

F55000667

PHYSIO-CHEMICAL STUDY OF SMOKE EMISSION BY AIRCRAFT INTERIOR MATERIALS

Part I

Physiological and Toxicological Aspects
of Smoke During Fire Exposure
I. N. Einhorn



JULY 1973

FINAL REPORT

Document is available to the public through
the National Technical Information Service,
Springfield, Virginia 22151

Prepared for

DEPARTMENT OF TRANSPORTATION
FEDERAL AVIATION ADMINISTRATION

Systems Research & Development Service

Washington D. C., 20591

US 8340 82
~~US 3740~~
F5000667R

1. Report No. FAA-RD-73-50, I		2. Government Accession No.		3. Recipient's Catalog No.	
4. Title and Subtitle PHYSIO-CHEMICAL STUDY OF SMOKE EMISSION BY AIRCRAFT INTERIOR MATERIALS - PART I PHYSIOLOGICAL AND TOXICOLOGICAL ASPECTS OF SMOKE DURING FIRE EXPOSURE				5. Report Date July 1973	
				6. Performing Organization Code	
				8. Performing Organization Report No. FAA-NA-73-70, I	
7. Author's I. N. Einhorn				10. Work Unit No. (TRAIS)	
9. Performing Organization Name and Address College of Engineering, University of Utah Division of Materials Science and Engineering For National Aviation Facilities Experimental Center Atlantic City, N.J. 08405				11. Contract or Grant No. 183-522-060	
				13. Type of Report and Period Covered Final October 1969 - June 1973	
				14. Sponsoring Agency Code	
12. Sponsoring Agency Name and Address Department of Transportation Federal Aviation Administration Systems Research and Development Service Washington D. C. 20591					
15. Supplementary Notes					
16. Abstract A concise review of the physiological and toxicological aspects of smoke during fire exposure has been presented. This report attempts to elucidate the parameters, both chemical and physical, which lead to smoke development, and subsequently, light obscuration, during their pyrolysis and combustion. Analysis of recent fire statistics covering losses during the past decade has been compiled and incorporated into the report. Various laboratory test procedures, both small-scale and large-scale, have been summarized and a critique presented outlining their usefulness and problems encountered in interpretation of results obtained using these test procedures. A review of the physiological and toxicological parameters affecting survival of humans during fire exposure is given. Consideration is directed toward the specific hazards encountered during aircraft accidents involving fire. Recent reviews of the medical literature pertaining to fire injury is discussed in detail.					
17. Key Words Aircraft Materials Pyrolysis Combustion Products Smoke Crash Fire Hazards Toxicity Fire Exposure Gas Chromatography				18. Distribution Statement Document is available to the public through the National Technical Information Service, Springfield, Virginia 22151	
19. Security Classif. (of this report) Unclassified		20. Security Classif. (of this page) Unclassified		21. No. of Pages 86	22. Price \$3.00 PC \$.95 MF

PREFACE

This report was prepared by Professor I. N. Einhorn, Director of the Flammability Research Center, College of Engineering, The University of Utah for the Federal Aviation Administration. The work was part of an R & D program of the Systems Research and Development Service, Washington, D. C., which was directed toward minimizing aircraft crash fire hazards.

This contract was administered under the direction of Mr. J. F. Marcy, Aircraft Safety Division, National Aviation Facilities Experimental Center (NAFEC), Atlantic City, New Jersey.

TABLE OF CONTENTS

	Page
INTRODUCTION	1
Purpose	1
BACKGROUND	1
Fire Statistics	1
Definition of Smoke	3
Fundamental Aspects of Combustion and Degradation of Polymeric Materials	3
Stage I-A Primary Thermal Processes	3
Stage I-B Primary Chemical Processes	5
Stage II Decomposition	5
Stage III Ignition	6
Stage IV Combustion	6
Sub-Stage IV-A Non-Flaming Degradation	6
Sub-Stage IV-B Flame Propagation	6
Sub-Stage IV-C Physical Response (Shrinking, Melting, Char Formation, Smoke Development)	7
Stage V Potential Physiological Hazard	8
Future Trends in the Development of Low Smoke-Generating Materials	9
Factors Governing the Smoke Development in Polymers	9
DISCUSSION	10
Laboratory Test Methods and Environmental Factors	10
Rohm and Haas XP-2 Chamber (ASTM D-2843-T)	10
National Bureau of Standards Smoke Chamber	14
The Lawrence Radiation Laboratory Smoke Chamber	15
Calculation of NBS Chamber Results	15
25-Foot Steiner Tunnel Test (ASTM E-84)	16
Comparison of Smoke Test Systems	20
Miscellaneous Test Procedures	21
Quantitative Determination and Characterization of Smoke	29
General Background	29
Analysis of Smoke Development in Polymers	30
Burning Conditions	35
Effect of Fire Retardants on Smoke Generation	38
Effect of Chemical Structure on Smoke Development	40

	<u>Page</u>
Physiological Aspects of Smoke	41
General Background	41
Physiological Factors Affecting Survival During Fire	
Exposure	44
Visual Parameters Affecting Survival	44
Escape Response	44
Toxicological Aspects of Combustion	45
General Background	45
Respiratory Burns	46
Smoke Poisoning	48
Toxic Effects From Gases and Thermal Degradation Products ...	50
Oxygen	50
Carbon Monoxide	51
Carbon Dioxide	59
Sulfur Dioxide	60
Hydrogen Sulfide	60
Aliphatic Hydrocarbons	60
Aromatic Hydrocarbons	61
Hydrogen Cyanide	61
Hydrogen Chloride and Related Compounds	61
Hydrogen Fluoride and Related Compounds	61
Acrolein	62
Toxicological Studies on Selected Plastics	62
Special Aspects of Smoke in Commercial Aircraft	63
General Background	63
SUMMARY	68
REFERENCES	69

LIST OF ILLUSTRATIONS

<u>Figure</u>		<u>Page</u>
1	Schematic Representation of Combustion and Thermal Degradation	4
2	Schematic Representation of Polymer Degradation	5
3	Schematic Drawing of XP-2 Smoke Chamber	10
4	An Idealized Smoke Obscuration Curve Obtained Using the XP-2 Chamber	11
5	The Effect of Sample Size on Light Obscuration as Measured Using the XP-2 Chamber	12
6	NBS Smoke Chamber (Front View)	17
7	Interior View of NBS Smoke Chamber Showing the Heater and Burning Test Specimen	18
8	Interior View of the NBS Smoke Chamber Illustrating the Flame Source, Sample Holder, and Radiometer Assembly	19
9	Diagrammatic Sketch of the Steiner Tunnel Test Apparatus - ASTM E-84 Test Method	20
10	Comparison of Light Absorbed With Weight Per Cent Smoke	23
11	Correlation of Results from 25- and 2-Foot Tunnels	24
12	Correlation of 30-30 Inclined Tunnel and 25-Foot Tunnel	25
13	Correlation Between Radiant-Panel and Tunnel Tests	26
14	Typical Smoke Development Curves for Two Materials	32
15	Geometrical Factor - V/AL	33
16	Smoke Obscuration Index (As Proposed by NBS)	35
17	Red Oak - Specific Optical Density as a Function of Burning Conditions	37
18	Effect of Ventilation on Maximum Smoke Density	38
19	Effect of Concentration of the Reactive Fire Retardant o,o-Diethyl-N,N'-bis (2 Hydroxyethyl) Aminophosphonate on Light Obscuration in Rigid-Urethane Foams	39

<u>Figure</u>		<u>Page</u>
20	Effect of the Non-Reactive Fire Retardant Tris, 2,3-Dibromopropylphosphate on Light Obscuration in Rigid-Urethane Foams	39
21	Electrocardiograms of Mice During Carbon Monoxide Tests	56
22	Reduction of Carboxyhemoglobin in Mice Blood	59
23	Radiant Heat Versus Exposure Time for Unbearable Pain and Third-Degree Burns	66

LIST OF TABLES

<u>Table</u>	<u>Page</u>
I Annual Fire Statistics (Based on Population)	2
II Trends in Fire Causes	2
III Geometric Factors Used in Smoke Density Calculations (XP-2 Chamber)	14
IV Comparison of Smoke Test Systems for Measuring Smoke Obscuration	21
V Weight Per Cent Smoke From Various Plastic Products	22
VI Smoke Density Compared to Smoke Weight	23
VII Flame-Spread Correlation Results with 30-30 Inclined Tunnel	25
VIII Radiant Panel Flame-Spread Data	27
IX Light Transmission in Various-Sized Compartments with Various Areas Emitting Smoke of Specific Optical Densities of 50 and 100 (Viewing Distance = 10 feet)	34
X Comparison of Smoke Evolution for Smoldering and Flaming Conditions	36
XI Smoke Development by Urethane Foams	40
XII Burn Mortality - New York City 1966 and 1967	47
XIII Respiratory Tract Complications in 257 Autopsied Cases	48
XIV Carbon Monoxide Poisoning in 185 Autopsied Cases, With Death Occurring Under 12 Hours	49
XV Signs and Symptoms of Toxicity of Reduced Levels of Oxygen Due to Fire Conditions	50
XVI Signs and Symptoms at Various Concentrations of Carboxyhemoglobin	51
XVII Physiological Response to Various Concentrations of Carbon Monoxide	52
XVIII Species Differences with Regard to CO-Hb Concentration in Blood	52
XIX Carbon Monoxide Hemoglobin Concentration and Time of Death (At Constant Concentration)	54

<u>Table</u>		<u>Page</u>
XX	Carbon Monoxide Hemoglobin Concentration and Time of Death (At Rising Concentration)	55
XXI	Physiological Response of Mice to Carbon Monoxide	58
XXII	Smoke Analysis of Several Common Materials (Concentration ppm Volume/Volume)	62
XXIII	Recent Toxicological Studies of Plastics During Pyrolysis and Combustion	63

PHYSIOLOGICAL AND TOXICOLOGICAL ASPECTS OF SMOKE DURING FIRE EXPOSURE

INTRODUCTION

Purpose

The purpose of this paper is to present a concise review of the physiological and toxicological aspects of smoke during fire exposure. The author has attempted to direct special emphasis toward the development of a fundamental understanding of the parameters, both chemical and physical, which lead to smoke development and, subsequently, light obscuration during the pyrolysis and combustion of polymeric materials.

This paper is divided into 8 separate phases:

1. General Background of Fire Statistics
2. Definition of Smoke
3. Fundamental Aspects of Combustion and Degradation of Polymeric Materials
4. Factors Governing Smoke Development
 - a. Laboratory Test Methods and Environmental Factors
 - b. Classification of Materials
 - c. Effect of Additives on Smoke Generation
5. Quantitative Determination and Characterization of Smoke
6. Physiological Aspects of Smoke
7. Toxicological Aspects of Smoke
8. Special Aspects of Smoke in Commercial Aircraft.

BACKGROUND

Fire Statistics

Recent reviews of fire statistics^{1,2,3} indicate that approximately 2.5 million fires occur in the United States annually, causing a property damage loss in excess of 2.5 billion dollars during 1971. Accurate final statistics covering fire loss during 1971 are just being compiled. Early estimates indicate that approximately 7.8 billion dollars were lost as a result of indirect causes. Thus, the total fire loss during 1971 was in excess of 10.0 billion dollars.

Because of persistent inflation, the number of fires per thousand population is a more reliable measure of fire prevention than is the figure for dollar loss. Table I presents a summary of the number of fires that occurred each year from 1960 through 1969 based on population.

TABLE I
ANNUAL FIRE STATISTICS (BASED ON POPULATION)

<u>Year</u>	<u>Fires Per 1,000 Population</u>	<u>Estimated Yearly Fire Losses</u>
1960	11.8	\$1,106,824,000
1961	12.0	1,209,042,000
1962	12.2	1,265,002,000
1963	13.1	1,405,558,000
1964	12.4	1,367,128,000
1965	12.1	1,455,631,000
1966	12.2	1,469,755,000
1967	12.1	1,829,920,000
1968	11.8	1,952,622,000
1969	12.0	2,447,600,000

During the 1960's there was little change in the number of fires per thousand population. Table II³ presents a comparison between the percentage distribution of the chief fire causes in 1969 as compared with 1959, based on the number of fires.

TABLE II
TRENDS IN FIRE CAUSES

<u>Cause</u>	<u>1959</u>	<u>1969</u>	<u>Trend</u>
Heating and Cooking	22.9%	14.4%	Substantial reduction
Smoking and Matches	18.0	11.5	
Electrical	13.9	14.0	
Flammable Liquids	6.5	4.8	
Open Flames and Sparks	6.0	6.2	
Lightning	3.3	2.3	
Children and Matches	3.9	8.2	Substantial increase
Exposure	2.8	1.9	Substantial increase
Incendiary or Suspicious	2.3	5.8	
Spontaneous Ignition	2.6	1.9	
Miscellaneous Known	11.3	12.1	
Unknown or Undetermined	6.5	16.9	Substantial increase
Totals	100.0%	100.0%	

The major areas of fire losses are:

Clothing and Apparel Fires
Interior Furnishings (e.g., carpets, mattresses, wall coverings)

Fires in Homes, Multi-Resident Dwellings, Institutions, and Public Buildings Transportation-Associated Fires

The major emphasis within the scope of this report will relate to the physiological and toxicological aspects of smoke produced during the combustion of materials utilized in aircraft interiors. Since few definitive studies have been reported in the open literature pertaining to aircraft fires, the author will supplement this report with appropriate references reported in the literature based on non-aircraft related fires.

Definition of Smoke

A dictionary definition⁴ of smoke is "the volatilized products of the combustion of an organic compound, as coal, wood, etc., charged with fine particles of carbon or soot; less properly, fumes, steam, etc."

Gaskill⁵ defined smoke as "the airborne products evolved when a material is decomposed by heat or burning (oxidation)." He further stated that "smoke may contain gases, liquid, or solid particles, or any combination of these."

Hilado⁶ defined smoke as "the gaseous products of burning organic materials in which small solid and liquid particles are also dispersed; smoke can also be defined as solid particles, such as carbon and ash, suspended in air." Hilado further stated "that the broader definition is the more appropriate because the nongaseous portion of smoke from some materials contain significant amounts of tarry or liquid droplets." Thus, little difference is noted in the three definitions of smoke described previously.

Fundamental Aspects of Combustion and Degradation of Polymeric Materials

Inasmuch as smoke is produced by the combustion and degradation of polymeric materials, an understanding of these processes is necessary to fully recognize the parameters governing smoke production in actual fire exposure.

The burning process of a unit mass of material can be considered to proceed in several states, depending upon the source of ignition, geometry, attitude, environment, and material characteristics, both molecular and macroscopic. The flow chart (Figure 1) presents a schematic representation of the stages mentioned above.

Stage I-A Primary Thermal Processes

Heat from an external source is applied to the material gradually raising its temperature. The rate of temperature rise depends upon the temperature and flow rate of the heat source, the temperature differential, as well as the basic characteristics of the material, such as specific heat, thermal conductivity, heat of chemical reaction, heat of fusion,

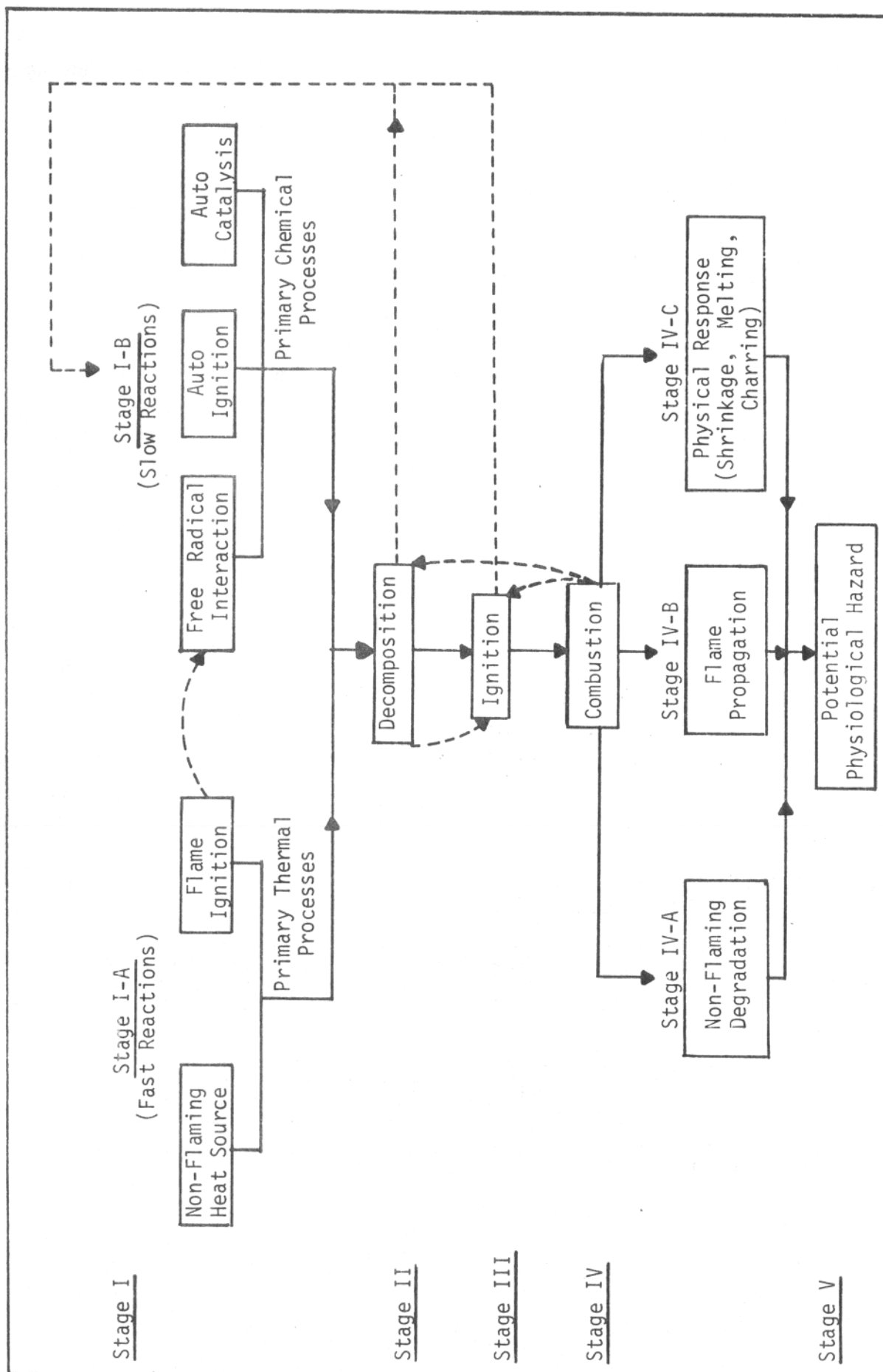


FIG. 1. SCHEMATIC REPRESENTATION OF COMBUSTION AND THERMAL DEGRADATION

heat of vaporization, or other changes which may take place during the heating of the material. The geometry of the material and its attitude may considerably affect the burning process. Such factors as pre-ignition heating, radiant feedback or feedaway, may substantially change the ignition and flame propagation characteristics after ignition.

Stage I-B Primary Chemical Processes

In addition to thermal energy, the external heat source may also introduce free radical species for chain-branching reaction. The heated material can be auto-reactive because of either a high heat of reaction or the generation of its own catalyst. In either case, the reaction rate is further accelerated in a manner which can then be independent of the primary thermal process. Lastly, the heated material can generate gaseous or adsorbed oxygen. In general, the accumulation of energy by such bootstrapping chemical processes is initially slow.

Stage II Decomposition

As soon as the materials reach their decomposition temperature, the following types of products may be formed as seen in the schematic representation of polymer degradation shown in Figure 2.

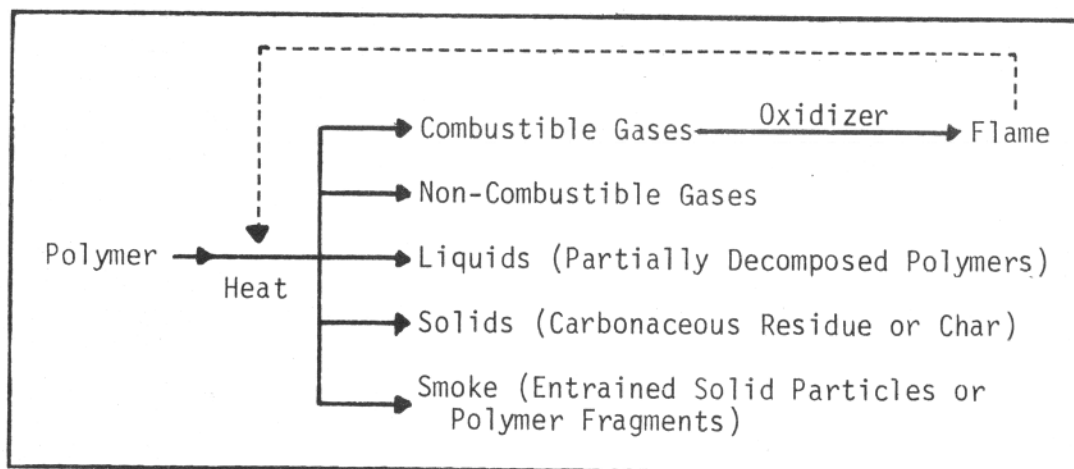


FIG. 2. SCHEMATIC REPRESENTATION OF POLYMER DEGRADATION

Elimination of combustible gases, i.e., gases which will burn in the presence of air, would effectively preclude burning. However, in most instances, this is impossible since most organic materials cannot be reduced to a highly-carbonaceous residue without the release of some volatile, hydrogen-containing compounds. Typical combustible gases are hydrogen, methane, ethane, ethylene, formaldehyde, and carbon monoxide. Examples of non-combustible gases (i.e., do not burn in the presence of air), are hydrogen chloride, hydrogen cyanide and carbon dioxide. The most desirable products of decomposition are the solid carbonaceous residues or chars since they help to preserve structural integrity and

protect adjacent masses from decomposition. They also prevent mixing of air with combustible gases.

The decomposition stage is greatly affected by the following factors:

- a. The temperature of initial decomposition.
- b. The heat of decomposition, or heat absorbed or released during decomposition.
- c. The manner in which the polymer decomposes, i. e., the relative amounts of the various products of decomposition.

Stage III Ignition

In the presence of a sufficient amount of oxygen or an oxidizing agent, the combustible gases ignite. Ignition depends upon the following characteristics of the material:

- a. The flash-ignition temperature, i.e., the temperature at which gases evolved from the material can be ignited by a flame or a spark.
- b. The auto-ignition temperature, i.e., the temperature at which reactions within the material become self-sustaining to the point of ignition.
- c. The minimum level of oxygen necessary to sustain ignition and combustion.

Stage IV Combustion

The most important characteristic of the material in this stage is its heat of combustion, i.e., the energy that is released during burning. The net thermal effect of combustion can be either negative or positive. If it is negative, an external supply of heat is necessary to support combustion; if it is positive, the excess of heat is made available to increase the temperature of the adjacent material.

Sub-Stage IV-A Non-Flaming Degradation

Many materials will degrade or smolder by a non-flaming process long before the advent of flame propagation. In fact, some materials do not combust in normal oxygen environments. This is not to say that these materials are not hazardous, for if they transport heat at a rapid rate, they may cause severe local burns. With the exception of those materials with high thermal conductivity, the basic characteristics mentioned here are those desirable for wearing apparel.

Sub-Stage IV-B Flame Propagation

Propagation results when the net heat of combustion is sufficient to bring the adjacent mass to the combustion stage. The ease with which the

material is brought to this stage depends upon its chemical structure, geometry, and attitude. It should be apparent that an oxidizing agent is generally required to sustain combustion. Some materials, in their degradation process, release oxygen and then will support combustion at a limiting oxygen index of less than 20 per cent; however, other materials require oxygen from the environment to support combustion. For the latter materials, such as textiles, the effect of weave, denier, etc., will greatly influence flame propagation. A typical example of the effects of fabric geometry can be seen in a comparison of flame propagation characteristics of a loose-knit sweater versus that of an angora-type fiber sweater. The loose-weave fabric will burn with a slow propagation rate because of small precursor heating of the adjacent material, while the angora fabric, with its high surface area, will enhance combustion and thus burn with a more rapid propagation. For this reason, propagation is often created as a surface phenomenon and hence surface flame spread is considered as a realistic measure of propagation for materials.

Sub-Stage IV-C Physical Response (Shrinkage, Melting, Char Formation, Smoke Development)

Straehl⁷ noted that synthetic fabrics such as polyamide and polyesters shrink considerably at relatively low temperatures. This shrinkage can be serious in clothing fires. Synthetic underwear shrinks onto the body when the outer wear burns; it makes, furthermore, excellent thermal contact with the skin and if the underwear catches fire, the results are likely to be fatal. The burning droplets from melting synthetics can make particularly deep and serious burns according to medical reports. Wool, as well as synthetics, can shed burning pieces, but the drips from wool can be caught by the hand because of the low thermal conductivity of wool. But drops of many synthetics are molten and of moderate thermal conductivity -- they stick and burn. The char from wool is a foam of low relative density, and like all foams, is a good insulator and makes poor thermal contact with the skin. It also has low heat capacity.

