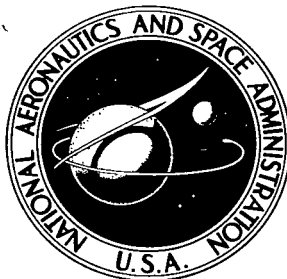| **CECILIA FELDICK**	**OBJECT**	Submission ID: 215195
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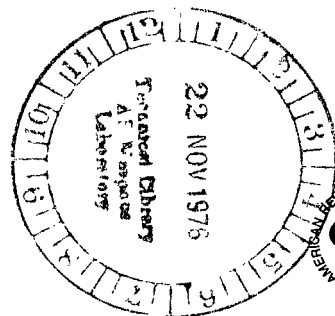
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GASEOUS EMISSIONS AND TOXIC HAZARDS ASSOCIATED WITH PLASTICS IN FIRE SITUATIONS - A LITERATURE REVIEW

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16. Abstract

This report discusses the hazards of plastics in fire situations, the gases emitted, the factors influencing the nature of these emissions, the characteristics of toxic gases, and the results of laboratory studies. The literature pertaining to the pyrolysis and oxidation of plastics was reviewed. An effort was made to define the state of the art for determining the toxic gases emitted by plastics under fire conditions. Recommendations are made and research needs defined as a result of this review.

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SUMMARY

This report summarizes the results of a literature search to determine the nature of toxic gas emissions from plastics subjected to fire conditions. It provides an overview of some of the results obtained by researchers in their studies to determine the identity and toxicity of gases emitted when polymers of varying types, forms, and compositions are heated under varying environmental conditions. Consideration is given to the effects these gases have on living organisms and their potential for toxic effects on man in a fire environment.

Toxic gases are an important cause of casualties in fires. A wide variety of toxic gases are produced at levels that can be extremely hazardous, both as single gases and in combinations of gases. Such combinations at times appear to be either more toxic or less toxic than the sum of the individual toxic levels of the gases involved. Chemical and physiological synergism and antagonism effects must be studied in much further detail.

Some commonly accepted notions concerning fire hazards are questioned. The role of smoke in fire situations requires further study as does that of carbon monoxide, heat, and other toxic gases. Although most investigators agree that carbon monoxide is the major hazard in gas inhalation, there is less agreement as to the role of other toxic gases and smoke. Further research is needed. Also, correlating laboratory research results to real fire situations must be further refined.

INTRODUCTION

The extensive use of polymers, including the natural polymers, in all phases of life constitutes a hazard to mankind when involvement in fire situations occurs. The gaseous pyrolysis and combustion products of plastics constitute serious hazards to life,

not only from oxygen deficiency, carbon monoxide, and smoke but also from the many other toxic gases emitted.

This literature review, or state-of-the-art report, attempts to describe the toxicological problems inherent in fire situations involving plastics and the results obtained by researchers in determining the identity and degree of hazard of the gases emitted by plastics in fires. This review is based on a search of the available open literature of the past 25 years that bears on the subject. Nearly 100 papers that contributed substantially to the results of this review have been included in the reference section. A bibliography cites additional pertinent reading material. Particular emphasis was placed on the toxicity characteristics of these gaseous emissions as they affect living organisms and their potential for toxic effects on man in a fire environment. The composition of these gases varies considerably with varying types of plastics, with additives, and with varying fire conditions. The nature of the hazards associated with such fires is also discussed.

In addition to the reference and bibliography sections, an author index is provided as well as an appendix listing the plastics discussed in the report and the more common toxic substances emitted by each when heated, with referral to appropriate references.

Certain terms used throughout this review should be explained: The polymer chain is no stronger than its weakest link and the temperature of initial thermal degradation is usually the temperature at which the least thermally stable bonds fail. Degradation may be of two types: pyrolysis, a chemical change brought about by the action of heat in the absence of oxygen; and thermal-oxidative degradation, which is influenced by both heat and oxygen. When the temperature increases to a point where the majority of the bonds fail, decomposition occurs. At a high enough temperature and in the presence of sufficient oxygen, the oxidation of the polymer fragments proceeds rapidly enough to produce heat and flame, or combustion.

AIRCRAFT INVOLVEMENT

A series of aircraft disasters in recent years has focused considerable attention on the growing list of problems connected with the burning of polymeric materials. The crash of a typical commercial transport at 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 of the 91 persons aboard, was one of the rare instances of what the Civil Aeronautics Board (CAB) termed a survivable crash with no fatalities at impact. The deaths were a direct consequence of the fire and the resulting smoke and toxic fumes. This type of incident clearly spells out the need for plastic materials that exhibit not only adequate flame

resistance and low smoke generation but also low-toxicity fire off-gases. Einhorn, et al. (ref. 1) have listed the hazards to life in the following order of decreasing importance for a typical airplane-crash fire:

(1) Flame propagation

(2) Smoke development

(3) Superheated air or gases

(4) Oxygen deficiency

(5) Toxicity of combustion product gases

Toxic hazards are listed last because of the time factor involved in physiological damage.

The National Advisory Committee for Aeronautics (now NASA) in an appraisal of hazards to survival in airplane crashes studied the factors that affect passengers under fire conditions by conducting full-scale crashes of transport and cargo airplanes. The time interval during which occupants could escape from a burning airplane was approximately 50 seconds before the effects of heat, carbon monoxide, or smoke obscuration made escape unlikely; heat limitations alone ranged from 50 to 300 seconds (ref. 2).

The Cleveland aircraft fire tests (ref. 3) in 1968 used currently available and commonly used materials. These tests established beyond a reasonable doubt that toxic products of combustion are the controlling factor in aircraft cabin fire survivability. This result was in sharp contrast to the previous theory that high temperature determines the survival limits.

