars).

Particular attention was placed on ignition properties, flame spread, rate of combustion, heat liberation and transfer, smoke evolution, and the toxicological effects of combustion products. All these are influenced by several factors, such as geometry or orientation of the material, chemical composition, physical properties, type of combustion (flaming or smoldering), the environment to which the material is exposed, the addition of flame retardants, and the degree of ventilation experienced. Of the properties listed above, flame or fire spread rate has been reported to be the most important in transit vehicle fires[22].

In reviewing the literature one of the most frequently expressed views was that there is, at most, very little correlation between small scale tests and actual, real fire (full-scale) conditions. While small scale tests can be used to screen materials, or provide a relative ranking based on a specific property, the conditions encountered in a full-scale situation are vastly different. A small scale test can provide data only for a specific set of conditions. In a real fire environment, conditions are changing constantly.

Obviously one cannot conduct a large number of full-scale tests for every possible situation because of cost and time limitations. Prudent judgement must be exercised in order to get the maximum amount of useful information from any test program. A useful guideline for a flammability testing program was given by Steingiser[40] in which he recommended the following: (a) selection of screening tests to measure ignition and surface flammability; (b) a test to determine smoke density; (c) a test to evaluate toxic combustion gases; (d) a test to measure the heat evolved; and finally, (e) a full-scale test on the complete assembly.

It should be noted that this report is not, nor was it intended to be, an exhaustive review of all the literature produced on materials flammability. It was to provide a general overview of the numerous aspects involved in the complex problem of flammability, and to serve as a starting point for a more detailed investigation of any of the

flammability characteristics required to meet the specific interest or need of the reader. For a more detailed discussion of any of these properties the original articles should be consulted.

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