Einhorn and Mickelson⁸ reported on the formation of char structure during the combustion of model urethane foams retarded with reactive and non-reactive fire retardant(s). The rigid urethane foam specimens, possessing a high degree of aromaticity in the polymer backbone and a cross-link density of less than 340 developed strong continuous char structure during burning. When the cross-link density exceeded 400, intumescence and slight melting occurred. As the cross-link density exceeded 500, there was no evidence of char formation and the samples were totally consumed. As the degree of aromaticity was reduced, the effective formation of char structure diminished. All flexible urethane foam samples, similar to those used in clothing liners and comfort cushioning burned to complete destruction.

It should be noted that direct relationships were noticed between the ease of combustion, char formation, and smoke development. For example, a polymer which burned rapidly and completely produced only moderate quantities of smoke, however, as a char was formed, the polymer formed a

greater resistance to flame propagation. The improved resistance, due in part to the thermal insulation of the underlying substrate by the char structure as well as by a diffusion control by the char thus limiting the outward evolution of highly combustible species into the flame front, led to a more incomplete combustion. The more incomplete the combustion process, the greater was the obscuring power of the resultant smoke. Evaluation of the data obtained in numerous laboratory experiments strongly indicated that the parameters that affect the development of improved thermal stability and flammability characteristics of cross-linked polymers, together with a greater generation of smoke, are:

1. the degree of aromaticity in the polymer backbone,
2. the nature and functionality of the monomers,
3. the molecular weight per cross-link density, and
4. the nature and method of incorporation of additives into the polymer system to retard combustion.

Stage V Potential Physiological Hazard

Numerous test methods have been promulgated to evaluate the flammability characteristics of materials. These methods of evaluating the combustion properties of fabrics may be divided into five general classes according to the properties they are intended to measure:

1. Ease of ignition
2. Combustion duration
3. Combustion behavior
4. Flame propagation
5. Gas and smoke evolution.

Only those tests used to measure and quantify gas and smoke evolution will be considered within the scope of this paper.

Special emphasis will be placed on the evaluation of physiological hazards to humans during fire exposure. Consideration will be directed toward the escape response and the effect of smoke in hindering this response.

In addition to certain physiological hazards encountered by humans during fire exposure, consideration must be directed toward the toxicological response to smoke. Normally one expects that flame contact is the major cause of injury and death during fire exposure. Perhaps the first event focusing attention to the hazards of fire from a plastic material was the Cleveland Clinic fire in 1929, in which X-ray films composed of highly-combustible nitrocellulose, caught fire and brought death to 125 persons. Analysis of the death pattern revealed that most of the deaths were not due to flame contact but were a consequence of the production of carbon monoxide and nitrogen oxides. Since then numerous other fires in this country have also led to deaths not only due to the actual flames, but to the gaseous products evolved from synthetic materials. Not too surprising, however, is the fact that research on the toxicological aspects of pyrolysis and combustion during fire exposure has

lagged so far behind other aspects pertaining to the flammability characteristics of polymeric materials that even a fair assessment of the toxic hazards cannot be adequately described at this time except in great generalities. The time has passed for the toxic consequences during combustion to be ignored or minimized.

When a polymeric material is heated, sufficient energy may be introduced into the system to break the weak chemical bonds between the polymer chains as well as to break the covalent bonds within the polymer chains.

Consideration must be given to those factors which will be responsible for the death or serious incapacitation of persons in or near the vicinity of a fire. The major factors affecting life support are listed below:

1. Direct consumption by the fire
2. Extremely high temperatures
3. Absence of oxygen
4. Presence of carbon monoxide
5. Presence of other gases
6. Presence of smoke
7. Development of fear.

From a toxicological point of view, factors 3 to 6 become important considerations since factors 1 and 2 will cause immediate death, while factor 7 may or may not lead to death, depending upon whether a panic-stricken person makes a rash decision such as jumping into the path of an oncoming vehicle or making contact with fallen power lines.

Exposure of humans to the various combustible gases as well as the particulate matter in smoke may bring about acute episodes of toxicity, ranging from minor irritant effects to death.

Future Trends in the Development of Low Smoke-Generating Materials

It is generally accepted that as conventional materials are modified by manipulation of their basic chemical structure or by the incorporation of additives to impart improved resistance to flame, they will produce more smoke during fire exposure. Several new trends will be discussed which offer potential for a realistic reduction of the smoke-generating tendency.

Factors Governing the Smoke Development in Polymers

Mickelson⁹ pointed out that there is no difficulty in enumerating a number of factors that may have an influence on the quantity of smoke generated during the combustion of polymeric materials. The major factor is discerning how each factor affects the smoke being generated when more than one factor is present. Mickelson⁹ divided the principal factors relating to smoke evolution into three classes:

- Class I - Laboratory Test Method and Environmental Factors
- Class II - Classification of Polymeric Material
- Class III - Effect of Additives on Smoke Generation

Each of these classes will be discussed in detail with numerous references made to literature references.

DISCUSSION

Laboratory Test Methods and Environmental Factors

Rohm and Haas XP-2 Chamber (ASTM D-2843-T)

One of the earliest procedures used for measuring the smoke generation of burning polymers was the XP-2 chamber developed by the Rohm and Haas Company and described by Rarig and Bartosic¹⁰ and Hilado.¹¹ Figure 3 is a schematic drawing of the XP-2 Smoke Chamber.

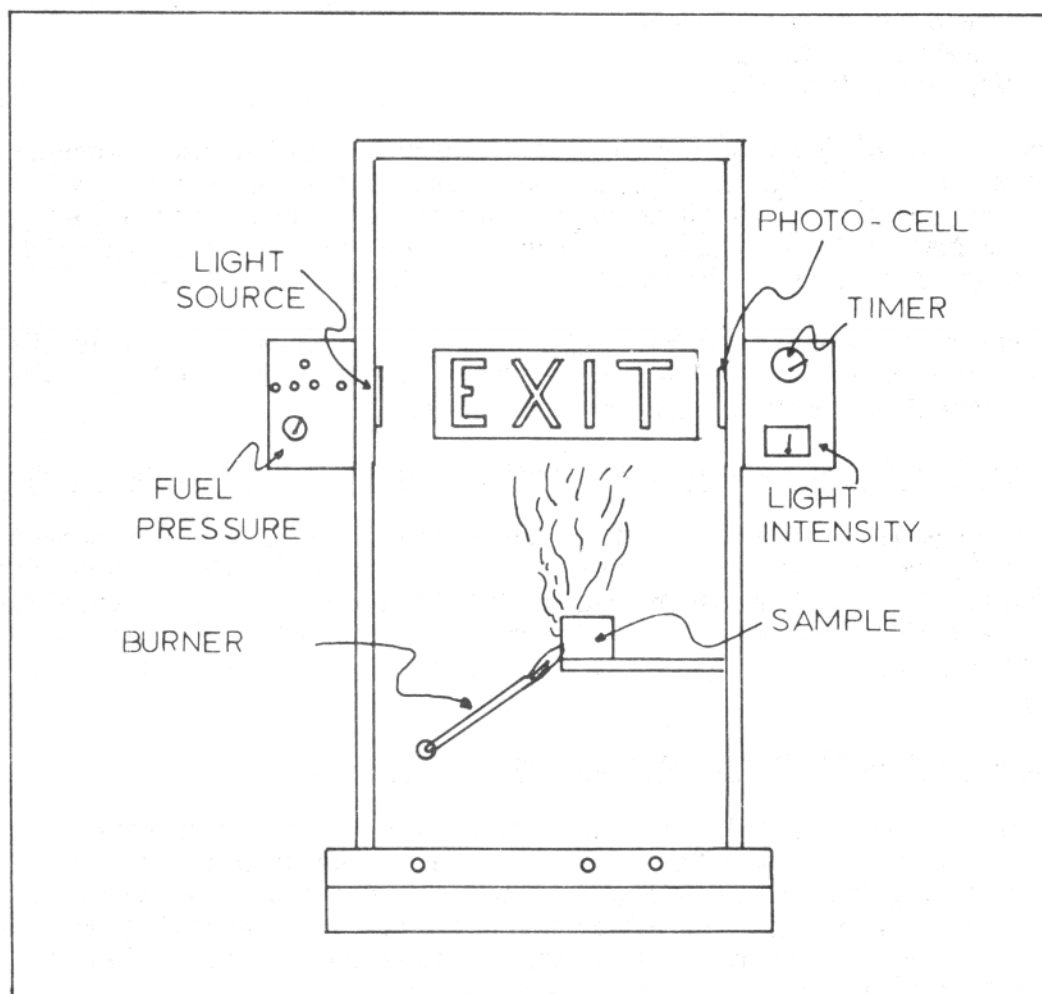


FIG. 3. SCHEMATIC DRAWING OF XP-2 SMOKE CHAMBER

This chamber measures 12 inches by 12 inches by 31 inches high and is constructed of anodized aluminum with stainless-steel fittings. The door is cast aluminum with an inset fire-resistant plate-glass panel to permit observation of the test specimens during burning.

A quantitative analysis of the smoke density over a 1-foot optical path is made by the use of a Weston Barrier Layer photocell incorporated in the walls of the chamber 11 inches above the sample support. Normally, the time necessary to reach 100 per cent light obscuration is used as a measure of the amount of smoke being produced. However, since the approach to 100 per cent obscuration is asymptotic, it is very difficult to obtain times to 100 per cent obscuration which are reproducible. Moreover, some samples can be burned completely without ever producing enough smoke to give 100 per cent light obscuration. A typical obscuration curve is shown in Figure 4.⁹

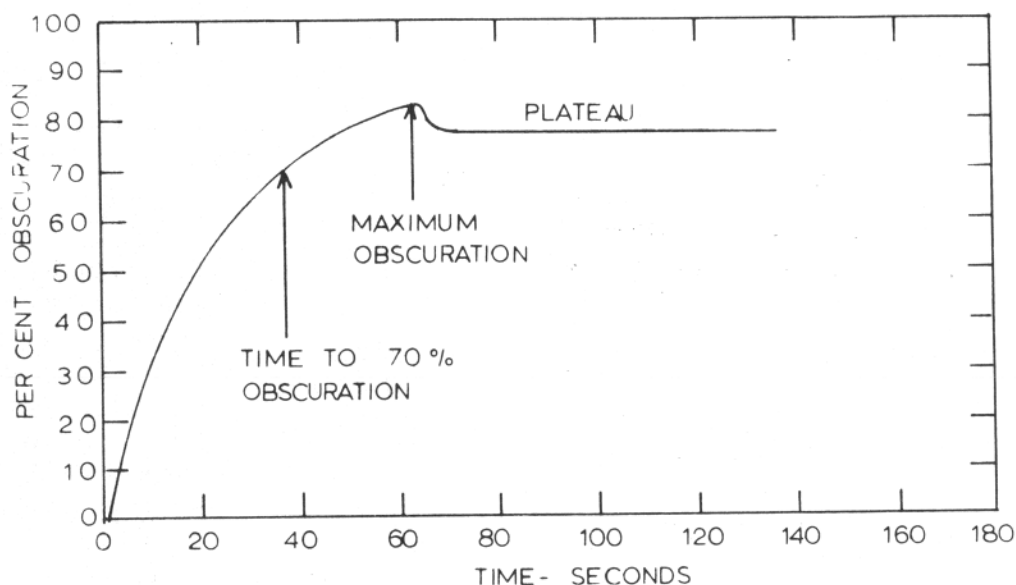


FIG. 4. AN IDEALIZED SMOKE OBSCURATION CURVE OBTAINED USING THE XP-2 CHAMBER

In making comparisons between polymeric materials, one might compare the maximum obscuration reached as does Hilado,¹¹ the time to reach some obscuration point as do Mickelson and Einhorn,¹² or the final plateau where it is assumed that the smoke has become uniformly mixed and there is no stratification of the smoke as do Stepniczka and DiPietro.¹³ Although these selected end points lead to different numbers being assigned to the smoke generated by polymers, they all differentiate between high smoke-producing materials and low smoke-producing materials. Mickelson and Einhorn chose to measure the time to 70 per cent obscuration because the fire-retarded urethane polymers produced copious amounts of smoke reaching an obscuration level of 100 per cent in 20 seconds or less. Since the approach to 100 per cent was asymptotic, it was difficult to establish a

reliable time to reach this point, whereas, it was found that the time to 70 per cent obscuration could be reproduced within plus or minus 0.4 seconds. Hilado has pointed out the advantage of using smaller samples (see Figure 5). When smaller samples are used, lower obscuration levels were obtained and thus it would not be necessary to measure the time to a specific percentage obscuration.

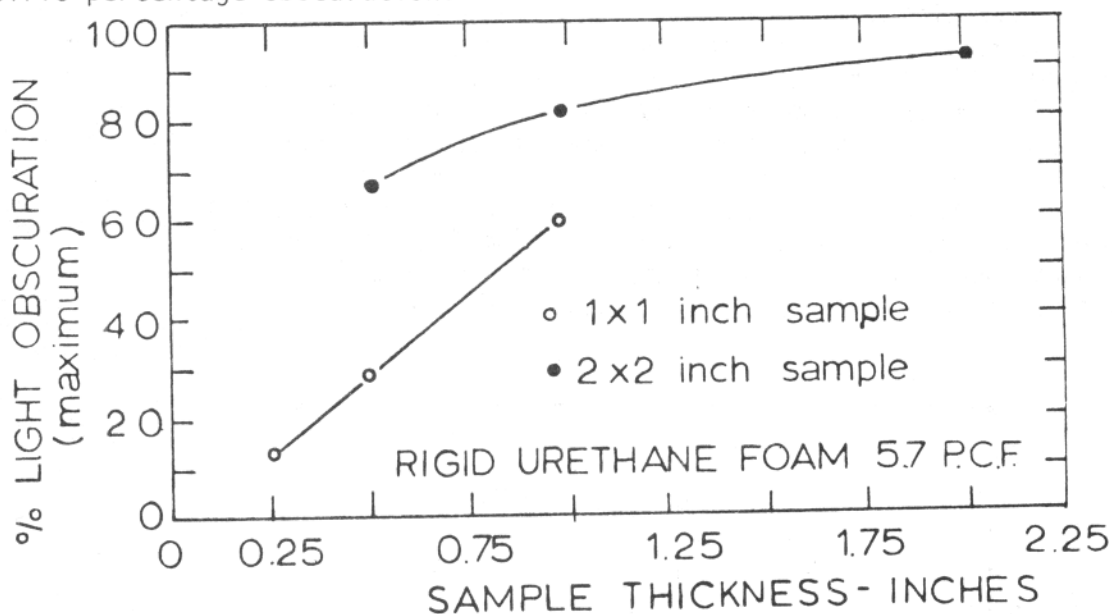


FIG. 5. THE EFFECT OF SAMPLE SIZE ON LIGHT OBSCURATION AS MEASURED USING THE XP-2 CHAMBER

It should be pointed out that good correlation was obtained between plastics evaluated for their smoke-producing characteristics in the XP-2 chamber and the results obtained when considerably larger quantities of the same plastics were combusted on wood-pallet fires. Materials which produced little smoke in the XP-2 chamber tests also produced little smoke in the larger-scale tests; materials which quickly obscured the light beam and exit sign during the XP-2 chamber tests produced copious amounts of smoke in the larger-scale fire tests.

There are several disadvantages to the XP-2 test procedure, the most serious of which is the condensation of soot on the windows of the light source and the photoelectric cell. After a test run, when the smoke has been evacuated from the chamber, the condensed soot may cause as much as an 80 per cent reduction in the light reaching the photocell. Hilado has reported the values of light reduction in the evacuated chambers along with the maximum light obscuration observed. This may be useful information because a material that produces a large amount of soot may not necessarily generate the type of smoke that causes severe obscuration. Einhorn tried two modifications in the chamber aimed at resolving this problem. In one experiment he provided an air curtain over the lens ports which markedly reduced the accumulation of soot and in a second series of experiments he placed a revolving plastic screen in front of the

lens port. This technique minimized the soot formation. However, when samples which produced heavy smoke concentration were combusted in the chamber with the revolving screen, only slight differences were observed in the obscuration times.

Another factor which introduced deviations in smoke measurements was the difficulty in maintaining an exact placement of the sample on the sample holder. Any deviation in this positioning will cause a variation in the amount of material exposed to the flame which will cause discrepancies in the amount of smoke measured during the burning process.

The obscuration produced by smoke in the XP-2 chamber is measured horizontally and since smoke stratifies, it may be that the obscuration indicated is not a true measure of the amount of smoke filling the chamber. Stepniczka and DiPietro¹³ chose the plateau as a more accurate indication of the true quantity of smoke filling the chamber since time has been provided for the uniform mixing of the chamber's contents. The increase in time provided by using this technique provides time for the agglomeration of the particulate matter making up the smoke. The agglomeration process changes the character of the smoke by altering the size distribution of the particulate matter.

Specimen size used in the XP-2 chamber has varied considerably. Specimen sizes reported in the literature range from 1 inch by 1 inch by 1/4 inch as reported in the original Rohm and Haas studies¹⁴ to samples as large as 2-inch cubes. The effect of specimen size in the XP-2 chamber has been studied within this range for cellular polymers by Hilado.¹¹ As mentioned previously, the use of smaller samples permit the direct measurement of maximum smoke obscuration.

Additional deviations in the quantity of smoke produced during a combustion test may result from variations in the wire screen used to support the specimen to variations in flame velocity and gas content. Further definitive studies are required to quantify these effects and to determine their relationships to factors involved in large-scale fires.

Hilado⁶ also reported on geometric factors pertaining to sample size. He noted that because the burner flame impinges on the specimen at an angle, two of the four sides and the bottom are usually exposed to flame when the sample had a base of 1 inch square. Actual laboratory tests indicated that when the sample size was increased to 4 inches square flame exposure was limited to the bottom surface only. Table III⁶ presents the geometric factors used in smoke density calculations when the sample is evaluated in the XP-2 chamber.

In the XP-2 chamber in which the volume is 4320 cubic inches and length is 12 inches, the nominal geometric factor for the standard 1-inch-square specimen is 360. Hilado⁶ believes that the 360 geometric factor should be used only with specimens of negligible thickness, such as films and fabrics.

TABLE III
GEOMETRIC FACTORS USED IN SMOKE DENSITY CALCULATIONS
(XP-2 CHAMBER)

Specimen Dimensions (Inches)	Exposed Area (Square Inches)	Specimen Volume (Cubic Inches)	Effective Thickness (Inches)	Geometric Factor (V/AL)
1x1x0	1.00	0.000	0.000	360
1x1x1/8	1.25	0.125	0.100	288
1x1x1/4	1.50	0.250	0.167	240
1x1x1/2	2.00	0.500	0.250	180
1x1x3/4	2.50	0.750	0.300	144
1x1x1	3.00	1.000	0.333	120
2x2x0	4.00	0.000	0.000	90
2x2x1/2	4.00	2.000	0.500	90
2x2x1	4.00	4.000	1.000	90
2x2x2	4.00	8.000	2.000	90

Einhorn, et al.,¹⁵ reported that certain fire-retarded samples evaluated in the XP-2 chamber would extinguish during the normal test period as a result of lack of sufficient oxygen or due to the reaction of the fire retardants in quenching the combustion process. Additional studies are necessary to evaluate the relationships observed as compared to actual large-scale fire conditions.

National Bureau of Standards Smoke Chamber

Recognizing the many problems encountered with the XP-2 chamber, Gross, et al.,¹⁶ developed a chamber for evaluating the smoking behavior of various materials.

This apparatus consists of a metal box 36 inches high by 36 inches wide by 24 inches deep. It is equipped with a glass door on the right-hand side of the front and an exhaust system on the left side near the top rear. The test specimens are 3 by 3 \pm 0.03 inches by the intended installation thickness up to and including 1-inch thickness. Specimens provided in thicknesses in excess of 1 inch, are sliced to 1-inch thickness and the original (uncut) surface tested. The specimen is mounted in a stainless-steel frame and held in place by an asbestos board backing and a spring clip. Specimens are wrapped in foil with the face cut away, to prevent smoke from leaking through the back of the sample holder. The sample area exposed is 2.56 inches by 2.56 inches (6.56 inches square). The heat is supplied radiantly from a horizontally-mounted 500-W electric heater, suitably enclosed and controlled. A frame containing horizontal rods is attached in front of the heater, so that channels attached to the sample holders will permit the sample to be slid (in the vertical position) in front of or away from the direct radiation.

An air-cooled, Gardon-foil radiometer, mounted in a frame similar to the sample holder, can be slid in front of or away from the heater. The sample and radiometer faces are positioned 1-1/2 inches from the face of the heater housing.

For a flaming exposure test, a six-tube burner is used. This burner is centered in front of and parallel to the specimen holder. The tips of the two horizontal tubes are centered 1/4 inch above the holder edge and 1/4 inch away from the specimen surface. Provision is made to rotate or move the burner out of position during nonflaming exposures. A metered premixed air and propane test gas is used as the fuel source.

The smoke obscuration is measured by means of a vertical light beam, 3 feet in height (bottom), and a photo-multiplier system (top), the output of which is fed to a recorder through a decade selector switch.

In operation, the heater is adjusted to yield a flux of 2.5W/cm^2 on the radiometer face, the light source is adjusted to 100 per cent transmission, the sample is positioned on the rods, and the door is closed. The test is started by sliding the sample in front of the heater, starting the recorder and a timer, shutting off the air supply to the radiometer, and (optionally) rotating the previously lit gas jet into position. The test is continued until the light transmission reaches a minimum and reverses itself.

The Lawrence Radiation Laboratory Smoke Chamber

The Lawrence Radiation Laboratory chamber is a duplicate of the NBS chamber, with the following added features:

1. A regulated ventilation system, which consists of a 1-inch diameter tube leading from a compressed-air supply, is located back to front in the lower right-hand side of the chamber. A variable-width slit cut longitudinally in the bottom of the cylinder permits the formation of a uniform sweep of air through the box from the lower right side upward to the left and out through the (open) exhaust port. Ventilation rates up to 20 chamber changes per hour are possible with this system.
2. A regulated radiant heat source adjustable up to 20W/cm^2 .

The LRL chamber is also equipped with a chamber pressure manometer and a regulatable oxygen-nitrogen supply (for establishing controlled atmospheres in the closed chamber).

Calculation of NBS Chamber Results

The results from the NBS chamber are calculated in terms of specific optical density (D_s), obscuration time (D_{s16}), and Smoke Obscuration Index (SOI), by means of the following equations:

$$D_s = \frac{V}{AL} \log_{10} \left(\frac{100}{T} \right)$$

$$SOI = \frac{D_m^2}{20 \times 100 \times D_{s16}} \left(\frac{1}{t_{90} - t_{70}} + \frac{1}{t_{70} - t_{50}} + \frac{1}{t_{50} - t_{30}} + \frac{1}{t_{30} - t_{10}} \right)$$

where T = percent light transmission at any time, t;

$$D = \text{optical density} = \log_{10} \left(\frac{100}{T} \right)$$

V = chamber volume

A = sample face area

L = light path length

All in consistent units;

D_s = specific optical density; i.e., optical density for smoke evolving from a sample of unit face area into a chamber of a unit volume and viewed through a light path of unit length;

D_m = maximum D_s obtained in a test;

D_{s16} = time for smoke to reach a critical (i.e., vision-obscuring) density;

t_{90} , t_{70} , etc. = time for D_s to reach 90 per cent, 70 per cent, etc. of D_m .

Note that SOI equates the visibility hazard to the product of the maximum smoke density and the average rate of density accumulation divided by the obscuration time. The SOI also includes an artificial factor of 1/100. Figure 6⁵ shows a front view of the NBS Smoke Chamber; Figure 7 is an interior view of the NBS Smoke Chamber showing the heater and burning test specimen. Figure 8 is an interior view of the NBS Smoke Chamber illustrating the flame source, sample holder, and radiometer assembly.

25-Foot Steiner Tunnel Test (ASTM E-84)

The Steiner Tunnel Test¹⁷ is essentially a test for surface flammability, but it also provides a measure of smoke production. The smoke development factor can be determined during the standard 10-minute tunnel test. This factor is a relative number comparing the amount of smoke developed by the material being tested to the amount of smoke developed by red-oak lumber under similar burning conditions. By passing the products of combustion through a light beam focused on a photo-electric cell, a continuous recording of the obscuration can be made. In this test, red oak has a smoke-developed factor of 100. Materials generating more smoke than red oak have values greater than 100, while those developing less have a factor less than 100. This test method is



FIG. 6. NBS SMOKE CHAMBER (FRONT VIEW)

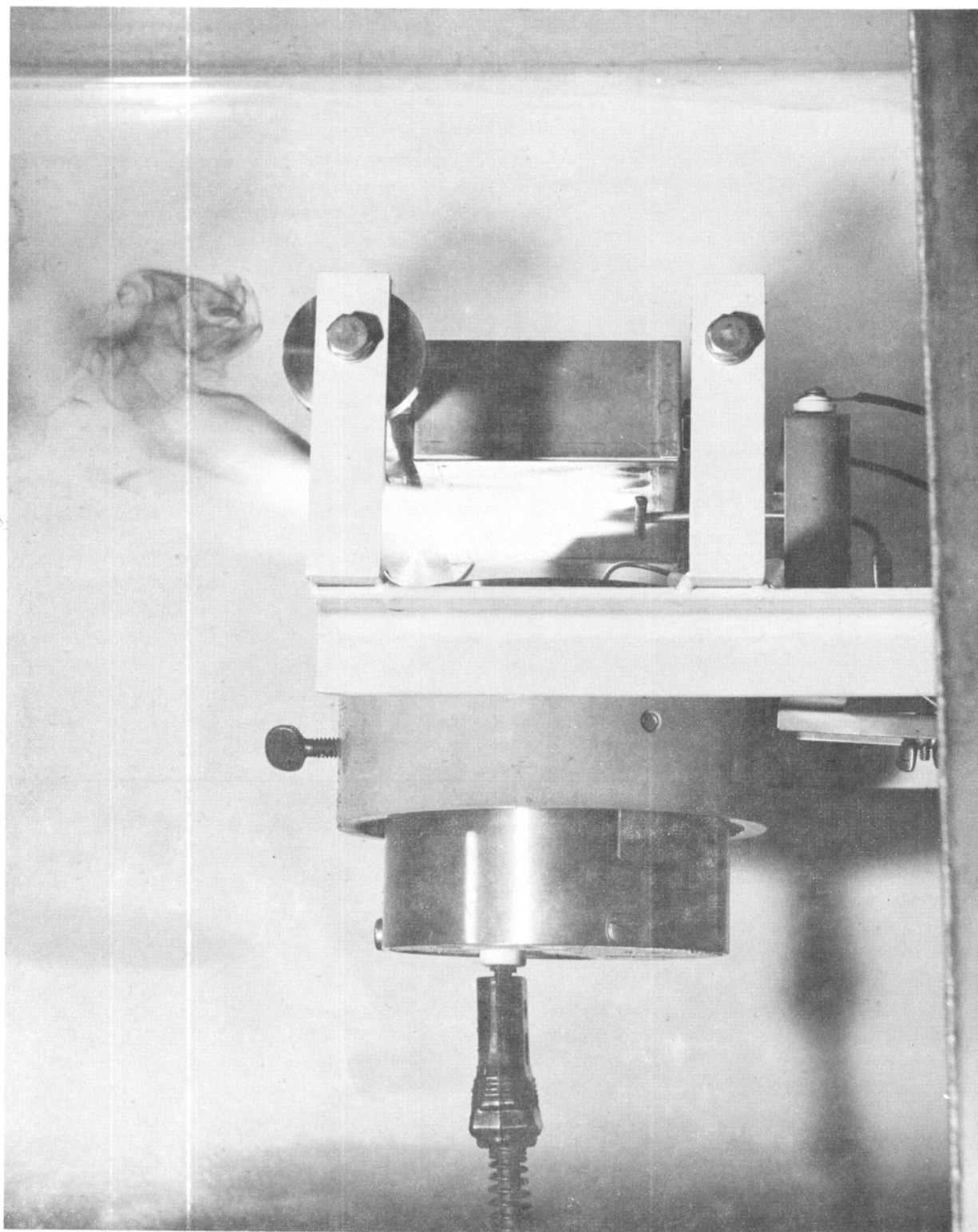


FIG. 7. INTERIOR VIEW OF NBS SMOKE CHAMBER SHOWING THE HEATER AND BURNING TEST SPECIMEN

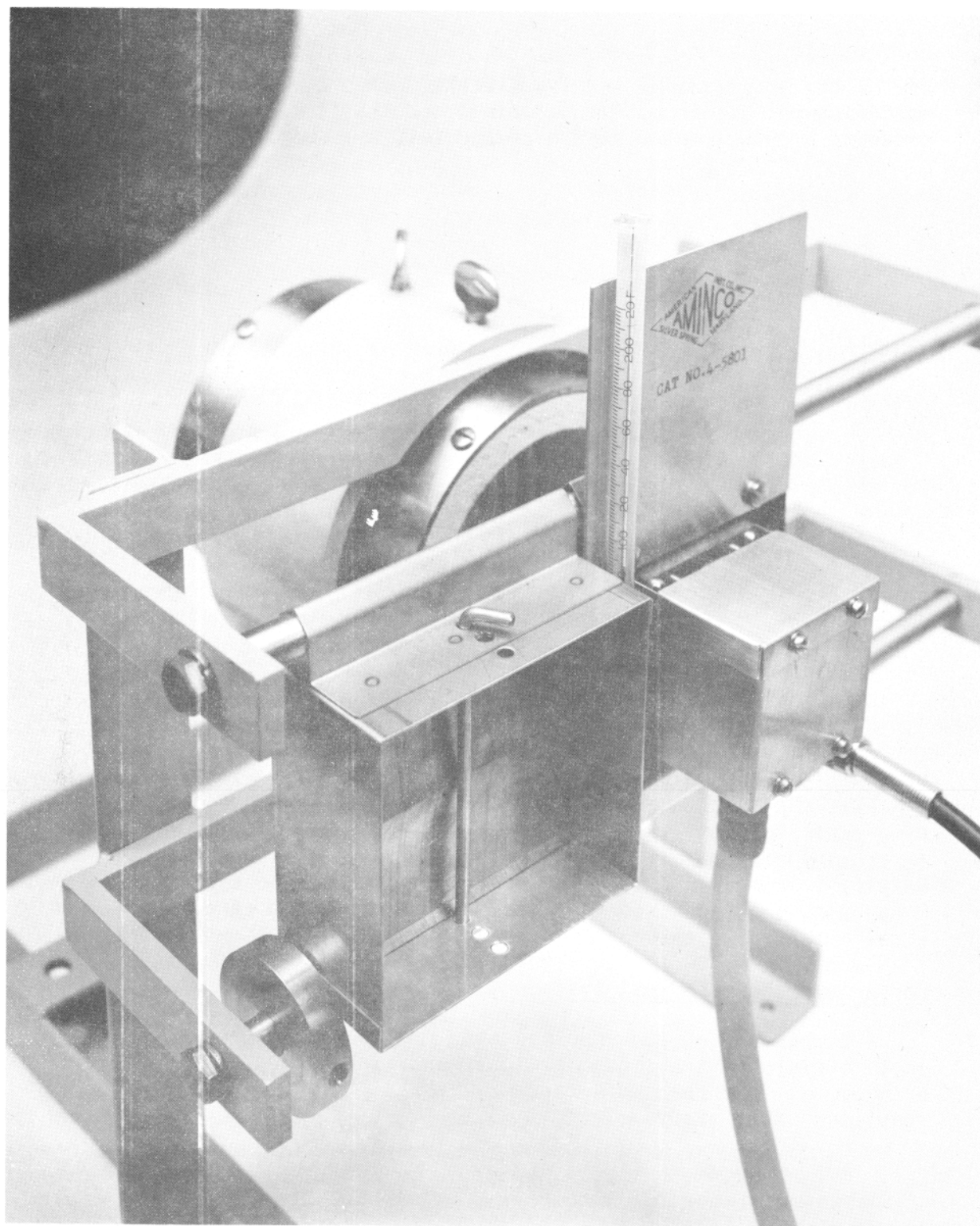


FIG. 8. INTERIOR VIEW OF THE NBS SMOKE CHAMBER ILLUSTRATING THE FLAME SOURCE, SAMPLE HOLDER, AND RADIOMETER ASSEMBLY

one of the most widely-used large-scale test procedures for materials specified for use in public buildings and institutions. Figure 9 presents a diagrammatic sketch of the test assembly.

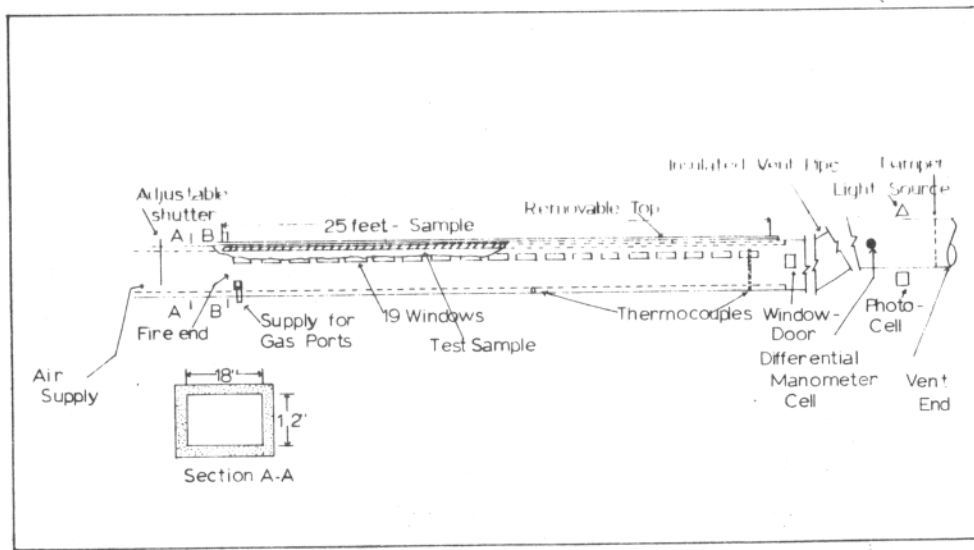


FIG. 9. DIAGRAMMATIC SKETCH OF THE STEINER TUNNEL TEST APPARATUS - ASTM E-84 TEST METHOD

Relatively good correlations have been obtained by Underwriters' Laboratories personnel on a Livonia-type construction compared to actual fire conditions which occurred during the Ford Rotunda fire. Further tests conducted on samples of acoustical tile, obtained from the Hartford Hospital, gave a good indication of the flame-spread and smoke-developed properties that could be anticipated and were experienced during the fire in that hospital.

Comparison of Smoke Test Systems

A comparison of the four systems, previously described, commonly used to evaluate the smoke developed and light obscuration characteristics of materials has been undertaken by Gaskill.⁵ Table IV presents the results of this study.

TABLE IV
COMPARISON OF SMOKE TEST SYSTEMS
FOR MEASURING SMOKE OBSCURATION

	Steiner Tunnel	XP2 Chamber	NBS Chamber	LRL Chamber
Sample size	Large	Small	Small	Small
Area (exposed)	36 ft ²	1 in. ² std (4 in. ² possible) ~ 0.1-1 in.	6.6 in. ²	6.6 in. ²
Thickness	Variable		0.002-1 in.	0.002-1 in.
Test duration (min)	10	4	~30 usually	~30 usually
Heat Source	Flame	Flame	Radiant + optional flame	Same as NBS
Flexibility	±50% ^a	40 psi to 5 psi	+20%	800%
Ventilation Rate	240 linear ft/min	None	None	Variable
Flexibility	±35% ^a	Possible	None	0 to 20 changes/hr
Heat-transfer mode	Primarily convection	Convection/ radiation	Radiation + some convection if flaming	Same as NBS
Smoke production mode	Pyrolysis + combustion progressing along surface. Some penetration.	Combustion—total involvement to partial involvement.	Pyrolysis without flame; pyrolysis + combustion with flame—both on surface + penetration.	Same as NBS; higher heats may result in mostly combustion smokes.
Smoke measurement:				
Method	Integrated rate	Integrated rate	Accumulation; maximum rate is measured, as is obscuration time.	Same as NBS
Reporting	Area under obscuration vs-time curve compared to that for red oak.	SDR (smoke density rating) in % of smoke obscuration-time curve.	Max density; max rate and time; obscuration time.	Same as NBS; material smoke obscuration index = sum of SOI's for various fire parameters.
Fire parameters possible	2	1	2	8
Equipment: Cost	\$40,000	\$1000	\$4000	\$4500
Portability	No	Yes	No	No
Work space (ft)	20 x 30	3 x 5	(Movable)	(Movable)

^aNot the standard method, but possible with the equipment.

Miscellaneous Test Procedures

Robertson¹⁸ attempted to measure smoke by collecting the smoke on a filter paper by using a vacuum source such as a high-volume particulate sampler. The weight of smoke collected per gram of material burned was used as a measure of the materials' smoking behavior.

Cass¹⁹ further modified this simple system and measured the weight per cent smoke from various plastic products. Table V presents a summary of his results. The Steiner Tunnel Test (ASTM E-84) is the most widely-used test procedure for construction materials. The NBS smoke chamber is gaining acceptance as a materials characterization standard.

TABLE V
WEIGHT PER CENT SMOKE FROM VARIOUS PLASTIC PRODUCTS

Material	Wt. % Smoke*
Wood, Red Oak	0.20, 1.10, 0.37, 0.27
Polymethyl methacrylate	3.9, 2.8
Self-extinguishing PMMA	
1. Containing P, Br, and Cl	9.0, 9.2
2. Containing P, Br, and Cl	10.4, 9.8
3. Containing P, Br, and Cl	13.4, 12.2
General Purpose Polyesters	16.7, 17.2
Self-extinguishing Polyesters	
1. Containing P, Br, and Cl	15.7, 15.6
2. Containing P and Cl	17.8, 19.2, 16.8, 18.3, 20.0
3. Containing P and Cl	11.1, 11.0, 12.4, 11.7
4. Containing P and Br	17.2, 18.1, 18.4, 15.6, 17.9, 16.6
Self-extinguishing Laminates	
1. Containing glass fiber, Halogen, P	11.1, 10.6
2. Containing glass fiber, Halogen, P	11.9, 12.0
3. Containing glass fiber, Halogen, P	7.3, 7.8
4. Containing glass fiber, Halogen, P, Sb ₂ O ₃	7.2, 8.0
Urethane Foam	
1. Containing P (S.E.)	11.5, 10.0, 10.6
2. Containing P and Cl	7.7, 9.2
Polyvinyl chloride	8
Vinyl-covered Fabric	
1.	8.5, 7.6, 7.4
2.	4.9, 5.5, 4.6
3.	6.5, 6.6, 6.8

* $\left(\frac{\text{Weight of particulate matter}}{\text{Weight of sample}} \times 100 \right)$

Cass¹⁹ cited as the chief objection to smoke the decreased visibility which hinders escape from fire in burning structures. A quantitative measure of the potential amount of smoke produced by a given fire combined with the light transmission of that smoke should indicate the degree of visibility existing under such conditions. Figure 10 shows the relationship between weight per cent smoke, as developed by Cass¹⁹ and light absorbed.

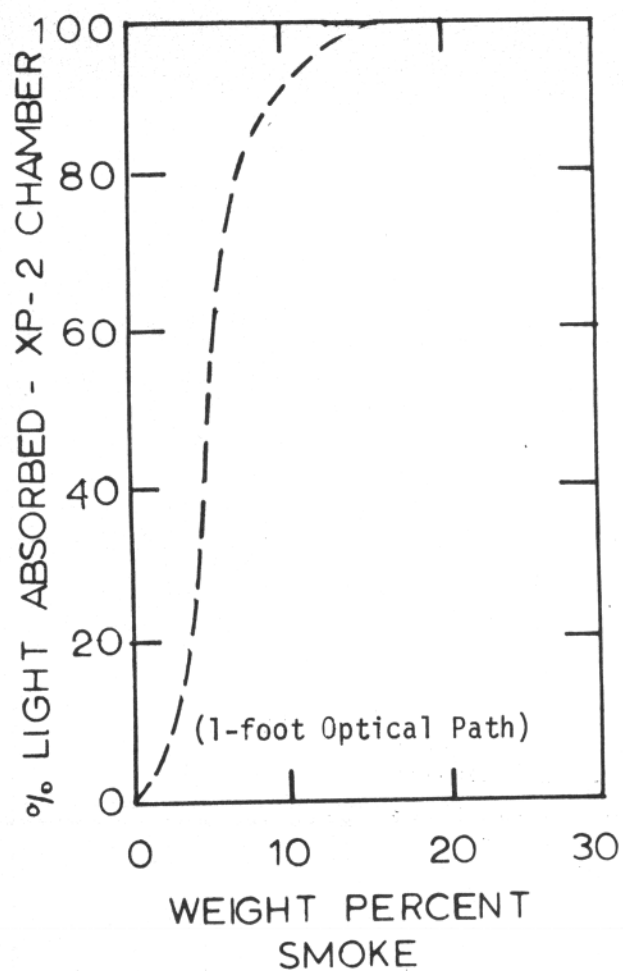


FIG. 10. COMPARISON OF LIGHT ABSORBED WITH WEIGHT PER CENT SMOKE

Cass¹⁹ further compared (see Table VI) smoke density to smoke weight.

TABLE VI
SMOKE DENSITY COMPARED TO SMOKE WEIGHT

Material	Maximum Optical Density (% Smoke)	Wt. % Smoke
Red Oak	2	1
PMMA	2	3
PMMA (S.E.)	98	11
Polyvinyl chloride	100	8
Polyester (flame-resistant)	99	18
Asbestos mill board	0	0

It should be noted that the chemical composition and structure of the test sample can affect the percentage of particulates in smoke. The nature of the particulate matter (size, size distribution, etc.) will affect the maximum smoke density but this is not a measure of physiological response and human vision.

Measurements described by Cass present, in the opinion of the author, only a partial consideration of the effects of smoke on vision and visibility. It is obvious that if a major fraction of a material being consumed by fire is changed to finely divided particulate matter, visibility will be greatly reduced. On the other hand, it is possible to have a complete loss of vision while a relatively small percentage of particulates are present. This phenomenon will be discussed in greater detail under the heading of physiological response to smoke.

Several tunnel tests are used to evaluate the flammability characteristics of materials. The Steiner Tunnel¹⁷ has been described previously. Small tunnels used as laboratory tools, have been described by Vandersall²⁰ and Levy.²¹ Figure 11 presents Vandersall's correlation of flame ratings between his two-foot tunnel and the twenty-five-foot tunnel.

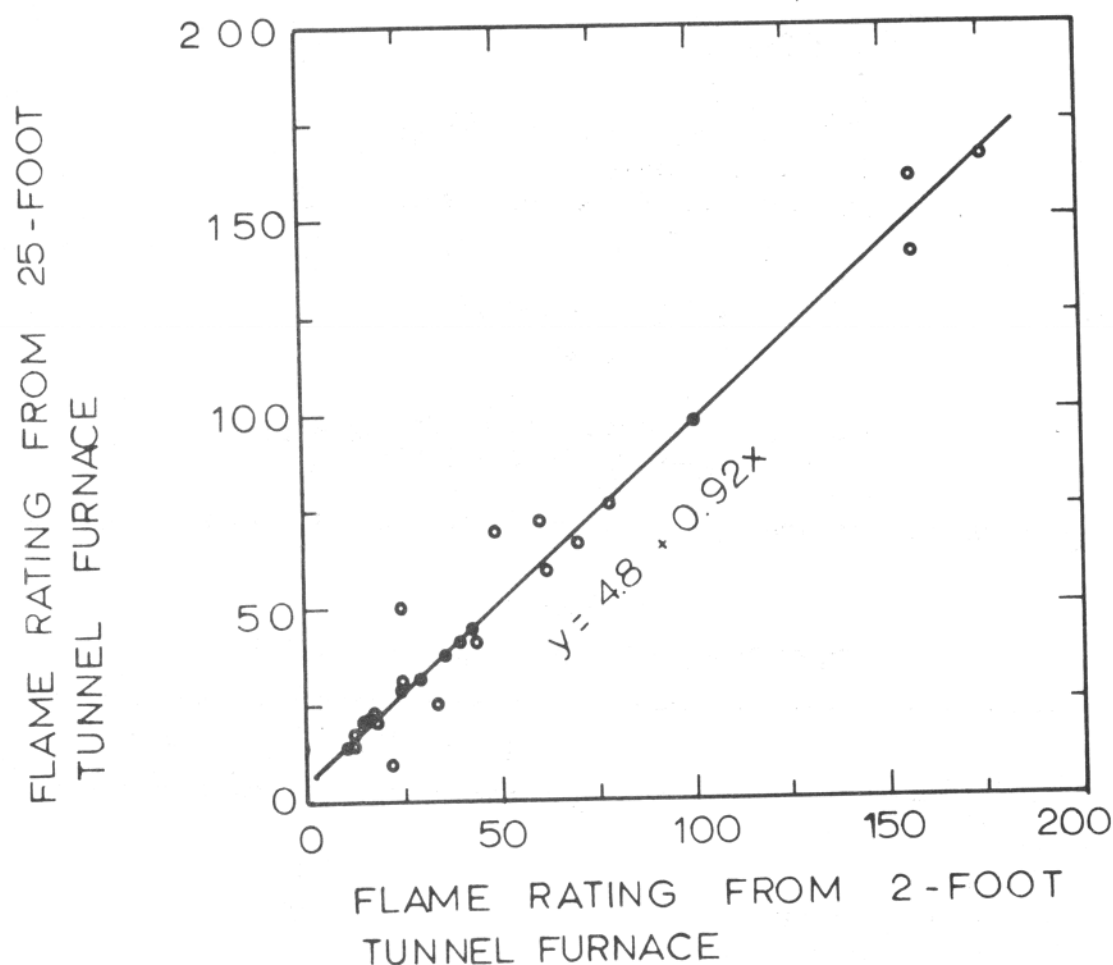
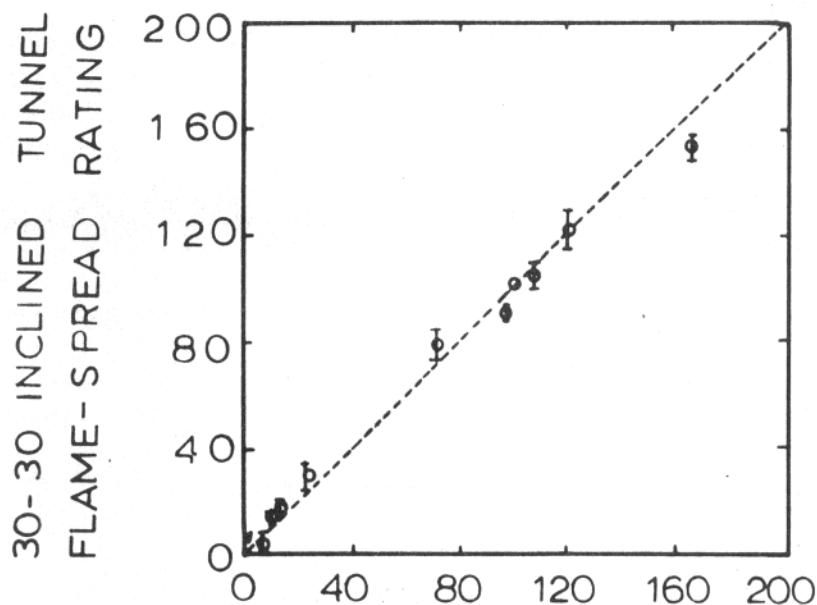


FIG. 11. CORRELATION OF RESULTS FROM 25- AND 2-FOOT TUNNELS

Figure 12 presents similar results obtained by Levy using his 30-30 inclined tunnel (See also Table VII).



E-84 TUNNEL TEST, FLAME SPREAD-RATING

FIG. 12. CORRELATION OF 30-30 INCLINED TUNNEL AND 25-FOOT TUNNEL

TABLE VII

FLAME-SPREAD CORRELATION RESULTS WITH 30-30 INCLINED TUNNEL

Material	Flame-Spread Ratings		Comment
	30-30 Inclined Tunnel	25-Foot Tunnel	
Asbestos - cement 1/4 inch	0	0	No smoke
Cellular glass - 9 pcf	3 - 5	5 - 8	No smoke
Acoustical tile - mineral type	13 - 16	10 - 15	Very little smoke
Tectum - 1 inch	15 - 20	15	Very little smoke
Phenolic foam - 3.5 pcf	22	< 25	Very little smoke, smolders
Acoustical tile - treated cellulose	24 - 33	25	Little smoke
Intumescent paint	28 - 30	25	Low smoke
Redwood - 1 inch	71 - 78	65 - 80	Low smoke
Birch - 1 inch	100 - 105	105 - 110	Smoky
Douglas fir plywood - 1/2 inch	113 - 127	100 - 169	Low smoke
Northern white pine - 1 inch	145 - 150	165	Smoky
Rigid vinyl foam - 2 pcf	83 - 86	---	Surface flash, melted 1 min.
Urethane - S.E. 2 pcf	100 - 109	---	Very smoky - high initial surface flash
Urethane - N.B. 2 pcf	102 - 105	---	Very smoky - high initial surface flash
Urethane - N.B. 2 pcf	111 - 116	---	Very smoky - high initial surface flash
Epoxy foam - 2.5 pcf	150 +	Very large	Very smoky, completely burned
Urethane - 6.5 pcf	150 +	Very large	Very smoky, high surface flash
Polystyrene - 1.5 pcf	150 +	Very large	Burned < 1-1/2 minutes
Polystyrene (E.R.) 2.0 pcf	Melted < 2 minutes		

Figure 13²² indicates the general form of the correlation between the ASTM E-162 Radiant Panel Test method and both the ASTM E-84 tunnel and the 8-foot tunnel method developed by the Forest Products Laboratory. The three methods should be expected to yield somewhat similar results over the range of flame-spread indices of about 10 to 150. Above and below this range there may be quite marked differences. As an example, there appears to be no evidence that highly flammable materials tested by the 8-foot tunnel method can show classifications above 180.

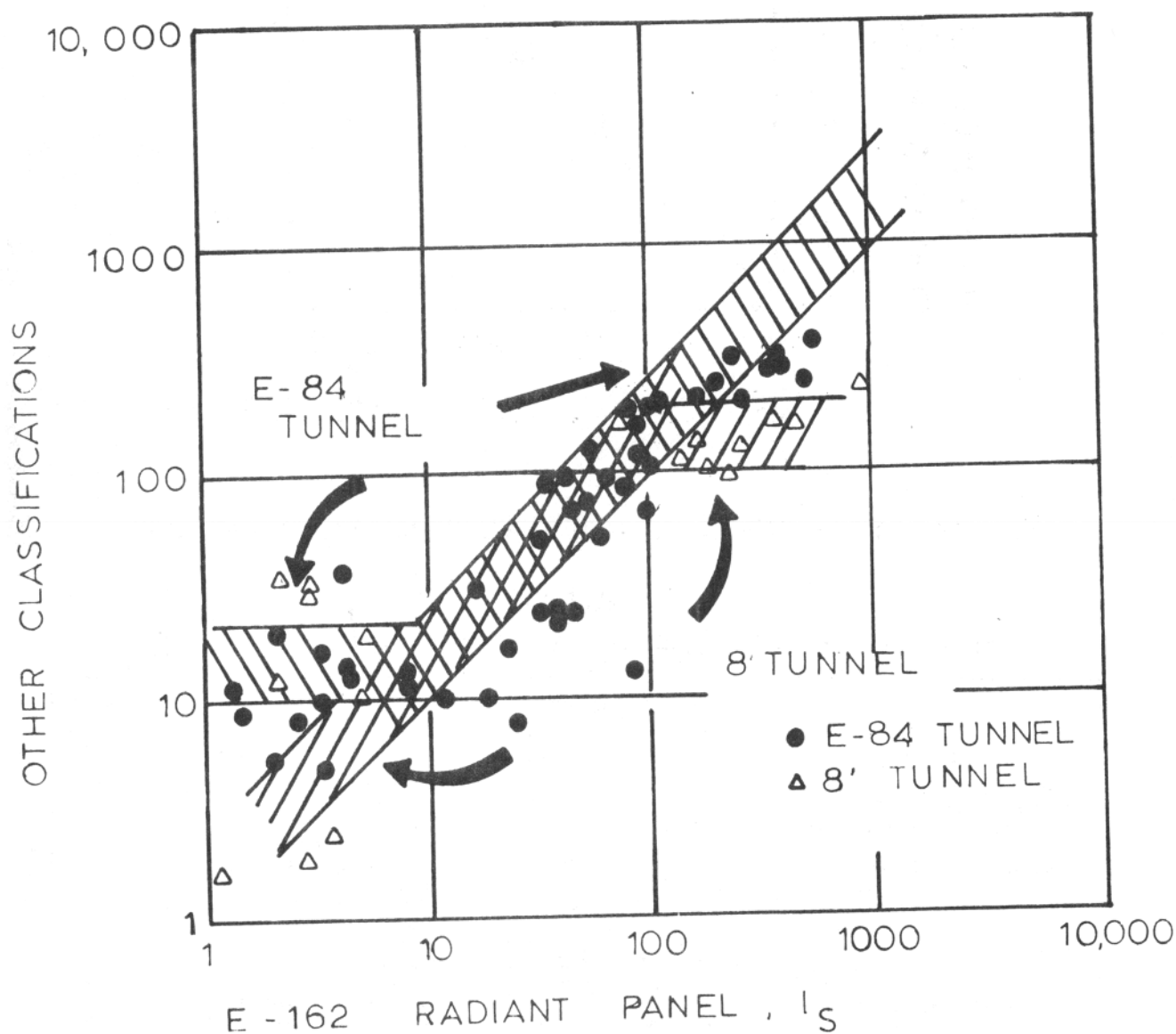


FIG. 13. CORRELATION BETWEEN RADIANT-PANEL AND TUNNEL TESTS

Table VIII²³ summarizes the flame-spread properties of selected materials determined using the radiant panel flame-spread apparatus. Included in this table are data obtained by the ASTM E-84 tunnel test. Analysis of the information presented in Figure 13 and Table VIII shows that a general correlation may be obtained between the two test procedures for most materials.

TABLE VIII
RADIANT PANEL FLAME-SPREAD DATA

Specimen	Name	Flame Spread Data					Classification by Other Methods			Smoke Data							
		Nominal Thickness, in.	Bulk Density, lb per cu ft	Moisture Content, per cent ^a	Number of Tests	Flame Spread Factor, F_g	Heat Evolution Factor, h	Flame Spread Index I_g	Coefficient of Variation, r , per cent	Underwriters' Laboratory Flame Spread Factor	SS-A-118b Classification	Flashover Time, min	Deposit, mg	Based on Red Oak	Underwriters' Laboratory Smoke Factor		
No. 17 ...	Fiberboard perforated tile, finish removed...	1/2	15.7	5.4	5	23.7	14.1	336	14.7	285	D	5.00	0.1	30	357		
No. 28 ...	Fiberboard A (FPL) ^c	1/2	20.0	8.0	9	15.3	18.2	278	5.1							0.4	130
No. 8 ...	Fiberboard J unfinished	1/2	18.0	7.0	9	18.2	12.8	236	5.0							0.2	70
No. 30 ...	Plywood exterior fir unfinished	1/4	42.3	6.8	4	8.5	17.0	143	32.2				0.3	100			
No. 18 ...	Hardboard Common II	7/32	59.8	3.8	5	4.5	30.2	136	12.4				4.1	1400			
No. 23 ...	Hardboard Common M (FPL)	1/4	63.5	3.8	6	4.1	29.7	121	6.9	113		6.15	5.2	1700	1900		
No. 16 ...	Fiberboard perforated tile	1/2	16.7	5.8	5	10.0	11.6	116	13.6				0.3	100			
No. 13 ...	Fiberboard J 1/4 paint A, 250 sq. ft. per gal. ...	1/2	18.3	6.5	5	8.4	12.2	107	44.0				0.4	130			
No. 24 ...	Red oak (FPL)	3/4	40.0	6.5	5	7.0	14.1	99	10.9	100	D		0.3	100	100		
No. 21 ...	Fiberboard C (FPL)	1/2	19.7	6.0	5	10.3	9.0	94	18.3	77	D		0.2	70	94		
No. 9 ...	Fiberboard J factory finish	1/2	20.2	6.6	5	9.9	8.4	83	15.9		D		0.2	70			
No. 12 ...	Fiberboard J 1/4 paint B, 250 sq. ft. per gal. ...	1/2	17.0	6.2	5	6.0	9.8	59	17.2				0.6	200			
No. 34 ...	Plastic C	1/8	81.5		5	4.9	11.5	56	8.4	130			9.7	3200	752		
No. 33 ...	Plastic B	1/8	98.0		5	3.7	8.4	30	19.5	60			5.7	1900	368		
No. 11 ...	Fiberboard J 1/4 paint B, 125 sq. ft. per gal. ...	1/2	17.8	6.9	5	4.1	6.4	27	26.0			10.35	0.9	300			
No. 26 ...	Gypsum board G (FPL)	3/8	50.5		5	4.2	3.6	14.3	44.5	10	C		0.0	0	0		
No. 3 ...	Gypsum board K	3/8	47.4		5	4.4	3.1	13.3	29.9				0.1	30			
No. 6 ...	Mineral base tile	3/4	19.3	3.4	5	7.8	1.5	10.5	60.0	10 ^b			0.0	0			
No. 25 ...	Gypsum board L	1/2	51.2		4	3.0	2.3	7.9	105.0	12.8			0.1	30	17		
No. 23 ...	Fiberboard I fire retardant, finish (FPL)	1/2	19.0	6.4	5	1.8	2.6	4.5	53.8	14	D		0.5	170	14		
No. 32 ...	Plastic A	1/8	89.4		5	1.0	4.0	4.0	42.3	20			3.3	1100	536		
No. 14 ...	Fiberboard L mineral spray	1/2	21.9	7.7	5	1.0	3.4	3.4	28.9				0.2	70			
No. 7 ...	Glass fiber batt	1	4.3	1.2	5	1.0	1.8	1.8	60.5				0.2	70			
No. 2 ...	Cellulose mineral board	7/8	47.8	7.5	5	1.0	1.3	1.3	48.6	9-10 ^b 10-15 ^b		16.45	0.1	30	0 ^b		
No. 8 ...	Glass fiber tile	3/8	10.3	0.6	5	1.0	1.2	1.2	77.7				0.3	100			
No. 15 ...	Fiberboard J 1/8 in. mineral surface	5/8	42.2	7.5	5	1.0	1.2	1.2	50.7		C		0.2	70			
No. 31 ...	Plywood exterior fir 1 aluminum foil	1/4	41.6	6.3	3	1.0	0.9	0.9	65.7		D		0.1	30			
No. 4 ...	Glass fiberboard	2	11.0	0.4	5	1.0	0.6	0.6	37.3		B		0.2	70			
No. 1 ...	Asbestos cement board	3/16	117.0	0.6	5	1.0	0.0	0.0		0	A	17.10	0.0	0			

^aBased on weight after drying at 221 (105 C).

^bTests on same materials but samples from other batches.

^cDesignates materials received from Forest Products Laboratory. Results of British Tests on somewhat similar materials.

In summary, one can conclude that there are a variety of test devices presently available for measuring smoke developed and the light-obscuring characteristics of materials during fire exposure. As shown previously, these small-scale and medium-scale devices are reported to correlate with each other and further, are supposed to present a realistic evaluation of the specimens under test as well as its performance in actual service.

Considerable information exists covering the fundamental physics and chemistry of combustion phenomena. But of the more practical aspects of combustion, how do we use this information to compare the flammability characteristics of materials or the interaction of materials in a total system? For example, it is the total system, the aircraft interior, the hotel room, the complete building, which is involved in a fire and one

must quantify the entire entity and not only its simple component parts. Thus, the major problem is - *How do we measure this value short of full-scale test procedures?*

The problem would be simpler if materials either burned or did not burn. However, most polymeric materials are in-between the two extremes and burn to varying degrees.

Most of the plastic industry's effort during the past twenty years has been channeled toward the development of test methods for a particular product in an effort to show it to be slightly better than some other material. In the development of such test methods, recognition has been given to the fact that under actual fire exposure conditions all the materials evaluated burn. Consideration is given only that under some artificial conditions one product is superior to another - change the conditions and a complete reversal of ratings may often be achieved. In view of the above, the American Society for Testing Materials recognizes this fact with the standard disclaimer:

"NO DIRECT CORRELATION BETWEEN THESE TESTS AND SERVICE PERFORMANCE SHOULD BE GIVEN OR IMPLIED"

Thus, the question could be asked, what should be the rationale of fire testing? Most fire researchers will agree that correlation between small-scale tests and actual fire experiences needs to be established.

Factors which determine the flammability characteristics of polymeric materials are:

- Sample Geometry and Orientation
- Sample Environment and Age
- Surface Area, and Porosity
- Concentration and Type of Additives
- Sample Density and Melting Point
- Degree of Aromaticity
- Cross-link Density
- Crystallinity
- Glass Transition Temperature
- Hydrogen Bonding
- Cohesive Bond Energy
- Degradation Temperature
- Convective Cooling Rate
- Specific Heat
- Absorptivity
- Thermal Conductivity
- Heat of Combustion

Considering the above factors which concern themselves with the physical and chemical properties of the material, a second list is presented which summarizes the parameters involved in designing a testing procedure:

What and where is the ignition source?
How fast is flame propagated?
Does the sample drip, spatter, char?
Does the material evolve flammable segments?
Does the material evolve toxic components?
What is the oxygen content of the sample and its environment?
What is the velocity and direction of air flow?
How much smoke is evolved?
How long does it take to burn through?
What is the size of the material under test?

- a. Small-scale (laboratory test)
- b. Intermediate-scale
- c. Large-scale

The terminology (and need for standardization) in fire-test evaluation can cause considerable confusion to those trying to interpret test results. Typical terminology found in fire-test reports in combustion literature are listed below:

Flameproof
Non-Burning
Self-Extinguishing
Slow Burning
Flammable
Non-Flammable
Fire Retardant
Burning
Flame Retardant
Fire Resistant
Non-Combustible

The above terms are definable but only when linked to a given material and a definite mode of testing.

The sample material examined by one test may be self-extinguishing while it may rate as combustible if another test is used.

Quantitative Determination and Characterization of Smoke

General Background

In recent years, firemen, building officials, personnel assigned to regulatory agencies, and to some extent the general public, have come to suspect that smoke from smoldering or burning materials may pose a greater threat to life than the heat generated in a fire.^{24,25}

In the past thirty years new problems have appeared in regard to fires. Many of these problems have been a direct outcome of man's ability to prepare synthetic materials to replace natural materials such as wood, cotton, silk, and metals. The heating and burning of these materials have

and are presenting dangers not only from the temperature or actual flames, but also from the variety of pyrolysis and combustion products generated from the fires. These potential problems now make it necessary to recognize the toxic aspects of fires and to devise methods for preventing and/or coping with them.

As mentioned earlier, the importance of toxic factors leading to death from fires was brought into national prominence from the Cleveland Clinic fire in 1929. In this tragic fire, X-ray films manufactured from the highly-combustible nitrocellulose ignited bringing death to 125 persons. Again, in 1942, a fire of national importance occurred in a popular Boston nightclub (Coconut Grove) bringing death to several hundred persons. In 1970 a number of fires in various parts of the United States and Europe focused additional attention on the tragedies resulting from fire. Thirty-two elderly residents of the Hamar Nursing Home, located in Marietta, Ohio, lost their lives due to a fire. Descriptions of the fire included accounts of dense clouds of black smoke most likely produced from carpeting, padding, paint, as well as from various types of furniture. Seventeen patients died in a private home for the aged in Montreal from a minor basement fire which lasted only 20 minutes. In November another fire in a gymnasium in France brought tragic deaths to 145 young people attending a dance.

The author served as an investigator of the fire in the Lil Haven Nursing Home (September 15, 1971) in Salt Lake City, Utah. Six patients died in a fire that lasted approximately 10 minutes. The first fire equipment arrived on the scene less than one minute after the rate-of-rise detector signaled the alarm. It is interesting to note that none of the six patients who died showed any evidence of body burns.

The propensity of certain plastic and elastomeric materials to ignite and burn with a rapid propagation rate has encouraged the industry producing these materials, as well as government agencies, to find ways of preventing or diminishing the flammability of the material.

Many polymeric materials contain chemical agents, called fire retardants, to reduce the original flammability characteristics of the material. The use of fire retardants is increasing at a prodigious rate each year. Unfortunately, as may happen on occasion, the treatment may bring about another problem equal to the problem which originally required the treatment. In this case, the flame retardants do improve the flammability characteristics of the materials, but by doing so, they increase the concentration and types of pyrolysis products which may be liberated during fire exposure. These products may have biological implications not previously appreciated.

Analysis of Smoke Development in Polymers

Gaskill⁵ has used the following procedure for conditioning samples prior to evaluation of smoke characteristics:

1. Samples are cut to size, dried overnight at 60°C, and conditioned for at least one week at room temperature at a relative humidity of 50 ± 2 per cent.
2. The samples are then tested in the smoke chamber under the following fire parameters:
 - a. Radiant heat exposure without flame in a sealed chamber.
 - b. Radiant heat exposure plus pilot flame in a sealed chamber.
 - c. Radiant heat exposure (only) under ventilation rates of 3, 6, 12, and 20 air changes per hour.
 - d. Radiant heat exposure plus pilot flame under ventilation rates of 3, 6, 12, and 20 air changes per hour.

The specific optical density may be determined from the light-transmission curves using the method of Gross, et al.¹⁶ The specific optical density which is used as a measure of the smoke evolved is defined as:

$$D_s = \frac{V}{LA} \log (100/T)$$

where:

- D_s = specific optical density
- V = chamber volume
- L = path length of light
- A = area of sample exposed to burning
- T = per cent light transmittance

Mickelson⁹ has presented two typical curves which might be obtained using the NBS smoke chamber. (See Figure 14).

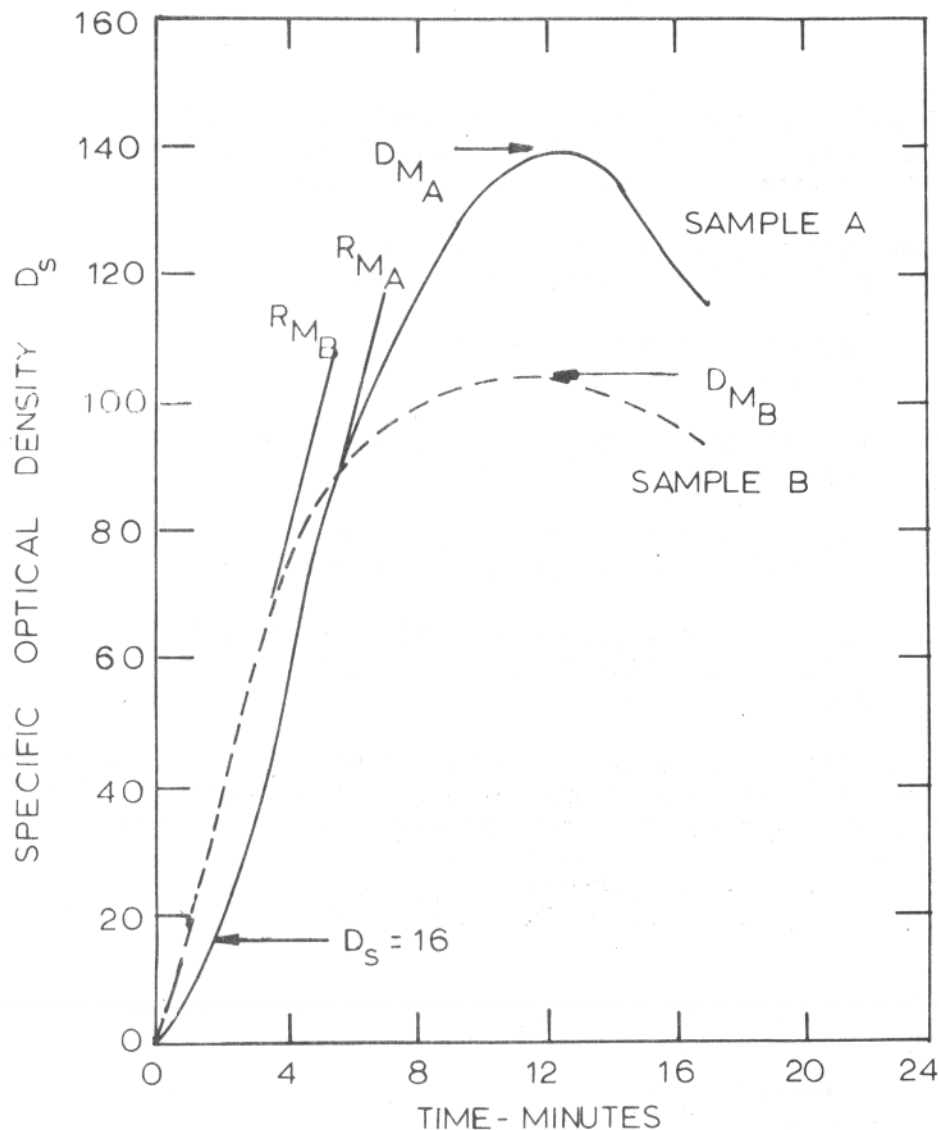


FIG. 14. TYPICAL SMOKE DEVELOPMENT CURVES FOR TWO MATERIALS

From the curves illustrated in Figure 14, it is obvious that a comparison between the smoking behavior of the two samples is most difficult. There are three parameters by which the smoking tendency of the two samples could be compared. The highest optical density, D_m , might be chosen as the indicator to show the difference between the smoking behavior of each material. Thus, in Figure 14, sample A would produce a greater amount of smoke than sample B.

Another criteria for comparison is to look for the time when the optical density has reached a prescribed value that is associated with a person's ability to find his way out of a smoke-filled room. The National Bureau of Standards has settled on a specific optical density of 16 as the indicator for this danger point. The significance of the critical time (time to reach an optical density of 16) is shown both in Figures 15 and in Table IX.

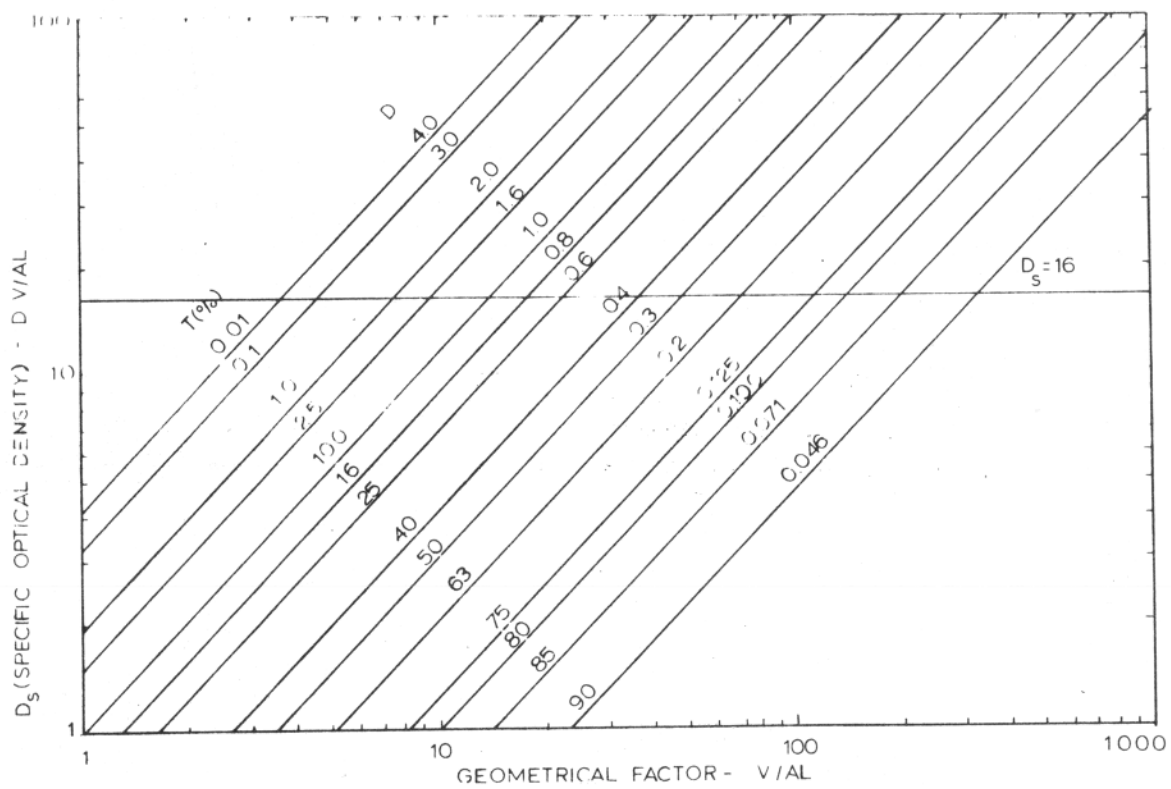


TABLE IX

LIGHT TRANSMISSION IN VARIOUS-SIZED COMPARTMENTS WITH VARIOUS AREAS
 EMITTING SMOKE OF SPECIFIC OPTICAL DENSITIES OF 50 AND 100
 (Viewing Distance = 10 feet)

Compartment Dimension (ft) Volume (ft ³)	12 x 10 x 8 960	50 x 8 x 8 3,200	40 x 40 x 8 12,800
Area smoking = 5 ft ²			
V/AL	19.2	64	256
% Transmission for			
D = 50	<1	<16	~55
D _s = 100	<0.01	~ 2.5	~40
Area smoking = 10 ft ²			
V/AL	9.6	32	128
% Transmission for			
D = 50	<0.01	~2.5	~40
D _s = 100	<0.01	<0.1	~16
Area smoking = 100 ft ²			
V/AL	0.96	3.2	12.8
% Transmission for			
D = 50	<0.01	<0.01	~0.01
D _s = 100	<0.01	<0.01	<0.01

V/AL = volume divided by area x length.

The data presented in Table IX show the per cent of light transmission for a viewing distance of 10 feet in three different-sized compartments with small, medium, and large areas yielding smokes of specific optical densities of 50 and 100. Visibility through these smokes is probable only in cases where small areas are smoking into very large volumes

For each test the specific obscuration index (SOI) is calculated. This concept, developed by Gross, et al.,¹⁶ equates the visibility hazard to the product of the maximum smoke density and the average rate of smoke increase divided by the critical time (the time in which the specific optical density reaches a value of 16). The derivation of the SOI is shown in Figure 16.

$$SOI = \frac{D_M \times R}{t_c}$$

D_M = maximum smoke accumulation
 R = average of linear rates of accumulation for each of the four 20% intervals between 10% and 90% of D_M
 t_c = time to reach a critical level, i.e., D_{s-16}

$$R = 1/4 \left[\frac{0.9 D_M - 0.7 D_M}{t_{0.9} - t_{0.7}} + \frac{0.7 D_M - 0.5 D_M}{t_{0.7} - t_{0.5}} + \frac{0.5 D_M - 0.3 D_M}{t_{0.5} - t_{0.3}} + \frac{0.3 D_M - 0.1 D_M}{t_{0.3} - t_{0.1}} \right]$$

$$= \frac{D_M}{20} \left[\frac{1}{t_{0.9} - t_{0.7}} + \frac{1}{t_{0.7} - t_{0.5}} + \dots \right]$$

Hence $SOI = \frac{D_M^2}{20 \times 100 \times D_{s-16}} \left[\frac{1}{t_{0.9} - t_{0.7}} + \frac{1}{t_{0.7} - t_{0.5}} + \dots \right]$

where $\frac{1}{100}$ is an artificial factor.

FIG. 16. SMOKE OBSCURATION INDEX (AS PROPOSED BY NBS)

A third method of comparison would be to use the maximum rate, R_M , at which smoke is being produced as the criterion. For the two samples shown in Figure 14, the maximum rates are about the same and it might be concluded that these two materials are equally bad producers of smoke.

Burning Conditions

For the tests mentioned previously, there are a variety of combustion conditions to which the sample is exposed. In the XP-2 chamber there is a direct flame contact between a propane torch and the sample. In the NBS chamber the sample is exposed to a constant radiation source (2.5 watts/square centimeter). The evolved gases may be ignited with a pilot flame if desired. Both smoldering and flaming samples may be evaluated using these chambers. Table X presents a summary comparing smoke evolution for smoldering and flaming specimens. This table was compiled by Mickelson⁹ and is a summary of earlier work carried out by Gross, et al.,¹⁶ and Gaskill.⁵

TABLE X

COMPARISON OF SMOKE EVOLUTION FOR SMOLDERING AND FLAMING CONDITIONS

<u>Material</u>	<u>Smoldering</u>		<u>Flaming</u>	
	<u>DM</u>	<u>S.O.I.</u>	<u>DM</u>	<u>S.O.I.</u>
Polyvinyl chloride	470 300*	93	535 600*	1400
Nylon	300	1	95	1
Silicone rubber	240	88	385	105
Polycarbonate	21	0	324	60
Urethane rubber (TDI - Polyester)	131	0	210	50
Polyethylene	468	65	150	3
Polystyrene	345 372*	22	468 660*	890

*Gross, et al.; all other values are the data of Gaskill.

Inspection of the data presented in Table X shows that a large difference exists in the quantity of smoke generated between the two burning products. It should be noted that the more flammable materials have a greater smoking tendency under smoldering conditions.

The effects of pre-ignition heating rates on the degradation process are variables which must be considered in a realistic study of the combustion process. Studies conducted by Christian,²⁶ Waterman,²⁷ Birky,²⁸ and Yuill²⁵ using rooms or room and corridor test facilities, have illustrated the effects of pre-ignition heating on the progress of experimental large-scale fire tests. Christian²⁶ summarized his results of a recent large-scale study (with reference to smoke) by stating, "incremental smoke produced by a finish material is equal to the difference between values measured in a finish fire and in a reference fire. Incremental smoke can be added to that of an appropriate room fire to evaluate total smoke production."

Another important factor that must be considered in the evaluation of the burning characteristics of materials is the availability of oxygen during the fire. Stuetz, et al.²⁹ and Einhorn³⁰ have discussed the effects of oxygen during the combustion of polymers. Stuetz showed that the limiting oxygen index (LOI) is a factor which affects the gas phase burning mechanisms. Einhorn showed that many polymers which form strong char structures fail to produce a homogeneous char when the oxygen content drops below a critical level. Char formation and char strength are factors which directly govern the combustion process and markedly affect the rate of smoke development.

Gaskill⁵ demonstrated the effects on smoke density by red oak combusted under flaming and non-flaming conditions. Figure 17 shows that

under radiant exposure the smoke density reaches a maximum value in about 20 minutes, with obscuration ($D_s = 16$) occurring in about 4 minutes. The maximum density is 400. For these conditions the smoke obscuration index is about 35. Under flaming conditions the maximum density is 75, obscuration occurs in about 8 minutes, and the obscuration index is essentially negligible.

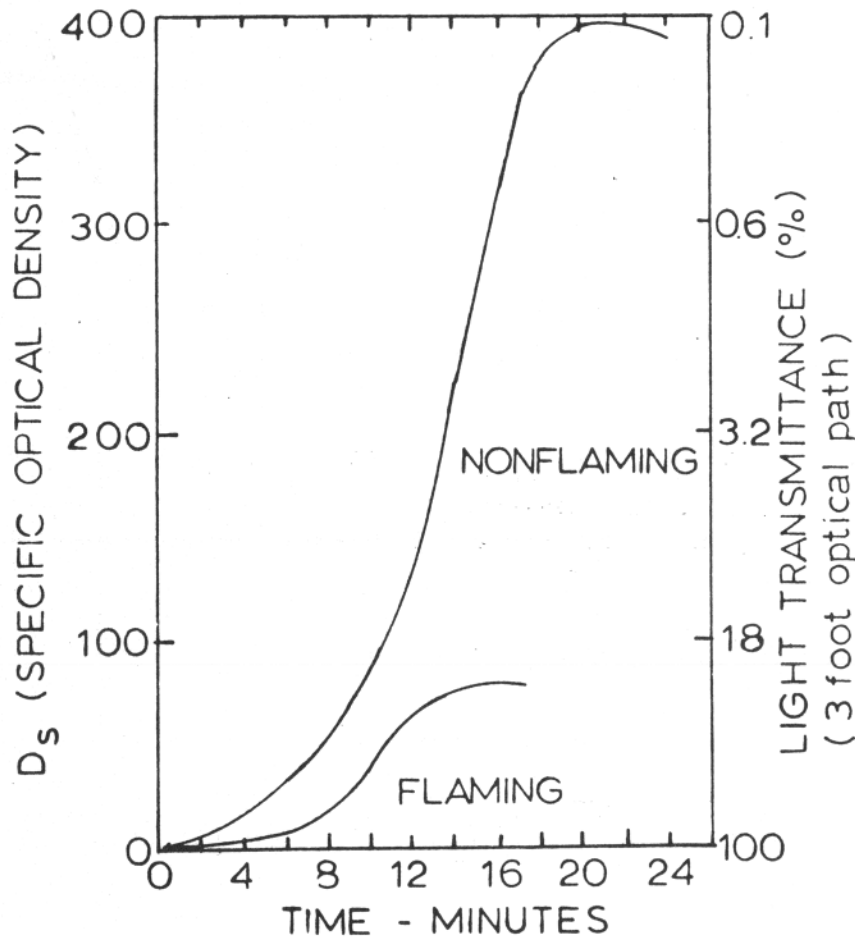


FIG. 17. RED OAK - SPECIFIC OPTICAL DENSITY AS A FUNCTION OF BURNING CONDITIONS

Gaskill⁵ noted that under ventilated conditions the maximum density decreased under non-flaming exposure to a value of 125 for the maximum ventilation of 20 changes per hour. This was still considered to be a dense smoke (see Figure 18). The red oak specimens under flaming conditions, with ventilation rates of 9 to 15 changes per hour, exhibited a reduction of smoke density to tolerable proportions.

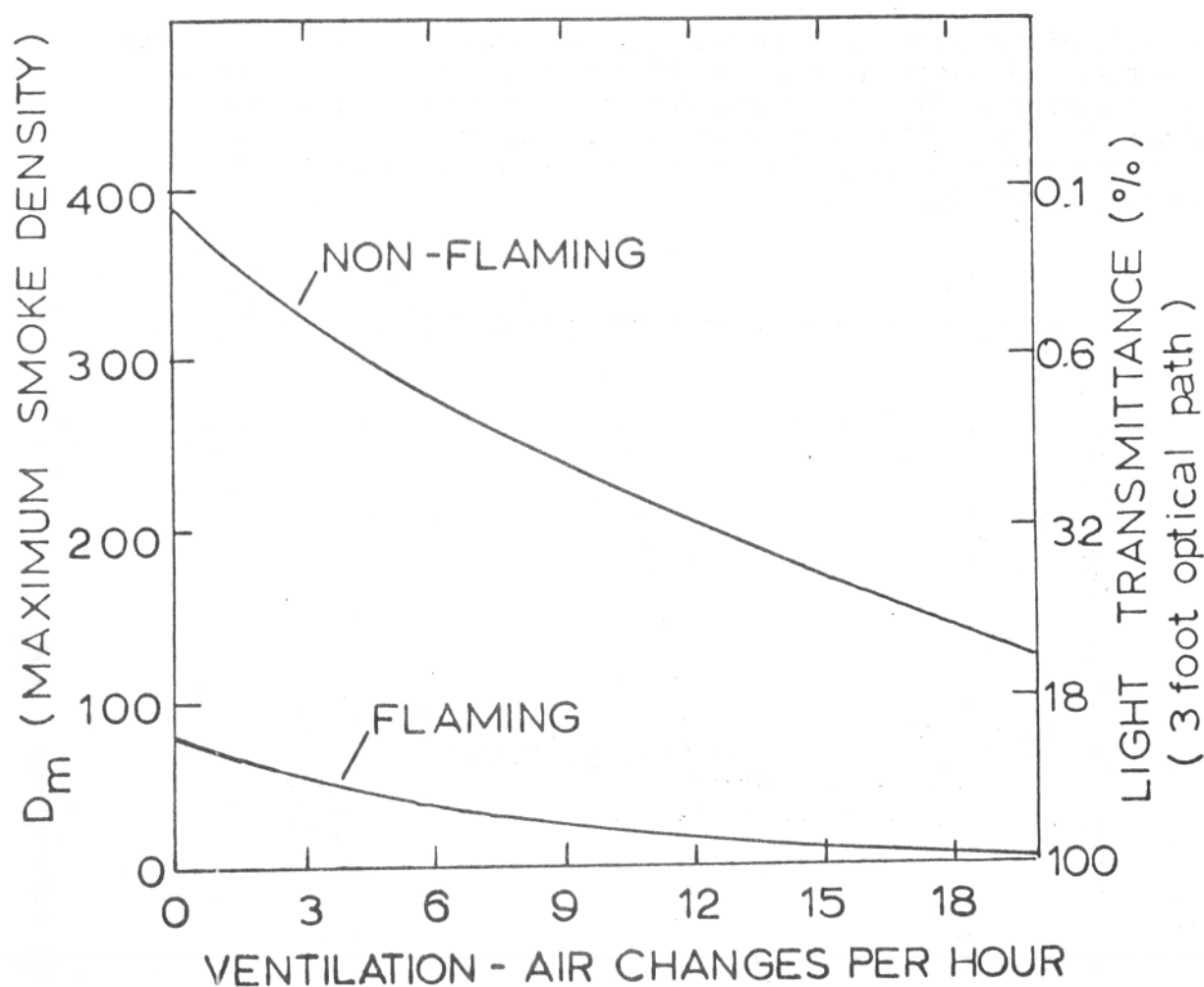


FIG. 18. EFFECT OF VENTILATION ON MAXIMUM SMOKE DENSITY

Effect of Fire Retardants on Smoke Generation

Einhorn, et al., ^{15,30,31} have demonstrated the effects of fire retardants and fire-retardant concentrations on the limiting oxygen index values and smoke obscuration values. Figures 19 and 20 illustrate the effect of concentration of reactive and non-reactive fire retardants on the light obscuration times in rigid-urethane foams.

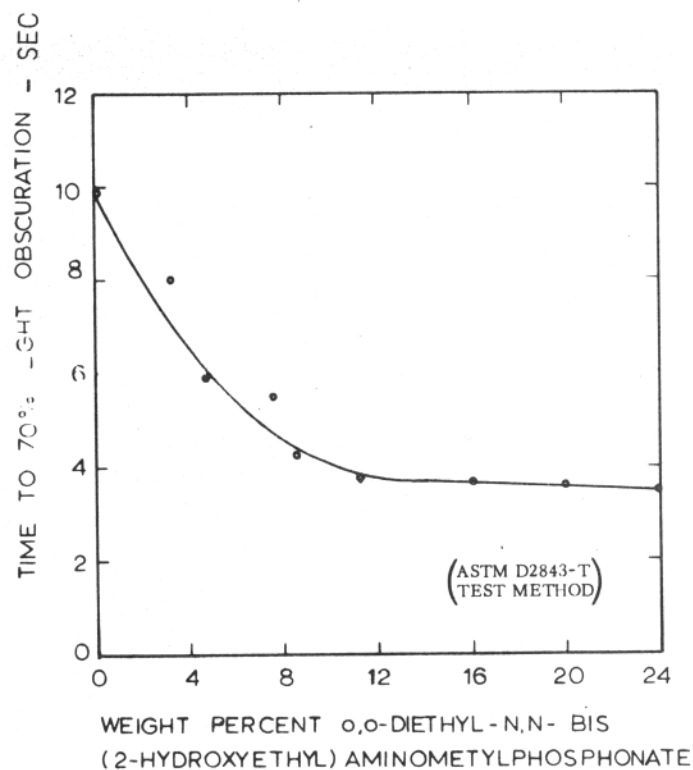


FIG. 19. EFFECT OF CONCENTRATION OF THE REACTIVE FIRE RETARDANT 0,0-DIETHYL-N,N-BIS (2-HYDROXYETHYL) AMINOMETHYLPHOSPHONATE ON LIGHT OBSCURATION IN RIGID-URETHANE FOAMS

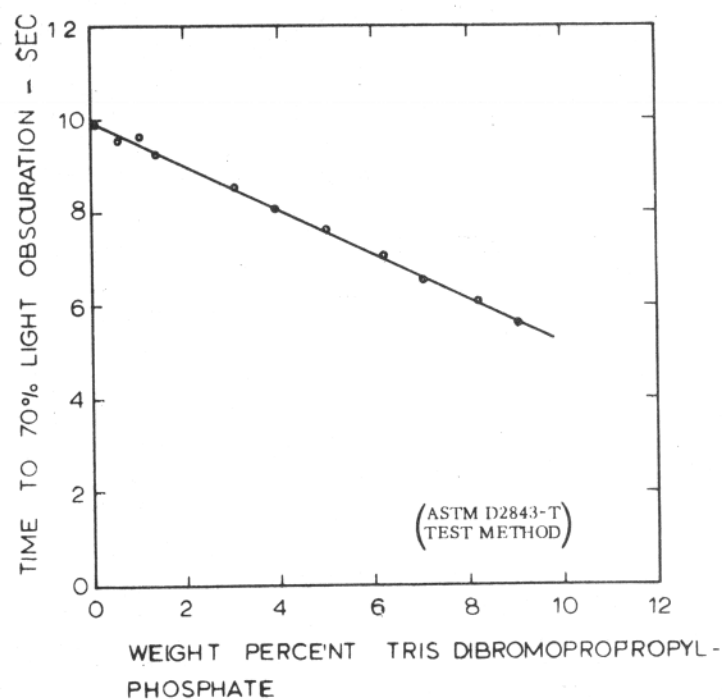


FIG. 20. EFFECT OF THE NON-REACTIVE FIRE RETARDANT TRIS, 2,3-DIBROMOPROPYLPHOSPHATE ON LIGHT OBSCURATION IN RIGID-URETHANE FOAMS

It should be noted that the reactive fire retardant, which imparts the greatest degree of protection, produces a more rapid light obscuration.

Effect of Chemical Structure on Smoke Development

Several investigators have studied the effects of chemical structure on the flammability characteristics of rigid-urethane foams.^{5,15,32,33,34,35} Table XI⁵ presents an excellent summary of chemical structure-smoke relationships in urethane foams.

TABLE XI
SMOKE DEVELOPMENT BY URETHANE FOAMS

Foam type	Density (lb/ft ³)	Blowing agent	Reaction to heat	Ventilation (changes/hr)	Nonflaming				Flaming			
					D _m	T _m (min)	D _s 16 (min)	SOI	D _m	T _m (min)	D _s 16 (min)	SOI
PAPI-ether (rigid, fire retardant)	2	CO ₂	Shrinks, chars, some tar	0	119	13	0.36	57	196	1	0.21	740
				3	82	8	0.35	45	168	2	0.23	685
				6	58	6	0.30	45	166	2	0.16	1070
				12	46	4	0.42	24	100	1	0.21	315
				20	34	2	0.47	18	109	2	0.25	246
PAPI-ether (rigid, fire retardant)	2	Fluorocarbon	Shrinks, chars, some tar	0	112	9	0.40	85	252	2	0.14	3400
				3	97	4	0.36	116	241	2	0.16	2600
				6	70	3	0.40	70	224	2	0.17	2700
				12	59	2	0.38	65	211	2	0.15	2700
				20	55	2	0.41	50	178	2	0.14	2300
PAPI-ester (rigid, fire retardant)	4	CO ₂	Shrinks and chars	0	454	16	0.39	475	525	6	0.18	4200
				3	359	14	0.47	245	528	7	0.16	5900
				6	299	13	0.50	177	512	7	0.18	4900
				12	227	10	0.43	145	480	7	0.18	2700
				20	159	10	0.40	93	416	5	0.18	3500
TDI-ester (fire retardant)	25	CO ₂	Melts and drips	0	431	20	1.0	132	534	6	0.5	1470
				3					508	6	1.0	650
				6	251	16	1.0	70	497	6	1.0	675
				12	153	14	1.0	40	357	6	1.0	330
				20	102	14	1.0	20	253	6	1.1	160
TDI-ether (non-fire retardant)	1.3	CO ₂	Shrinks, melts, flaming drips	0	515	26	0.52	270	319	5-12	0.80	990
				3					251	5	0.90	234
				6	300	34	0.55	87	245	6	1.0	126
				12	177	23	0.63	48	227	6	0.92	196
				20	105	32	0.59	20	136	6	0.86	80
TDI-ester (fire retardant)	2.5	CO ₂	Shrinks and melts to tarry mass	0	161	13	0.43	105	70	4	0.20	310
				6	89	4	0.44	80	50	1	0.45	56
				12	66	2	0.43	56	40	1	0.48	32
TDI-ether (fire retardant)	1.8	CO ₂	Chars, shrinks	0	290	7	0.44	620	285	2	0.17	4500
				3					280	1	0.16	4800
				6	210	5	0.35	280	265	1	0.18	3900
				12	160	4	0.44	155	260	1	0.16	4200
				20	130	4	0.46	130	240	1	0.18	3200
MDI-sucrose (fire retardant)	2	Fluorocarbon	Shrinks and chars	0	170	10	0.30	190	500	2	0.13	12000

Considerable information is listed in the literature pertaining to the smoking characteristics of a wide variety of polymeric systems.^{36,37,38,39,40,41,42,43} Since most other classes of polymers follow the general guidelines mentioned previously in this study, the reader is directed to the above-mentioned references for further information pertaining to specific classes of polymers.

Physiological Aspects of Smoke

General Background

A review of the information presented in the INTRODUCTION shows that a vast amount of information is presently available pertaining to fire statistics. Much of the information gathered provides the basis for an understanding of the magnitude of an increasing public loss. Little information is available that relates to human response during fire exposure.

A series of disasters in recent years has focused considerable attention on the growing list of problems connected with the burning of polymeric materials such as fibers, coatings, elastomers, foams, and reinforced plastics. The crash of the United Airlines Boeing 727 jetliner at the Salt Lake City Airport in November 1965 was one of the most dramatic incidents illustrating the dangers arising from intense heat, toxic fumes, and dense smoke. This tragedy, which took the lives of 43 persons out of the 91 aboard, was one of the rare instances of what the Civil Aeronautics Board termed "survivable" crash with no fatalities on impact. Yet the big question remained: *What was the contribution of the plastic materials inside the plane to the development of fumes and smoke?* Previous attempts by industry to fire retard plastics produced improved resistance to flame contact, however, hazards due to smoke generation were, in general, not fully understood and recognized. Disasters of the Salt Lake City type clearly spell out the need for the use of plastic materials that exhibit both adequate flame resistance, as well as low-smoke generation. The necessity exists, therefore, for the development of plastics with these properties and the more accurate evaluation of such materials to allow prediction of their behavior in emergency situations.

A critical analysis of the hazards to life support in fires involving plastics has been carried out by the author. The burning process takes place in several steps.

1. A destructive distillation of the plastic takes place, producing gases whose nature depends on the composition of the material.
2. Oxygen unites with free carbon to form carbon monoxide. At this time dense smoke is usually formed, presenting additional hazards.
3. When sufficient oxygen is present, it combines with the flammable gases produced in the first step, as well as with carbon monoxide. If sufficient excess oxygen is available to combine with all the combustible materials, the carbon monoxide burns to form the relatively harmless carbon dioxide. Ordinarily, the products of complete combustion are less harmful than those of incomplete burning.

Thus, consideration of those parameters affecting the combustion of plastics has led the author to list the hazards to life support in the following order of decreasing importance for confined space fires:

1. Asphyxiation — caused by rapid depletion of available oxygen
2. Attack by superheated air or gases (maximum survivable temperature)
3. Smoke development
4. Toxicity hazards of combustion products
5. Flame propagation.

Fires involving very rapid flame propagation as contrasted to slow burning deep-seated fires would, of course, alter the order in which the hazards are listed above. A sixth factor must be considered which probably outweighs the factors mentioned above. It is the combined effect of all five factors.

The Fire Gas Research Report⁴⁴ states that where oxygen is reduced to 12-15 per cent under fire conditions, muscular coordination for skilled movements is lost; between 10 and 14 per cent, consciousness continues, but judgment is faulty and muscular effort leads to rapid fatigue. Breathing ceases when the oxygen content falls below 6 per cent. Oxygen concentrations below 6 per cent will cause death at ambient temperatures in 6 to 8 minutes.

Shorter, et al.,⁴⁵ reported that temperatures in excess of 300°F (149°C) were capable of causing loss of consciousness or death within several minutes. The temperatures recorded in several controlled experimental fires in buildings exceeded the maximum survivable level within 5 to 10 minutes. This period of time is expected to be greatly reduced in aircraft fires due to the large concentrations of available fuel.

Smoke development measurements have been made by a number of experimental techniques. Dense smoke discharged into the atmosphere by burning wood, cotton, paper, or plastics contains toxic products of thermal decomposition including carbon monoxide, hydrogen cyanide, hydrogen halides, a number of organic irritants, such as acetic acid, formic acid, formaldehyde, furfural, etc. During the early stages of a fire, the smoke may contain so little carbon monoxide that the major injuries resulting from smoke inhalation may be caused by the irritants. These attack the mucous membranes of the respiratory tract and may create conditions favoring the onset of pneumonia. In cases of actual exposure, the physiological effects of inhaling smoke depend upon its physical state. When the smoke is very hot, it will destroy tissues by burning, regardless of its chemical composition; when cooled, the smoke may be non-irritating because the irritants have been removed by condensation and settling.

In addition to causing injury or death by the methods previously described, dense smoke may prevent exit from the area of combustion by

obscuring vision. This same obscuration effect may prevent location of the source of the fire and thus hinder fire control.

Many investigations have been conducted on single materials under controlled laboratory conditions. In actual fires, combustion of single materials is seldom encountered, and there is ample evidence to show that the sum of the toxicity potential of two or more gases or vapors may synergistically affect life.²⁶ When encountered in a fire, the toxicity of such mixtures may be further increased by low oxygen concentrations and high temperatures. Carbon dioxide, for example, causes stimulation of the respiratory center of the brain; and if breathed in excess during a fire, it causes an abnormally high intake of other gases causing toxic or lethal concentrations which might have been avoided if carbon dioxide had been absent.

Although the lungs and associated structures are principal sites of action for irritant fire gases, corrosive vapors such as acids and acetaldehyde will also affect the unprotected skin and the cornea of the eye. Whatever the tissue exposed, the effect will cause inflammation. If the concentration of irritant gas or vapor is high or the exposure prolonged, fluid accumulates in the respiratory organs, being drawn from the blood and tissues. This condition is called tracheal, bronchial, or pulmonary edema, according to the level in the respiratory tract which is affected.

To date, the major concern of those engaged in the development of fire-retardant materials has been the reduction of the ignition tendency and flame propagation. Thus, it has been possible to meet code and regulatory requirements regarding flame spread, but in the opinion of the author, the total hazard resulting from incomplete combustion has been increased.

In addition to an increase in hazards caused by improper methods of fire-retardation of plastics, recent studies conducted by the author have shown that the flammability characteristics measured by small-scale testing procedures, with slow heating rates, do not correspond with the performance of the same materials in actual large-scale fire exposures. The incorporation of a fire retardant into a polymeric composition will lower the thermal degradation temperature of the polymer.¹⁵ If the material is exposed to a flame in an environment of rapidly-diminishing oxygen content, the fire-retardant material may burn more readily than the non-fire-retardant composition. Further studies using sensitive thermal analytical procedures have shown that incorporation of non-reactive low molecular weight retardants may lead to sublimation of the retardant prior to actual flame contact resulting in a material which also will burn more readily than the non-retarded material.

Physiological Factors Affecting Survival During Fire Exposure

The factors that critically limit survival responses during fire exposure must be defined. In actual fire exposure it is difficult, if not impossible, to separate the physiological parameters from the toxicological parameters. Within the scope of this paper, the author has made this separation in order to illucidate that which is presently understood about the response of humans in fires and to indicate those areas where further study is required.

In many respects, it is more important to determine limits for survival than the mechanism of death from exposure to noxious gases or hypoxia.

Visual Parameters Affecting Survival

Considerable attention was directed earlier to the measurement by optical techniques of the quantity of smoke produced during the combustion process. It should be noted that while many chemical and physical factors can affect the quantity of smoke produced, the size and concentration of particulates in this smoke, and the chemical composition of the smoke, the optical techniques commonly used can measure only the light obscuring potential of smoke and cannot measure the physiological factors relating to human survival during fire. The particulates contained in smoke can and do affect the vision of firefighters using gas masks and sustained breathing equipment. The results obtained using the XP-2 chamber or the NBS chamber can relate directly to the ability of firefighters to see under fire conditions. On the other hand, persons encountering smoke in a fire may not be able to see due to such factors as lacrimation caused by components in the smoke. Einhorn, et al.,⁴⁶ reported that fluorocarbons exposed to pyrolysis or combustion caused severe opacification of the cornea in test animals exposed to their degradation products. The hydrogen fluoride, fluorine gas, and carbonyl-difluoride, identified in the smoke produced was in sufficient concentration to etch glass coverslips. Thus, even though relatively low smoke was generated during the pyrolysis or combustion process, humans exposed in a similar environment might have their sight hampered to an extent that they would not be able to escape a fire area in time to prevent exposure to lethal concentrations of toxic fumes or temperatures sufficient to cause death.

Escape Response

Little reliable data is available concerning the escape response of humans during fire exposure. The influence of hypoxia alone and in combination with carbon monoxide and noxious gases must be determined both at ambient temperatures and at rates of temperature increase that are encountered in "typical" fires. Numerous investigators have reported cases where a victim has died during a fire with no visible barrier observed to easy escape. Victims of fires, such as cigarette ignition of mattresses or furniture, where long periods of smoldering have preceded

actual ignition often are found away from the ignition source. Analysis confirms relatively high blood carboxyhemoglobin concentrations which may have been the cause of death. But questions must be asked as to possible loss of sight, prior to death, the possible effect on nerve impulse, the possible effects on muscle activation or contraction, or other effects similar to these which may have prevented escape from a hazardous area even though the victim realized that he must egress the area.

Noxious gases which find their way into the circulation, either because they are odorless or are in low concentrations, may act in still unknown ways in producing neuromuscular dysfunction. The peculiar affinity of carbon monoxide for hemoglobin and cyanide radicals for cytochrome oxidase are two well-known examples. Other bases may also affect oxidative metabolism at various levels either by influencing oxygen transport or intermediary metabolism. The enzyme systems concerned directly with muscle activation and contraction may also be affected.

Studies comparing responses to hypoxia of various types of CO interaction have disclosed significant differences. Since arterial P_{O_2} may be normal despite a reduced oxygen-carrying capacity, reflexes which normally increase respiratory rate and tissue blood flow are not activated.^{47,48} Recovery from hypoxia associated with CO intoxication is greatly prolonged in comparison to recovery from hypoxia alone.^{49,50}

A reduced partial pressure of oxygen is found in a poorly-ventilated environment in which there is combustion. Combined with the presence of carbon monoxide and other gases impairing oxidative metabolism, very little reduction in ambient oxygen tension may be lethal. From observations of subjects at high altitude, lassitude and lack of motivation progressing to somnolence are the primary behavioral responses to hypoxia.⁵¹ These effects threaten survival both at altitude and during accidental fire. The ability to continue automatic motor activities such as running depends both upon the central nervous control of this activity and the neuromuscular system. The ability of these systems to continue normal function during fire exposure must be determined. It should be possible to assess the relative importance of central nervous and peripheral neuromuscular systems as responsible for loss of motor control. As yet unknown mechanisms dependent upon particular combinations of noxious gases may be operating which can significantly impair peripheral motor mechanisms. Noxious gases may exert specific effects upon activation and/or contraction properties of skeletal muscles. Failure to respond appropriately under the stressful circumstances of a fire may depend upon loss of these peripheral motor mechanisms.

Toxicological Aspects of Combustion

General Background

The most controversial and most complicated aspect of fire research is that phase of study directed toward an understanding of the toxicological properties of materials during fire exposure. Hundreds of articles have appeared in the literature reporting the nature and quantitative

analysis of pyrolytic decomposition products. Bulletin 53⁵² published by Underwriters' Laboratories cites two hundred ninety-seven references dealing with toxicity studies using animals which were exposed to a wide range of environments under many experimental conditions. In the summary of this report it was stated that considerable variance was observed in the experimental results and that little correlation was obtained by different investigators.

If laboratory animals are subjected directly to the pyrolytic decomposition products at temperatures normally encountered in real fires, they perish from the effects of heat before being overcome by the decomposition products.

In recent investigations Einhorn et al.⁴⁶ studied the effect of temperature on lethality (LD 100) of laboratory rats of varying body weight. A preliminary heat transfer mechanism was postulated. Although an induction period was observed due to the insulating characteristics of the animal's fur, the relatively large surface-to-volume ratio resulted in their inability to survive extensive thermal shock to the degree that humans can.

Previous studies utilizing animals have suffered from several defects in design. First, the number of animals was small. Second, there was often a lack of control. Third, there were few standardized pre- and post-exposure tests of the animals' responses. Fourth, routine necropsy examinations of all major organs were not the rule.

A further weakness in many investigations pertaining to toxicological aspects of combustion is the failure to simulate conditions of common prototype fires such as aviation fires, home fires, automobile or boat fires, etc. For example, the likely time of exposure and the likely conditions of exposure such as temperature and varying oxygen concentration have not been key factors in the experiments. Analysis of decomposition products resulting from pyrolysis or combustion has indicated major changes in the nature of the products due to condensation, recombination, or cross-reactions when the temperatures of combustion are modified. Experimental design considerations must also be given to changes in the degradation of a single material as compared to the degradation of the same material in the presence of one or more materials of different chemical composition.

Respiratory Burns

In 1962, Phillips and Cope⁵³ labeled respiratory tract damage as "a principal killer" in burn victims. In 1967, Stone⁵⁴ reported respiratory involvement in 15 per cent of 197 burn patients studied. Zikria⁵⁵ analyzed the causes of death among fire fatalities which had occurred in New York City during the years 1966 and 1967. (See Table XII).

TABLE XII
BURN MORTALITY - NEW YORK CITY 1966 AND 1967

<u>Post-Burn Survival Time</u>	<u>Total Cases (Survival Time)</u>		<u>Autopsied Cases (311)</u>	
	<u>Cases</u>	<u>%</u>	<u>Cases</u>	<u>%</u>
<12 hours	283	53	185	60
>12 hours	158	30	72	23
Not known	93	17	54	17
Total	534	100	311	100

Three hundred and eleven of 534 fire victims were autopsied, 60 per cent of whom died at the site of the fire or on the way to the hospital. Seventy per cent of these early fatalities had respiratory involvements.

One hundred and five of the fire fatalities had less than 40 per cent body surface burns; 77 per cent of these could have been expected to survive, if statistical prediction were based solely on the extent of the body surface burns.^{56*} Respiratory involvement was found as a primary diagnosis among the majority of these fatalities. Specifically, 43 per cent had smoke poisoning and/or asphyxiation; 50 per cent had carbon monoxide poisoning; and 27 per cent had pathologically evident damage to the tracheobronchial tree and lungs. These figures clearly indicate the magnitude and seriousness of the problem of inhalation injuries in fire victims.

It is generally accepted that the tracheobronchial tree and pulmonary tissues can sustain heat damage, chemical damage, anoxic damage, or any combination of these injuries during fire exposure. Pressure damage may also occur when the fire is accompanied by an explosion.

Until the late 1960's many investigators doubted that caloric inhalation damage could occur in the tracheobronchial tree because of the low specific heat of gases. Moritz⁵⁷ experiments on dogs using high-temperature torches as the source of combustion, seemed to indicate the

*Medically the "rules of nine"⁵⁶ are used to express the extent of a burn. One arm is 9 per cent, a leg is 9 per cent, front and back 9 per cent, etc. The per cent of the body involved is important for both treatment and for plotting survival figures. If a 3rd degree burn involves 50 per cent of the body surfaces, the mortality rate is about 50 per cent. If a 3rd degree burn involves 70 per cent or more of the body surfaces, survival is nil. A healthy adult may survive a 10 - 15 per cent 3rd degree burn without too much difficulty; a healthy child may survive a 5 - 10 per cent 3rd degree burn without too much difficulty.

physical impossibility of caloric damage. In 1968 Zikria, et al⁵⁵ and Stone⁵⁸ demonstrated heat fixation of the tracheal mucosa in fire victims as well as the presence in varying degrees of injury to the tracheobronchial tree. All the victims who had severe tracheobronchial damage were dead at the scene of the fire or soon after.

It is possible that the caloric burns of the tracheobronchial tree may occur by the inhalation of incompletely combusted products which continue to burn on the way down the tracheobronchial tree.

Smoke Poisoning

Zikria⁵⁵ indicated that smoke poisoning was the primary diagnosis in 119 victims of the 185 early burn fatalities studied (Table XIII).

TABLE XIII
RESPIRATORY TRACT COMPLICATIONS IN 257 AUTOPSIED CASES

	<u>Post-Burn Survival Time</u> (<12 Hours)		<u>Post-Burn Survival Time</u> (>12 Hours)	
	<u>Cases</u>	<u>%</u>	<u>Cases</u>	<u>%</u>
Smoke Poisoning and/or Asphyxia only	99	53.5	4	5.6
Respiratory Tract Damage and/or Pulmonary Damage only	11	5.9	28	38.9
Both	20	10.8	1	1.4
Neither	<u>55</u>	<u>29.9</u>	<u>39</u>	<u>54.1</u>
Total	185	100.0	72	100.0

Lethal levels of carbon monoxide poisoning were discovered in 45 of 185 early deaths by Zikria.⁵⁹ (See Table XIV).

TABLE XIV
CARBON MONOXIDE POISONING IN 185 AUTOPSIED CASES,
WITH DEATH OCCURRING UNDER 12 HOURS

	<u>Carboxyhemoglobin Saturation</u>	<u>Cases</u>	<u>%</u>
Laboratory Determination		(130)	(70.3)
Usually lethal	>50%	45	24.3
Significant	11% - 49%	64	34.6
No contribution	7% - 10%	21	11.4
Clinical Diagnosis only		14	7.6
No indication		<u>41</u>	<u>22.1</u>
Total		185	100.0

In real fire exposure it becomes nearly impossible to ascertain which one of two agents (excluding absence of oxygen, presence of carbon monoxide, and perhaps direct evidence of large quantities of particulate matter in the upper respiratory tract) caused death. It becomes even more difficult to ascertain the toxic potential of a specific material when it burns or is heated. Presently, the simplest approach is to have some knowledge of what gases are formed and to seek toxic information on the individual compounds if such knowledge is available. From this point on, the problem of identifying the role of a single product on life support becomes greatly magnified since the combination of products being inhaled may not, and generally does not, produce the same biological response as when only one of the compounds is inhaled.

When man is placed in contact with a chemical agent, it can produce an acute toxic effect in a number of ways, the most important of which are listed below:

1. The compound may act as a primary irritant upon the skin and/or on mucous membranes.
2. The compound may be absorbed into the blood stream, leading to definite toxic symptoms and signs, and which may result in death on continued exposure.
3. The compound may act as a sensitizing agent, producing antibodies to the antigen. A repeated exposure to the same, or nearly similar compound may produce allergic manifestations ranging from mild to very serious.

4. The compound may be absorbed in very low concentrations, producing no definite signs and symptoms of toxicity, but may affect mental functions.

The first two can lead to rapid death during fire exposure, or if not death, may result in sufficient damage to cause hospitalization. The third (sensitizing agent) consequence has not received much attention in regard to fires but it should not be overlooked, at least in those cases where death does not occur or even in those instances in which no apparent harm is noted. An allergic response may, however, develop at another date but may have been initiated due to the fire or the pyrolysis of a polymeric material. Finally, low levels of a compound may be sufficient to alter mental functions which, in turn, lead to serious accidents or consequences for the person as well as for a larger number of individuals.

Toxic Effects From Gases and Thermal Degradation Products

Oxygen (See also page 42)

In this case the important factor is the absence of oxygen rather than the release of oxygen due to fire or pyrolysis of polymeric materials. Complete lack of oxygen will lead to death within a few minutes and lesser concentrations of oxygen in the air than normal will produce a number of signs and symptoms of hypoxia in persons exposed to that environment. Even if death does not occur due to the lower levels of oxygen in the immediate atmosphere, denial of sufficient oxygen to brain tissue for short periods of time will produce irreparable brain damage. Higher concentrations of oxygen, but still below that considered normal, will affect the brain cells in a reversible manner, but during this period the person will have behavioral changes which may produce faulty judgment leading to serious accidents and possible death or grave injuries to himself as well as to others. Table XV⁵² presents estimates of the signs and symptoms due to oxygen deficiency.

TABLE XV
SIGNS AND SYMPTOMS OF TOXICITY OF REDUCED LEVELS OF OXYGEN
DUE TO FIRE CONDITIONS

% of Oxygen in Air	
20% (or above)	Normal
12% to 15%	Muscular coordination for skilled movements lost
10% to 14%	Consciousness continues but judgment is faulty and muscular effort leads to rapid fatigue
6% to 8%	Collapse occurs quickly but rapid treatment would prevent fatal outcome
6% (or below)	Death occurs in 6 to 8 minutes

Carbon Monoxide

Out of all the gases generated from the burning of a material (both natural and synthetic), the gas which produces the most deaths in real fire situations is carbon monoxide. Even though present air has levels of carbon monoxide in parts per million, animals and man apparently can tolerate concentrations up to 100 ppm for short periods of time (up to 8 hours) without any undue harm. Fire conditions, however, can release large concentrations of CO in air and these levels can lead to death in very short periods of time. The main action of carbon monoxide after it is inhaled is to combine reversibly with hemoglobin (Hb) to form carboxyhemoglobin (CO-Hb). This reaction displaces oxygen in the blood and leads to apoxia and death if the reaction is not reversed. Carbon monoxide also interferes with oxygen release in the tissues but this appears to be of secondary importance as compared to combining with hemoglobin. Both animal and human studies have demonstrated that correlations can be made between signs and symptoms of toxicity and the per cent CO-Hb formed. Table XVI⁶⁰ summarizes this information and shows that concentrations below 10 per cent produce no signs or symptoms. Most medical personnel and toxicologists agree that, in general, most persons will not show toxic symptoms below a level of 20 per cent carboxyhemoglobin. From this level on, however, extremely toxic manifestation will occur and death will be imminent in concentrations of 60 per cent or more.

TABLE XVI
SIGNS AND SYMPTOMS AT VARIOUS
CONCENTRATIONS OF CARBOXYHEMOGLOBIN

% CO-Hb	Signs and Symptoms
0 to 10	No signs or symptoms
10 to 20	Tightness across forehead, possible slight headache, dilation of the cutaneous blood vessels
20 to 30	Headache and throbbing in the temples
30 to 40	Severe headache, weakness, dizziness, dimness of vision, nausea, vomiting and collapse
40 to 50	Same as above, greater possibility of collapse; syncope and increased pulse and respiratory rates
50 to 60	Syncope, increased respiratory and pulse rates, coma, intermittent convulsions and Cheyne-Stokes respiration
60 to 70	Coma, intermittent convulsions, depressed heart action and respiratory rate, and possible death
70 to 80	Weak pulse, slow respiration leading to death within hours
80 to 90	Death in less than an hour
90+	Death within a few minutes

Henderson, et al.,⁶¹ reported on the physiological response to various concentrations of carbon monoxide. (See Table XVII).

TABLE XVII
PHYSIOLOGICAL RESPONSE TO VARIOUS
CONCENTRATIONS OF CARBON MONOXIDE

Response	CO in Air	
	PPM by Vol.	Vol. %
Concentration allowable for an exposure of several hours	100	0.01
Concentration inhaled for 1 hour without appreciable effect	400 - 500	0.04 - 0.05
Concentration causing just appreciable effects after 1 hour of exposure	600 - 700	0.06 - 0.07
Concentration causing unpleasant, but not dangerous symptoms after 1 hour	1000 - 1200	0.10 - 0.12
Dangerous concentrations for exposure for 1 hour	1500 - 2000	0.15 - 0.2
Concentration fatal in exposures of less than 1 hour	4000 and above	0.4 and above

In order to determine the relationship between the concentration of carbon monoxide in the air and the CO-Hb content, several investigators have exposed laboratory animals at various concentrations of carbon monoxide and measured the time required to reach a given blood level. Table XVIII summarizes the work of Hofmann and Oettel⁶² pertaining to the blood CO-Hb levels between rat and man.

TABLE XVIII
SPECIES DIFFERENCES WITH REGARD TO CO-Hb CONCENTRATION IN BLOOD

CO Concentration PPM	Rat		Man	
	20% CO-Hb	50% CO-Hb	20% CO-Hb	50% CO-Hb
10,000	in minutes	in minutes	in minutes	in minutes
5,000	in minutes	in minutes	in minutes	in minutes
2,000	in minutes	15 minutes	20 minutes	60 minutes
1,000	15 minutes	240 minutes	60 minutes	300 minutes
500	30 minutes	-	90 minutes	-
250	90 minutes	-	360 minutes	-

NOTE: Negative sign indicates 50% level not reached. Rats will die at 70% CO-Hb concentration within 30 minutes.

It should be recognized (as illustrated in Table XVIII), that saturation curves for humans are not directly applicable to rats, because these animals inhale a larger volume of air per unit time in relation to their body weight and their blood can thus be more rapidly saturated with carbon monoxide.

Considerable differences in the reported lethal concentrations of carbon monoxide are found in the literature. This may be due in part to the animals used, the conditions of exposure, or the methods used to monitor the environment. For example, Kishitani⁶³ reported the lethal concentration of CO-Hb in mice to be approximately 40 per cent. This is considerably lower than previous references mentioned in this paper.

Kishitani⁶³ exposed mice, in groups of three, to concentrations of carbon monoxide ranging from 0.1 to 1.8 per cent by volume of air. Exposure time was set at 15 minutes in order to correlate with safe evacuation times predicted for individuals trapped in real fire exposures. Electrocardiograms of the mice were recorded during the tests in order to determine the effect of carbon monoxide on the heart. Table XIX presents the relationship between CO-Hb concentration and the time of animal death at constant concentration. Table XX presents similar information at rising concentrations of carbon monoxide. Autopsy observations showed the blood vessels colored a bright scarlet color typical of carbon monoxide poisoning. Delicate changes were noted in the electrocardiogram with the rise in carbon monoxide concentration. At high carbon monoxide concentrations myocardium anoxia was recognized. Figure 21 presents the electrocardiograms taken of mice exposed at varying carbon monoxide concentrations.

TABLE XIX
CARBON MONOXIDE HEMOGLOBIN CONCENTRATION
AND TIME OF DEATH (AT CONSTANT CONCENTRATION)

CO Concentration (%)	Mouse	CO-Hb (%)	Time of Death* (min.sec.)
0.1	A	5.0	L
	B	0.0	L
	C	6.5	L
0.2	A	18.0	L
	B	23.5	L
	C	--	L
0.3	A	30.0	L
	B	25.0	L
	C	27.0	L
0.4	A	35.0	L
	B	29.5	L
	C	32.0	L
0.5	A	29.5	L
	B	31.5	L
	C	31.0	L
0.6	A	42.0	5'00"
	B	40.5	L
	C	43.5	9'00"
0.7	A	45.5	L
	B	46.0	12'00"
	C	36.0	L
0.8	A	24.0	4'30"
	B	50.0	L
	C	35.0	L
0.9	A	43.5	L
	B	52.5	7'00"
	C	44.0	L
1.0	A	48.0	8'30"
	B	48.5	5'30"
	C	--	11'15"
1.1	A	51.5	6'00"
	B	45.5	L
	C	40.0	2'45"
1.2	A	42.0	L
	B	41.0	10'20"
	C	42.5	2'00"
1.3	A	36.0	L
	B	41.5	L
	C	38.0	L
1.4	A	40.0	4'00"
	B	41.0	3'00"
	C	39.0	4'00"
1.6	A	52.5	3'30"
	B	27.0	L
	C	49.5	3'30"
1.8	A	34.0	1'45"
	B	48.5	2'45"
	C	49.0	3'45"

*L: living after 3 days

TABLE XX

CARBON MONOXIDE HEMOGLOBIN CONCENTRATION AND TIME OF DEATH
(AT RISING CONCENTRATION)

Conditions of Rising Concentration (Value of α at $C=\alpha\{1-\exp(-vt/V)\}$)	Mouse	CO-Hb(%)	Time of Death* (min.sec.)
0.1	A	10.5	L
	B	1.0	L
	C	0.0	L
0.2	A	1.0	L
	B	1.0	L
	C	19.0	L
0.3	A	6.0	L
	B	11.5	L
	C	13.5	L
0.4	A	--	L
	B	--	L
	C	--	L
0.5	A	21.0	L
	B	26.0	L
	C	29.0	L
0.6	A	25.5	L
	B	26.5	L
	C	22.0	L
0.8	A	27.5	L
	B	20.0	L
	C	24.0	L
1.2	A	37.0	L
	B	32.5	L
	C	30.0	L
1.4	A	27.5	L
	B	32.5	L
	C	26.5	L
1.6	A	34.5	L
	B	34.0	L
	C	27.5	L
1.8	A	30.0	10'30"
	B	33.0	15'00"
	C	33.5	10'30"
2.0	A	35.0	12'30"
	B	34.5	15'00"
	C	34.5	12'00"
2.2	A	36.5	12'00"
	B	37.0	8'00"
	C	34.0	12'00"

*L: living after 3 days

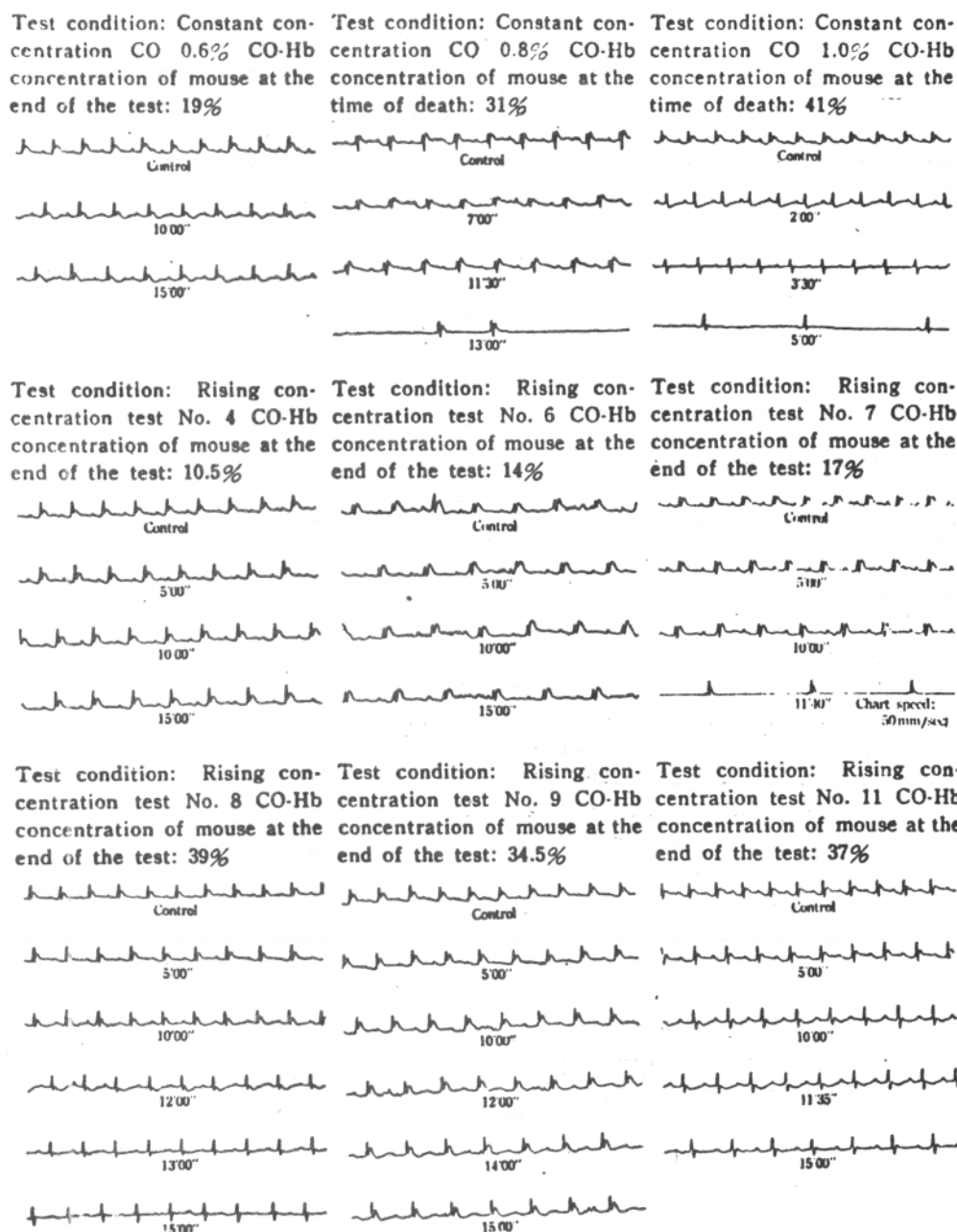


FIG. 21. ELECTROCARDIOGRAMS OF MICE DURING CARBON MONOXIDE TESTS

In recent years attention has been given to possible toxic effects of carbon monoxide at levels where signs and symptoms of toxicity are not noted, as for example, below 10% CO-Hb. Schulte has explored this problem and has found that concentrations as low as 5% CO-Hb can affect certain psychomotor abilities.⁶⁰ For example, in experiments with humans he noted that both the rate of errors and the time needed to complete an arithmetical chore would increase. He also employed other tests in his human experiments and came to the conclusion that low levels of carbon

monoxide could have, and most likely do have, an affect upon judgment and situational decisions and responses.*

If low concentrations of carbon monoxide can indeed affect decision making and other psychomotor responses this may provide a possible answer for the inability of victims to escape an area wherein they have been exposed to high concentrations of carbon monoxide.

Carbon monoxide has 300 times the affinity for hemoglobin than does oxygen. When carbon monoxide is included in inhaled air the following reaction occurs in the lung cells:



Although this is a reversible reaction, as the affinity for carbon monoxide is stronger than for oxygen, oxygen hemoglobin ($O_2 \cdot H_b$) no longer can be formed. As the carboxyhemoglobin is formed, the hemoglobin loses its capacity to transport oxygen resulting in an oxygen shortage in tissues and organs.

Table XXI presents a summary of the physiological effects of carbon monoxide as a function of concentration and exposure time.

*Some investigators have reported that certain cigarette smokers may at times show up to 10% CO-H_b in their blood, depending upon the number of cigarettes smoked and the manner in which they are smoked. Other figures, however, generally show a level of less than 5%.

TABLE XXI
PHYSIOLOGICAL RESPONSE OF MICE TO CARBON MONOXIDE

CO Concentration (%)	Mouse	Time of Occurrence of Behavior (min.)*				
		No Symptoms	Sluggish Movement	Stumbling, Paralyzed Limbs, Lying on Stomach	Convulsions, Rolling on Sides	Death
0.1	A	15.0(5.5)				
	B	15.0(0.0)				
	C	15.0(6.5)				
0.2	A		(18.0)			
	B		(23.5)			
	C					
0.3	A			14.0(30.0)		
	B		6.5	9.0(25.0)		
	C			8.0(27.0)		
0.4	A		4.0	7.0(35.0)		
	B		4.0	10.0(29.5)		
	C		5.0	6.0(32.0)		
0.5	A		3.0	4.0(29.5)		
	B		3.0	4.0(31.5)		
	C		3.0	4.0(31.0)		
0.6	A			2.0	4.5	5.0(42.0)
	B			2.3(40.5)		
	C		2.0		7.3	9.0(43.5)
0.7	A		1.5	2.0	3.0(45.5)	
	B		1.5		7.5	12.5(46.0)
	C		1.5		4.0(36.0)	
0.8	A				3.0	4.5(24.0)
	B				4.0(50.0)	
	C			4.5	6.8(35.0)	
0.9	A			1.0	2.3(43.5)	
	B			1.0	2.0	7.0(52.5)
	C			1.0	1.3(44.0)	
1.0	A					
	B					
	C					
1.1	A			1.0	4.8	6.0(51.5)
	B			1.0	4.8	
	C			1.0	2.0	2.8(40.0)
1.2	A		0.8	3.0(42.0)		
	B		0.8		1.5	10.3(41.0)
	C		0.8		1.5	2.0(42.5)
1.3	A			1.3	3.5(36.0)	
	B			1.3	2.8(41.5)	
	C			1.3	2.8(38.0)	
1.4	A					4.0(40.0)
	B					3.0(41.0)
	C					4.0(39.0)
1.6	A		0.5	0.8	1.3	3.5(52.5)
	B		0.5	0.8(27.0)		
	C		0.5	0.8	2.5	3.5(49.5)
1.8	A				1.8	1.8(34.0)
	B				1.8	2.8(48.5)
	C				1.8	3.8(49.0)

*Figures in parentheses indicate CO-Hb concentration (%) at that time.

Consideration must be given to methods which favor the rapid reversal of the concentration of carboxyhemoglobin in the blood. Einhorn, et al.⁴⁶ exposed laboratory animals exhibiting convulsions during the agonal episode, which is consistent with a cerebral hypoxia due to carbon monoxide poisoning, to pure oxygen. The convulsions ceased within a minute and the animals were grooming themselves within thirty minutes. Kishitani⁶³ exposed mice to fresh air after carbon monoxide exposure and observed a rapid return to normal carboxyhemoglobin levels. (see Figure 22).

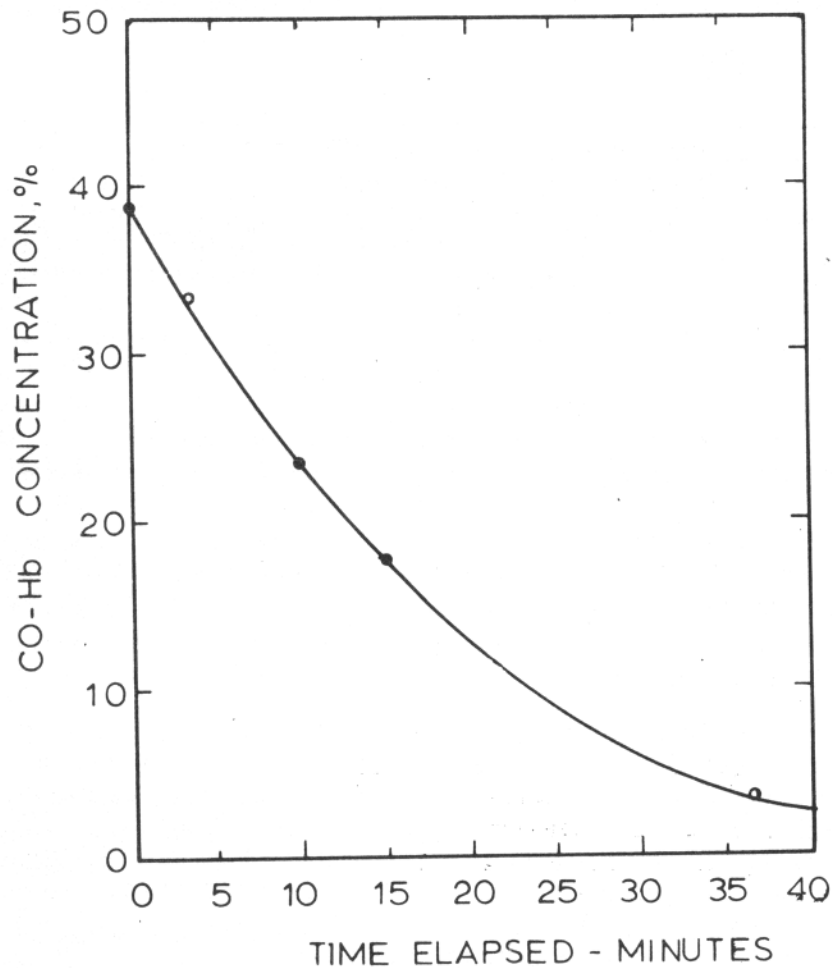


FIG. 22. REDUCTION OF CARBOXYHEMOGLOBIN IN MICE BLOOD

Further studies are necessary to determine if this reversal of carboxyhemoglobin content will persist when animals are exposed to a variety of toxic gases under temperature conditions approaching those experienced in actual fires.

Carbon Dioxide

All fires will produce some levels of carbon dioxide which, in turn, may be inhaled by those in the vicinity of a fire. Since CO_2 is an important constituent of the body process, CO_2 is not considered as a toxic agent at normal concentrations. Inhalation of carbon dioxide will, however, stimulate respiration which, in turn, will increase inhalation of possible toxic components from the combustion and non-combustion gases present from the fire. It is not correct to assume, however, that toxic signs and symptoms will not occur in man. For example, inhaling of CO_2 in concentrations of 10 per cent have caused in segments of test groups, headaches and dizziness, as well as other symptoms. Higher concentrations (above 20 per cent) can lead to narcosis in animals and in most people.

Sulfur Dioxide⁶⁴

Certain natural materials, as well as man-made materials such as natural and synthetic rubbers, may have sufficient sulfur content to generate sulfur dioxide directly or indirectly when the materials are exposed to heat and fire. This gas (SO_2) is a pungent, heavy gas and is extremely toxic to animals and humans. The threshold limit value (TLV) is given as 5 ppm.* Sulfur dioxide, in contact with water (moisture), will form sulfuric acid which, in turn, produces the extremely irritant response when the gas has contact with skin. Mucous membranes, in particular in the respiratory tract and in the eye, are highly susceptible to the irritant effects. Exposure to high concentrations of the gas lead to death most likely because of asphyxiation (blockage of air transport in the upper respiratory tract). Chronic exposure to sulfur dioxide appears to have greater toxic effects upon those having cardiorespiratory diseases than those not suffering with these ailments. Epidemiologic studies have also led to suggestions that a cause-effect relationship may exist for the high incidence of death during episodes of smog.

Hydrogen Sulfide⁶⁴

Hydrogen sulfide, or the familiar "rotten egg" gas, is an extremely rapid and powerful systemic toxic agent. Concentrations as low as 50 ppm will generally cause toxic symptoms and concentrations such as 1,000 ppm will cause death. Lower levels in the air (below 200 ppm) can be extremely dangerous to mucous membranes through the irritant properties of the gas. In humans hydrogen sulfide will cause headaches, nausea, confusion, and weakness and may lead to unconsciousness. Because of the rapid metabolism of the compound, death can be prevented if the persons are removed from the source of the exposure. Death generally is due to central respiratory paralysis.

Aliphatic Hydrocarbons⁶⁴

Thermodegradation of all organic polymers will produce a variety of aliphatic compounds having a range of molecular weights. The lower molecular weight compounds will produce narcosis in animals and man but as the series is ascended, the biological activity will decrease. With certain polymers there may be present unsaturated hydrocarbons when the polymer is degraded and these compounds will generally have a greater toxic effect than the saturated compound. In these mixtures there may also be present acids, alcohols, and aldehydes, each contributing a toxic property.

*Threshold Limit Value (TLV) - concentration of a compound in the air which, if exceeded, may cause toxic signs and symptoms. The concentration is a weighted average over an eight-hour period of exposure.

Aromatic Hydrocarbons⁶⁴

These compounds, starting with benzene and leading to other aromatic structures, will have both irritating properties as well as systemic toxicity. As the structure of the aromatic molecule is altered, the toxicity may be increased or decreased. Several of these aromatic compounds, such as benzene, will be absorbed not only by inhalation but by absorption through the skin. Levels of 100 ppm and above are considered dangerous to health. Styrene is a degradation product of polystyrene and is considered as safe in concentrations below 100 ppm. Levels above 100 ppm can produce irritation to mucous membranes, symptoms of toxicity and impairment of neurological functions.

Hydrogen Cyanide⁶⁴

Hydrogen cyanide may be a lethal agent when ingested as the salt in a dose of less than 1/4 gram. Concentrations above 20 ppm in the air are considered as dangerous to health. Initial inhalation of the vapors of HCN will cause a reflex stimulation of breathing which, in turn, will lead to greater concentration of the gas entering the body. Within a very short time the person becomes unconscious and if not removed from the source, certain death will result. Cyanide will inactivate certain enzymes in the body such as cytochrome oxidase and this will, in turn, prevent utilization of oxygen by tissue.

Hydrogen Chloride and Related Compounds⁶⁴

Degradation of polyvinyl chloride produces as one of its major degradation products, hydrogen chloride. Other compounds may result including vinyl chloride ($\text{CH}_2 = \text{CHCl}$) and phosgene. On combining with water, hydrogen chloride forms hydrochloric acid. This acid is less corrosive than sulfuric acid and does not produce a severe tissue response on skin but will have destructive damage on mucous membranes. If inhaled, the upper respiratory tract will be severely damaged and this may lead to asphyxiation and death. Vinyl chloride appears to be less toxic than HCl but will produce narcosis when inhaled.

Hydrogen Fluoride and Related Compounds⁶⁴

Fluorinated polymers, if heated to sufficiently high temperature, will release a group of low molecular weight, saturated and unsaturated fluorinated hydrocarbons. These compounds, in particular hydrogen fluoride, are extremely toxic when inhaled in sufficient concentrations. Hydrofluoric acid results when HF combines with water. This acid is extremely corrosive to all tissue. Inhalation of this compound will produce serious damage to the mucous membranes in the respiratory tract which may lead to death, or death may be due to systemic toxicity of the compound itself. Tetrafluoroethylene may also be present but this compound is much less toxic and has been found to be non-toxic to animals exposed to levels of 40,000 ppm over a four-hour period. The highly toxic octofluoroisobutylene may also form on heating polytetrafluoroethylene.

Acrolein

Acrolein is a three-carbon compound possessing the chemical formula CH_2CHCHO . This compound due to its extreme lachrymatory affect serves as its own warning agent. It affects particularly the membranes of the eyes and respiratory tract. The maximum allowable concentration is 0.1 ppm. Table XXII⁵⁹ presents the concentration of acrolein and other toxic aldehydes found in the smoke released during the combustion of several common materials.

TABLE XXII
SMOKE ANALYSIS OF SEVERAL COMMON MATERIALS
(Concentration ppm Volume/Volume)

Toxic Compound	Wood	Kerosene	Cotton	M.A.C.*
Acrolein	50	< 1	60	0.1
Formaldehyde	80	<10	70	5.0
Acetaldehyde	200	60	120	200
Butyraldehyde	100	< 1	7	Not Tested

*Industrial maximum allowable concentration

Zikria,⁵⁹ in a recent paper, pointed out that carbon monoxide alone cannot account for the pulmonary edema, tracheobronchial and pulmonary parenchymal damage resulting from smoke poisoning. He exposed dogs to standardized smokes of wood and kerosene, without heat, in a smoke chamber. The animals exposed to kerosene smoke did not have any pulmonary edema, tracheobronchial or parenchymal damage, and all survived. On the other hand, the animals exposed to wood smoke did develop pulmonary edema and tracheobronchial and parenchymal damage, causing 50 per cent of the test animals to die within 1 - 3 days after exposure.

Deichmann and Gerarde⁶⁵ reported that acrolein in a concentration of 5.5 ppm has been shown to cause irritation of the upper respiratory tract; at higher concentrations, pulmonary edema occurs; and at concentrations of 10 ppm, death occurs within a few minutes. Sim and Pattle⁶⁶ subjected human volunteers to acrolein. They reported that inhalation of acrolein causes lacrimation and irritation of all exposed mucous membranes at concentrations of as little as 0.805 ppm.

Toxicological Studies on Selected Plastics

The chemical composition, physical structures such as surface area, geometry, attitude, rate of heating, surrounding environment, and relative humidity are but few of the parameters governing the combustion of plastics. Any single factor, mentioned previously, or combination of these factors will also affect the toxicity of the combustion products.

Table XXIII presents a selected list of recent studies pertaining to the toxicological aspects of plastics during pyrolysis or combustion.

TABLE XXIII
RECENT TOXICOLOGICAL STUDIES OF
PLASTICS DURING PYROLYSIS AND COMBUSTION

Plastic Material	Investigator(s)
<u>Cellular Plastics</u>	
Isocyanurate Foam	Seader, Einhorn ⁶⁷
Polystyrene	Martin ⁶⁸
Polyvinyl chloride	Martin ⁶⁸
Polyurethanes	Martin ⁶⁸
Phenolics	Martin ⁶⁸
Polystyrene	Hofmann, Oettel ⁷¹
<u>Fluorinated Polymers</u>	
Fluorinated copolymers	Einhorn, Seader ⁶⁷
Fluorinated copolymers	Einhorn, Seader, Muhlfeith, Drake ⁴⁶
Vinyl chloride	O'Mara, Crider, Daniel ⁷³
Polytetrafluoroethylene	Coleman, Scheel, Kupel, Larkin ⁷⁴
Polytetrafluoroethylene	Scheel, Lane, Coleman ⁷⁵
Polytetrafluoroethylene	Scheel, McMillan, Phipps ⁷⁶
Polytetrafluoroethylene	Coleman, Scheel, Gorski ⁷⁷
Polytetrafluoroethylene	Birnbaum, Scheel, Coleman ⁷⁸
Polytetrafluoroethylene	Woritz, Kuon ⁷⁹
Polyvinylchloride	Cornish, Abar ⁸³
<u>Spacecraft and Aircraft Materials</u>	
Miscellaneous elastomers, coatings, foams	Manned Spacecraft Center Report ⁸⁰
Aircraft Interior Materials	Gross, Loftus, Lee, Gray ⁸¹
Spacecraft Materials	Epstein, Heicklen ⁸²
<u>Fire Retardant Paint</u>	
Intumescent Coatings	Einhorn, Seader ⁶⁷
Intumescent Coatings	Einhorn, Seader, Muhlfeith, Drake ⁴⁶
<u>Building Materials</u>	
Building Materials	Pryor, Johnson, Jackson ⁶⁹
Building Materials	Sumi, Tsuchiya ⁷⁰
Building Materials	Hafer, Yuill ⁷²
Building Materials	Waterman ²⁷

Special Aspects of Smoke in Commercial Aircraft

General Background

Commercial aviation has advanced considerably during the past 2 decades. The piston-engine aircraft so common during the 1950's and

1960's, has all but been replaced by jet-powered aircraft. Approximately 120 million passengers were carried by domestic airlines during 1969 and the Civil Aeronautics Board estimated that this number will exceed 300 million by 1975.

The average number of seats available during the early 1960's was less than one hundred per plane. By 1980 the average airline will have approximately 200 seats per plane. The Boeing 747 aircraft presently carries approximately 300 passengers. A production prototype now under evaluation carries almost 500 seats. Several other aircraft are now being tested, which will carry between 200 and 300 seats for air-bus or local city-to-city service. Such aircraft present a greater potential for major disasters due to their large passenger-carrying capability.

The greatest potential for accident occurs during take-off and landing operations. Although not specifically defined in the Federal Air Regulations, historically in the aviation history, a "survivable accident" means a crash landing wherein the crash forces encountered do not extensively disrupt the structural integrity of the cabin and cockpit and cause incapacitating injuries to passengers.

The author has reviewed the statistics compiled from official government records summarizing aircraft accidents for the years 1960 and 1964.⁸⁴ The following data were obtained when consideration was given to accidents involving only landings or take-offs:

	<u>1960</u>	<u>1964</u>
Total people involved	2128	1608
Passengers - fatal	156	92
Passengers - serious injury	30	44
Passengers - minor/no injury	1617	1277
Crew - fatal	21	19
Crew - serious injury	0	8
Crew - minor/no injury	237	190

Thus, approximately 7-8 per cent of the people involved in a landing or a take-off accident were fatally injured. Since many accidents of this class result in fire, it is believed that the majority of victims perish as a result of asphyxiation, exposure to high temperature, exposure to lethal concentrations of toxic degradation products, are burned by body contact with the flame source, or die as a result of a combination of two or more of the above factors. Evaluation of a Salt Lake City crash of a United Airlines Boeing 727 in November 1965, showed that the 43 deaths which occurred, out of a total of 91 persons on board at the time of the accident, were a direct consequence of the fire and resulting smoke and toxic fumes. Impact injuries were not responsible for any of the fatalities.

Tests conducted by the Federal Aviation Administration⁸⁵ have shown that the aluminum fuselage construction employed in today's aircraft is not capable of withstanding burn-through to the interior of the cabin for more than 1 minute in a severe fuel fire and in many instances, this time is considerably reduced.

Recent research has been directed toward gaining a better understanding of actual conditions encountered during aircraft accidents.⁸⁶ One factor studied in this series of tests was to determine escape time in a simulated aircraft fire. Escape time was defined as the elapsed time from the instant of fuel ignition to that time when a human tolerance limit was reached which could prevent an aircraft occupant from escaping through his own efforts. This parameter was used earlier by Pinkel, et al⁸⁷ in their crash test program in the early 1950's. The human tolerance limits which were used to determine escape time were:

1. Unbearable pain due to heat exposure to the skin
2. Collapse due to carbon monoxide exposure
3. A momentary exposure to an air temperature of 390 degrees Fahrenheit as a respiratory limit.

Fatal burns to passengers subjected to a severe cabin fire environment could be expected to occur within a few seconds as shown in Figure 23.^{88,89}

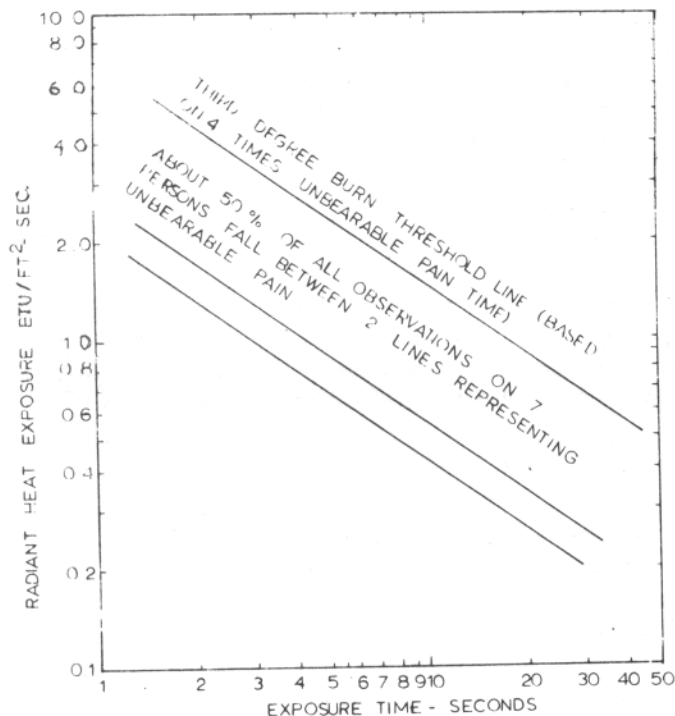


FIG. 23. RADIANT HEAT VERSUS EXPOSURE TIME FOR UNBEARABLE PAIN AND THIRD-DEGREE BURNS

Recent research programs have been directed toward the development of materials which will provide a greater period of safety in an aircraft accident.^{90,91,92}

A new generation of high-temperature polymers, poly(urea-isocyanurate-imide)terpolymers have been developed which do not produce appreciable smoke or toxic degradation products during combustion.⁹³ A series of polysaccharide polymers are also being developed by the Ventron Corporation in cooperation with the Flammability Research Center of the University of Utah. These polymers have oxygen indices ranging from 73 to 100 and do not give off appreciable smoke during the combustion process.⁹⁴

Marcy and Johnson⁹⁵ studied the flaming and self-extinguishing characteristics of aircraft cabin interior materials. They concluded that many plastic materials exhibit both heavy smoke and acrid odor. They further recommended that new test methods and requirements be developed to limit the maximum allowable smoke and toxic combustion products below hazardous levels.

Sarkos⁹⁶ described a test which consisted of exposing a titanium fuselage to an external fuel fire. The titanium fuselage remained intact and prevented fuel-flame penetration; however, the silicone cabin pressure sealant and silicone-bonded insulation autoignited and burned, causing early cabin heating, significant smoke and toxic gases, and a flash fire.

A critical analysis of survival in emergency escape from passenger aircraft was carried out by Snow, et al.⁹⁷ Human factors in three aircraft accidents involving 261 passengers of whom 105 lost their lives, were studied in depth by the Office of Aviation Medicine, Department of Transportation, Federal Aviation Administration. The first accident involved a United Airlines DC-8 aircraft which crashed during landing at Stapleton Field, Denver on July 11, 1961. This aircraft, which experienced hydraulic problems prior to landing, made a normal touchdown, then veered off the runway, sheered off both main landing gears and struck a parked truck. Soon after the aircraft stopped, two major fires broke out. This fire produced an acrid black smoke which was blown toward the aircraft by a 7-knot wind from the northeast. When the right window exits were opened, this smoke invaded the passenger cabin. During evacuation, the principal environmental hazard was smoke. When the aft galley door was opened, a chimney-effect developed, drawing outside smoke into the right window exits, down through the aft section of the cabin and out the open door. The accident report states "although occasional tongues of flame were blown in through the right window exits, destructive invasion of the cabin by fire occurred only after 98 passengers had escaped and 16 others had been incapacitated by smoke.

In a recent study,⁹⁸ data relating to FAA and manufacturer test evaluations of DC-8 aircraft equipped with ceiling-mounted escape slides were analyzed. Usually such tests are carried out under optimal lighting conditions, without smoke and with maximal crew assistance. In contrast, in actual accidents, while environmental factors such as fire and smoke may stimulate greater urgency, overall speed of evacuation may be slowed due to poor visibility, human error, and mechanical failure in opening exits or deploying slides.

Complete necropsies were performed on seven of the victims of the Denver crash and gross external examinations were made on the remainder of the victims. All bodies displayed extreme 3rd- and 4th-degree burns. No sign of impact trauma were noted and no other significant pathology was observed in the autopsied victims. Blood carboxyhemoglobin concentrations ranged between 30 and 85 per cent.

The second aircraft, a United Airlines Boeing 727, crash-landed at the Salt Lake City Municipal Airport on November 11, 1965. This accident has been described earlier in this paper. When the fire was extinguished, 41 bodies were found onboard the aircraft. Gross external descriptions were made on all victims and complete necropsies performed on 10. Burns involving more than 50 per cent of the body surface were found on all 41 bodies. In the majority (25) 4th-degree (charring) burns were predominant. The remaining 16 displayed extensive 1st-, 2nd-, and 3rd-degree burns. No fractures of the skull or extremities were palpable in any victim nor were any other signs of mechanical trauma evident.

The ten necropsied victims displayed no pre-existing disease which might have influenced survival. The major viscera were intact, there were no signs of hemorrhage, fracture, or other mechanical trauma. Carbonaceous matter was present in the larynx and the trachea of all victims. In 8 of the 10 necropsies microscopic examinations revealed carbon pigment present in the lumen of the smaller bronchi. Varying degrees of capillary congestion, alveolar hemorrhage and edema were noted in all instances. Carboxyhemoglobin determinations were made on 35 victims. All displayed saturation levels above 10 per cent. Individual values ranged from 13 to 82 per cent with a mean of 36.9 per cent.

The third crash occurred at Fiumicino Airport in Rome on November 23, 1964. This crash involved a crew of 11 and 62 passengers. Two explosions occurred within 40 seconds of the crash. Of 17 survivors 10 were treated for minor injuries and released, 7 were hospitalized. Four of these were treated solely for burns, 2 for fractures, and one for sustained burns and fractures. Carboxyhemoglobin ranged from 13.8 to 49.0 per cent (mean 23.0 per cent). In general, death was attributed to thermal burns and/or asphyxia. Carbonization was extreme in all cases.

An analysis of the aircraft accidents discussed, shows that fire injury and death are attributed to the same factors as those encountered in other confined-space fires. The principal difference in aircraft fires, due to the large quantity of highly-flammable fuel is the increased hazards due to flame and rapid smoke development.

SUMMARY

The fundamental aspects of combustion and degradation of polymeric materials has been reviewed with special emphasis placed on the physiological and toxicological factors resulting from exposure to smoke.

The parameters governing smoke development during pyrolysis and combustion were discussed. Techniques utilized in the characterization of smoke were mentioned and factors influencing smoke development noted.

A status-of-the-art survey of the literature was presented pertaining to the physiological and toxicological aspects of combustion. It is obvious that considerable research is required to determine the mechanism of death and injury resulting from smoke exposure.

REFERENCES

- ¹DiPietro, J., "An Overview of Flammability of Polymeric Materials - Yesterday, Today and Tomorrow," Polymer Conference Series, Flammability Characteristics of Polymeric Materials, University of Detroit, Detroit, Michigan (June 16-20, 1969).
- ²Einhorn, I. N., "An Overview of Flammability of Materials," Polymer Conference Series, Flammability Characteristics of Polymeric Materials, University of Utah, Salt Lake City, Utah (June 15-20, 1970).
- ³Fire Journal, Vol. 64, No. 5 (September 1970), pp. 65-69.
- ⁴The College Standard Dictionary of the English Language, Funk and Wagnalls, New York, New York.
- ⁵Gaskill, J. R., "Analysis of Smoke Development in Polymers During Pyrolysis or Combustion," Polymer Conference Series, Flammability Characteristics of Polymeric Materials, University of Utah, Salt Lake City, Utah (June 15-20, 1970).
- ⁶Hilado, C. J., "The Effect of Chemical and Physical Factors on Smoke Evolution From Polymers," Polymer Conference Series, Flammability Characteristics of Polymeric Materials, University of Detroit, Detroit, Michigan (June 8-12, 1970).
- ⁷Straehl, L., "Textile Flammability and Consumer Safety," Gottlieb Duttweiler Institute for Economic and Social Studies, Ruschlikon, Zurich (1969).
- ⁸Einhorn, I. N., and Mickelson, R. W., "Char Formation in Rigid Urethane Foams," Proceedings of the Division of Organic Coatings and Plastics, American Chemical Society, 20, (2) (April, 1968), pp. 291-310.
- ⁹Mickelson, R. W., "The Factors Influencing the Smoking Characteristics of Polymers," Polymer Conference Series, Flammability Characteristics of Polymeric Materials, University of Utah, Salt Lake City, Utah (June 21-26, 1971).
- ¹⁰Rarig, F. J., and Bartosic, A. J., "Evaluation of the XP-2 Smoke Density Chamber," Symposium on Fire Test Methods - Restraint and Smoke, ASTM, STP 442, American Society for Testing and Materials (1967), p.106.
- ¹¹Hilado, C. J., "Smoke From Cellular Polymers," Fire Technology, Vol. 5, (1969) p. 130.
- ¹²Mickelson, R. W., and Einhorn, I. N., "The Effect of Additives on the Smoking Tendency of Urethane Foams," Proceedings of the Division of Organic Coatings and Plastics, American Chemical Society, 28 (April, 1968), p. 272.

- ¹³Stepniczka, H., and DiPietro, J., "Flammability Characteristics of Cotton and Polyester Fibers," Presented at the TRI Meeting, New York, New York (March 11, 1971).
- ¹⁴Rohm and Haas Company, NFPA Quarterly, 57 (January 1964), pp. 276-287.
- ¹⁵Einhorn, I. N., Kanakia, M. D., and Seader, J.D., "Physio-Chemical Study of Smoke Emission by Aircraft Interior Materials," Part II: Smoke and Fire Characteristics of Rigid and Flexible Foams, DOT Contract No. DOT-FA-70-NA-445 (November 1972).
- ¹⁶Gross, D., Loftus, J. J., and Robertson, A. F., "Method for Measuring Smoke and Burning Materials," Symposium on Fire Test Methods - Restraint and Smoke, 1966, ASTM, STP 422, American Society for Testing and Materials (1967), p. 106.
- ¹⁷Briber, A., "Testing and Evaluation of the Flammability Characteristics of Polymers and Plastics," Polymer Conference Series, Flammability Characteristics of Polymeric Materials, University of Detroit, Detroit, Michigan (June 16-20, 1969).
- ¹⁸Robertson, A. F., "Recent Developments in Flammability and Smoke Measurements," Polymer Conference Series, Flammability Characteristics of Polymeric Materials, Wayne State University, Detroit, Michigan (June 13-17, 1966).
- ¹⁹Cass, R. A., "Smoke Control Design," Journal of Cellular Plastics, Vol. 3, No. 1 (January 1967), p. 41.
- ²⁰Vandersall, H. L., Journal of Paint Technology, Vol. 39 (1967), p. 494.
- ²¹Levy, M. M., "A Simplified Method for Determining Flame Spread," Journal of Cellular Plastics, Vol. 3, No. 4 (April 1967), pp. 168-173.
- ²²Robertson, A. F., "Surface Flammability Measurements By The Radiant-Panel Method," Special Technical Publication 344, American Society for Testing and Materials, Philadelphia (1962).
- ²³Robertson, A. F., Gross, D., Loftus, J. J., "A Method For Measuring Surface Flammability of Materials Using a Radiant Energy Source," Fifty-ninth Annual Meeting of the American Society for Testing and Materials (June 17-22, 1956).
- ²⁴Pryor, A. J., and Yuill, C. H., "Mass Life Fire Hazard," Southwest Research Institute, San Antonio, Texas, Report NRDC-TR-3 (1966), pp. 127-130.
- ²⁵Yuill, C. H., "A Study of Fire Safety Aspects of Plastics in Building Construction," Southwest Research Institute, San Antonio, Texas, LIV-3 (1960).
- ²⁶Christian, W. J., "Fire Response in Buildings," Polymer Conference Series, Flammability Characteristics of Polymeric Materials, University of Utah, Salt Lake City, Utah (June 15-20, 1970).

- ²⁷Waterman, T. E., "Effect of Building Occupancy and Design to Use of Combustible Materials of Construction," IITRI Summary Report, Society of the Plastics Industry (October 1968).
- ²⁸Birky, M., National Bureau of Standards, Flammability Research Section, private communication.
- ²⁹Stuetz, D. E., Barnes, B. P., DiEdwardo, A. H., and Zitomer, F., "Polymer Flammability," Polymer Conference Series, Flammability Characteristics of Polymeric Materials, University of Utah, Salt Lake City, Utah (June 15-20, 1970).
- ³⁰Einhorn, I. N., "Fire Retardance of Polymeric Materials," Journal of Macromolecular Science - Reviews in Polymer Technology, Vol. D1, No. 2, (1971), pp. 113-184.
- ³¹Einhorn, I. N., "The Chemistry of Fire Resistant Materials and Suppression," Fire Research Abstracts and Reviews (in press).
- ³²Einhorn, I. N., Mickelson, R. W., Shah, B., and Craig, R., "Smoke Developments in Urethane Foams," Journal of Cellular Plastics, Vol. 4, No. 5 (May 1968), pp. 188-197.
- ³³Anderson, J. J., "The Relationship of Crosslink Density to the Flammability Characteristics of Polyurethane Foams," Polymer Conference Series, Flammability Characteristics of Polymeric Materials, Wayne State University, Detroit, Michigan (June 13-17, 1966).
- ³⁴Bachus, J. K., Dorr, W. C., Gemeinhardt, P. G., and Saunders, J. H., "Thermal Degradation of Rigid Urethane Foams," Journal of Cellular Plastics, Vol. 1, No. 1 (January 1965), pp. 178-186.
- ³⁵Dichert, E. A. and Toone, G. C., Modern Plastics, Vol. 42 (January 1965), p. 197.
- ³⁶"Symposium on Fire Test Methods," 1962, ASTM Special Technical Publication No. 344, Philadelphia, Pennsylvania (1963).
- ³⁷"Fire Test Methods - Restraint and Smoke," ASTM Special Technical Publication No. 422, Philadelphia, Pennsylvania (1966).
- ³⁸Lyons, J. W., "The Chemistry and Uses of Fire Retardants," Wiley - Interscience, New York, New York (1970).
- ³⁹Thiery, P., "Fireproofing," Elsevier Publishing Company, Ltd., New York, New York (1970).
- ⁴⁰Ranney, M. W., "Flame Retardant Polymers," Noyes Data Corporation, Park Ridge, New Jersey (1970).

- ⁴¹Perkowski, W. S. and Cheatham, R. G., "Flammability and Design Considerations for Commercial Airplane Interior Materials," Polymer Conference Series, Flammability Characteristics of Polymeric Materials, University of Detroit, Detroit, Michigan (June 16-20, 1969).
- ⁴²Ranney, M. W., "Flame Retardant Textiles," Noyes Data Corporation, Park Ridge, New Jersey (1970).
- ⁴³Einhorn, I. N., and Seader, J. D., Editors, "Treatise on the Flammability Characteristics of Polymeric Materials," Program Design, Inc., Cleveland, Ohio (1971).
- ⁴⁴Fire Gas Research Report, Vol. 45, No. 3 (1952), pp. 280-306.
- ⁴⁵Shorter, G. W., McGuire, J. H., Hutcheson, N. B., and Leggett, R. M., "The St. Lawrence Burns," National Fire Protection Association Quarterly, Vol. 53, No. 4 (1960), pp. 399-416.
- ⁴⁶Einhorn, I. N., Seader, J. D., Muhlfeith, C. M., and Drake, W. O., "Flammability and Toxicological Characteristics of Isocyanurate Foams, Intumescent Coatings and Fluorel," Final Report, NASA Contract, NAS 2-6063 (March 1971) and Polymer Science & Engineering, Vol. 12, No. 3 (May 1972).
- ⁴⁷Chalmers, J. P., et al., "Distribution of Peripheral Blood Flow in Primary Tissue Hypoxia Induced by Inhalation of Carbon Monoxide," Journal of Physiology, 192 (1967), pp. 549-559.
- ⁴⁸Ross, J. J., et al., "Observations on the Role of Diminished Oxygen Tension in the Functional Hyperemia of Skeletal Muscle," Circulation Research, Vol. 15 (1964), pp. 473-484.
- ⁴⁹Drinker, C. K., "Carbon Monoxide Asphyxia," New York: Oxford University Press (1938), p. 138.
- ⁵⁰Dell, P., et al., "Effect of Hypoxia on the Reticular and Cortical Diffuse Systems, Cerebral Anoxia and the Electroencephalogram, Meyer, J. S., and Gastant, H., Editors, G. C. Thomas Pub. (1961), p. 56.
- ⁵¹Pugh, I. G. C. E., "The Effect of Acute and Chronic Exposure to Low Oxygen Supply on Consciousness," Schaeffer, K. E., Editor, Environmental Effects on Consciousness, New York: Macmillan (1962), pp. 106-116.
- ⁵²Dufour, R. E., "Survey of Available Information on the Toxicity of The Combustion and Thermal Decomposition Products of Certain Building Materials Under Fire Conditions," Bulletin of Research, No. 53, Underwriters' Laboratories, Inc., Northbrook, Illinois (July 1963).
- ⁵³Phillips, A., and Cope, O., "Burn Therapy II: The Revelation Respiratory Tract Damage As a Principal Killer of the Burned Patient," Annals of Surgery, Vol. 90 (1962), p. 812.

- ⁵⁴Stone, H. H. and Martin, J. D., "Pulmonary Injury Associated With Thermal Burns," *Surgery, Synecology, and Obstetrics*, 129 (1969), p. 1242.
- ⁵⁵Zikria, B. A., Sturner, W. A., Astarjeon, N. K., Fox, C. L., and Ferrer, J. M., "Respiratory Tract Damage in Burns," *Pathophysiology and Therapy Annals, New York Academy of Science*, 150 (1968), p. 618.
- ⁵⁶Crikelair, G. F., "Medicine Aspects of Clothing Burns," *Textile Flammability and Consumer Safety*, Gottlieb Duttweiler Institute for Economic and Social Studies, Ruschlikon, Zurich (1969).
- ⁵⁷Moritz, A. R., Henriques, F. C., Jr., and McLean, R., "The Effects of Inhaled Heat on the Air Passages and Lungs," *American Journal of Pathology*, 21 (1945), p. 311.
- ⁵⁸Stone, H. H., Rhame, D. W., Corbitt, J. D., Gerin, K. S., and Martin, J. D., "Respiratory Burns: A Correlation of Clinical and Laboratory Results," *Annals of Surgery*, 165 (1967), p. 157.
- ⁵⁹Zikria, B. A. "Inhalation Injuries in Fires," Symposium on An Appraisal of Halogenated Fire Extinguishing Agents, National Academy of Sciences - National Research Council, Washington, D. C. (April 11-12, 1972).
- ⁶⁰Schulte, J. H., *Archives of Environmental Health*, 7 (1963), p. 524.
- ⁶¹Henderson, Y., Haggard, H. W., Teague, M. C., Prince, A. L., and Wunderlich, R., *Journal of Industrial Hygiene*, 3, 79 (1921) through *Industrial Hygiene and Toxicology*, Second Revised Edition, Vol. II, Fosseth, D. W., and Irish, D. D., Editors, Interscience Publishers, New York (1963).
- ⁶²Hofmann, H. T., and Oettel, H., *Modern Plastics*, 94 (October 1969).
- ⁶³Kishitani, K., "Study on Injurious Properties of Combustion Products of Building Materials at Initial Stage of Fire," *Journal of the Faculty of Engineering*, Vol. XXXI, No. 1 (1971).
- ⁶⁴Autian, J., "Toxicological Aspects of Flammability and Combustion," *Treatise on the Flammability Characteristics of Polymeric Materials*, Einhorn, I. N., and Seader, J. D., Editors, Program Design, Inc., Cleveland, Ohio (1971).
- ⁶⁵Deichmann, W. B., and Gerarde, H. W., *Symptomatology and Therapy of Toxicological Emergencies*, Academic Press, New York, New York (1964).
- ⁶⁶Sim, V. M., and Pattle, R. E., "Effects of Possible Smog Irritants on Human Subjects," *Journal of the American Medical Association*, 1908 (1957).
- ⁶⁷Seader, J. D., and Einhorn, I. N., "Analysis of Volatile Combustion Products and A Study of Their Effects on Laboratory Animals," *Journal of Polymer Science and Engineering*, Vol. 12, No. 1 (March 1972).

- ⁶⁸Martin, K. G., "Degradation of Rigid Cellular Plastics Under Fire Conditions in Buildings," *Reviews of Pure and Applied Chemistry*, 21, 121 (1971), pp. 121-143.
- ⁶⁹Pryor, A. J., Johnson, D. E., and Jackson, N. N., "Hazards of Smoke and Toxic Gases Produced in Urban Fires," Southwest Research Institute Project No. 03-2402 OCD Contract DAHC 20-70-C-0212, Houston, Texas (September 1969).
- ⁷⁰Sumi, K., and Tsuchiza, Y., "Toxic Gases and Vapors Produced at Fires," *Canadian Building Digest*, National Research Council of Canada (December 1971).
- ⁷¹Hofmann, H. T., and Oettel, H., "Relative Toxicity of Thermal Decomposition Products of Expanded Polystyrene," Paper presented Wurzburg, Germany (September 20, 1967).
- ⁷²Hafer, C. A., and Yuill, C. H., "Characterization of Bedding and Upholstery Fires," Southwest Research Institute Contract CST-792-5-69, Houston, Texas (March 31, 1970).
- ⁷³O'Mara, M. M., Crider, L. B., and Daniel, R. L., "Combustion Products From Vinyl Chloride Monomer," *American Industrial Hygiene Association Journal*, Vol. 32, No. 3 (March 1971), pp. 153-156.
- ⁷⁴Coleman, W. E., Scheel, L. D., Kupel, R. E., and Larkin, R. L., "The Identification of Toxic Compounds in the Pyrolysis Products of Polytetrafluoroethylene (PTFE)," *American Industrial Hygiene Association Journal*, Vol. 29, No. 1 (January-February 1968), pp. 33-40.
- ⁷⁵Scheel, L. D., Lane, W. C., and Coleman, W. E., "The Toxicity of Polytetrafluoroethylene Pyrolysis Products - Including Carbonyl Fluoride and a Reaction Product, Silicon Tetrafluoride," *American Industrial Hygiene Association Journal*, Vol. 29, No. 1 (January-February 1968), pp. 41-48.
- ⁷⁶Scheel, L. D., McMillan, L., and Phipps, F. C., "Biochemical Changes Associated With Toxic Exposures to Polytetrafluoroethylene Pyrolysis Products," *American Industrial Hygiene Association Journal*, Vol. 29, No. 1 (January-February 1968), pp. 49-53.
- ⁷⁷Coleman, W. E., Scheel, L. D., and Gorski, C. H., "The Particles Resulting from Polytetrafluoroethylene (PTFE) Pyrolysis in Air," *American Industrial Hygiene Association Journal*, Vol. 29, No. 1 (January-February 1968), pp. 54-60.
- ⁷⁸Birnbaum, H. A., Scheel, L. D., and Coleman, W. E., "The Toxicology of the Pyrolysis Products of Polychlorotrifluoroethylene," *American Industrial Hygiene Association Journal*, Vol. 29, No. 1 (January-February 1968), pp. 61-65.

- ⁷⁹Woritz, R. S., and Kuon, B. K., "The Inhalation Toxicity of Pyrolysis Products of Polytetrafluoroethylene Heated Below 500 Degrees Centigrade," American Industrial Hygiene Association Journal, Vol. 29, No. 1 (January-February 1968), pp. 19-20.
- ⁸⁰"Toxicity and Identification of Thermolysis Products of Spacecraft Elastomers," Manned Spacecraft Center, Houston, Texas, Private Communication.
- ⁸¹Gross, D., Loftus, J. J., Lee, T. G., and Gray, V. E., "Smoke and Gases Produced by Burning Aircraft Interior Materials," National Bureau of Standards, Building Science Series, 18 (February 1969).
- ⁸²Epstein, G., Heicklen, J., "Relative Toxicity of Selected Polymeric Materials Due to Thermal Degradation," Air Force Report No. SAM 50-TR-70-115, The Aerospace Corporation (December 15, 1969).
- ⁸³Cornish, H. H., and Abar, E., "Toxicity of Pyrolysis Products of Vinyl Plastics," Archives of Environmental Health, Vol. 19 (July 1969), pp. 15-21.
- ⁸⁴Civil Aeronautics Board, Aircraft Accident Report, SA 388, File No. 1-0032 (June 7, 1966).
- ⁸⁵Geyer, G. B., "Effect of Ground Crash Fire on Aircraft Fuselage Integrity," Federal Aviation Agency, NAFEC, Report NA-69-37, AD 698806 (December 1969).
- ⁸⁶Conley, D. W., "Post-Crash Fire-Fighting Studies on Transport Category Aircraft," Report No. RD 65-50 (AD 621676), Federal Aviation Agency Systems Research and Development Service, Atlantic City, N. J. (May 1965).
- ⁸⁷Pinkel, I., Preston, G. M., and Presman, G. J., "NACA Aircraft Crash Fire Tests," National Fire Protection Quarterly, Vol. 47, No. 2 (October 1958), pp. 121-138.
- ⁸⁸Boettner, K., "Effects of Heat on Man," Journal of American Medical Association, Vol. 144, No. 9 (October 28, 1950), pp. 732-738.
- ⁸⁹Boettner, K., "Effects of Heat on Man," National Fire Protection Association Quarterly, Vol. 42, No. 4 (April 1949), pp. 265-268.
- ⁹⁰Neel, C. B. and Fish, R. H., "Protection of Aircraft in Ground Crash Fires," Polymer Conference Series, Flammability Characteristics of Polymeric Materials, University of Utah, Salt Lake City, Utah (June 21-26, 1971).
- ⁹¹Blockley, W. V., and Taylor, C. L., "Studies in Humane Tolerance For Extreme Heat," Technical Report No. 5831, U. S. Air Force (February 1950).

- ⁹²Webb, P., "Pain Limited Heat Exposures, Temperature - Its Measurement and Control in Science and Industry," Vol. 3, Part 3, Reinhold Publishing Company, New York, New York (1962), pp. 245-250.
- ⁹³Drake, W. O., and Einhorn, I. N., "Flammability Characteristics of Poly(Urea-Isocyanurate-Imide) Terpolymers," Ph.D. thesis, Division of Materials Science and Engineering, University of Utah, Salt Lake City, Utah (April 1972).
- ⁹⁴U. S. Patent 3551365 assigned to Dr. R. Matalon, Cherry Hill, New Jersey (December 29, 1970).
- ⁹⁵Marcy, J. F., and Johnson, R., "Flaming and Self-Extinguishing Characteristics of Aircraft Cabin Interior Materials," Final Report NA-68-30 (05-68-13), Department of Transportation, Federal Aviation Administration, National Aviation Facilities Experimental Center, Atlantic City, New Jersey (July 1968).
- ⁹⁶Sarkos, C. P., "Titanium Fuselage Environmental Conditions in Post-Crash Fires," Report No. FAA-RD-71-3, Department of Transportation, Federal Aviation Administration, Systems Research and Development Service, Washington, D. C. (March 1971).
- ⁹⁷Snow, C. C., Carroll, J. J., and Allgood, M. A., "Survival in Emergency Escape From Passenger Aircraft," Report No. AM-70-16, Office of Aviation Medicine, Department of Transportation, Federal Aviation Administration, Oklahoma City, Oklahoma (October 1970).
- ⁹⁸Aerospace Industries Association of America, Technical Group Report, "Evacuation Crashworthiness Development Program," Washington, D. C. (1968).