In more recent years the Federal Aviation Agency (FAA) also has studied the smoke and gases produced by burning aircraft interior materials. In one study of the flammability and smoke characteristics of 100 representative interior materials, indicator tubes were used to detect a number of toxic gases (ref. 4). No attempt was made to determine high concentrations of carbon dioxide (CO_2) or low concentrations of oxygen. For the materials tested, the highest concentrations were of carbon monoxide (CO) at 2000 parts per million parts of air (ppm), hydrogen chloride (HCl) at 2500 ppm, and hydrogen cyanide (HCN) at 90 ppm. In general, HCl was produced by polyvinyl chloride (PVC) and modacrylics, hydrogen fluoride (HF) by polyvinyl fluoride, and HCN by wool, urethane, modacrylics, and acrylonitrile-butadiene-styrene (ABS). Carbon monoxide was produced by almost all samples in varying amounts (ref. 5).

An FAA survey of 717 accidents involving commercial turbine-powered aircraft that occurred worldwide between 1952 and 1971 (ref. 6) revealed at least 182 accidents where postcrash fire occurred. Of these 182 accidents, 122 were impact survivable to some degree; yet 1050 fatalities resulted from fire, of which up to 35 percent might have been prevented had the technology for minimizing fire hazard been optimal.

Three survivable, relatively low crash-force, air carrier accidents were reported by Mohler (ref. 7). Carbon monoxide caused toxic incapacitation during the brief period

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available for emergency evacuation prior to cabin destruction by fire. Acrid smoke caused laryngospasm and this resulted in breathing difficulties. Hydrogen cyanide was also present in amounts that would be incapacitating and frequently fatal, especially in combination with CO. A full-scale mockup test showed that cabin CO levels reached 10 000 ppm in 90 seconds and 26 000 ppm in 180 seconds. This is above normally accepted fatal levels (3500 ppm). Levels of HCN exceeded 4000 ppm in 90 seconds, which is also above the fatal level (135 ppm for 30 min). Further investigations revealed that when animals are exposed to a combination of CO and HCN, a physiological effect occurs that exceeds the effect of either CO or HCN acting alone. In CO poisoning alone, coma and death begin at about 60 to 70 percent CO blood carboxyhemoglobin levels; in HCN poisoning alone, coma and death occur at 5 micrograms per milliliter of blood. With CO and HCN acting together, lethal effects occur with 20 percent CO blood carboxy-hemoglobin levels and blood cyanide levels of 2 micrograms per milliliter (ref. 7).

Table I summarizes the main toxic gases evolved from typical aircraft materials during a fire (ref. 8). At first sight it might appear that plastics containing the nitrile $(-C \equiv N)$ group, such as acrylonitrile, ABS, modacrylics, and nitrile rubber, would give rise to a very high concentration of HCN. But this has generally been found not to be the case. The $C \equiv N$ bond is weak and breaks preferentially. The situation is different for plastics containing halogens, which preferentially evolve the hydrogen halides (e.g., HCl and HF). Woolley (ref. 9) found that the formation of HCl from PVC, for example, is almost quantitative and that the formation of other poisonous organochlorine compounds such as phosgene occurs only to a minor extent.

According to an FAA study published in December 1965 (ref. 10), the most important factor affecting the degree of fire hazard present inside the aircraft cabin was the flammability of the materials in which the fire originated. These large-scale fire tests showed that the interior materials used in a passenger cabin can produce a flash fire with little or no warning. Heat, smoke, and CO levels generated by the fire until about the time of the flash fire were below human survival limits. This was also borne out during the full-scale fire tests involving passenger cabins conducted for the FAA by the National Aviation Facility Experimental Center. In these tests, personnel donned self-rescue breathing apparatus only during a few of the more severe tests for greater safety and comfort. However, with the occurrence of a flash fire there is a rapid increase in flame propagation, smoke density, temperature, air pressure, CO, and oxygen deficiency.

Although traditionally it has been thought that lack of oxygen is a major hazard in any fire, there is little evidence to support this argument in an aircraft fire. If passengers are to survive an in-flight fire, the fire can be of only a relatively small nature and toxic gases are then the major problem. In the ground fire (crash) case, evacuation

TABLE I. – GASES EMITTED BY ORGANIC MATERIALS DURING FIRE

Toxic gas or vapor	Source
Carbon monoxide, carbon dioxide	All organic materials
Hydrogen cyanide, oxides of nitrogen (NO, NO_2), ammonia	Wool, silk, plastics containing nitrogen (urethanes, acrylonitrile, acrylonitrile-butadiene-styrene, modacrylics, nylon, melamine, urea-formaldehyde)
Halogen acids (hydrogen chloride, hydrogen fluoride, hydrogen bromide)	Polyvinyl chloride (PVC), fluorinated plastics, fluorocarbon sealants, fire-retardant plastics
Sulfur dioxide	Most rubbers, polysulfide sealants, sulfur-containing plastics (e.g., polysulfone)
Phenol	Phenolic resins
Formaldehyde	Acetal resins
Formic acid, acetic acid	Cellulosics, rayon
Acrolein	Wood, paper
Aldehydes	Phenol-formaldehyde, wood, nylon, polyester resins
Benzene	Polystyrene, PVC, polyester resins

must be achieved rapidly before the levels of smoke and toxic gases rise. Again the primary considerations are toxic gases rather than oxygen deficiency (ref. 8).

Smoke, rather than heat or CO, has proved to be the most severe factor affecting the safety and comfort of aircraft passengers during the early stages of a fire. At this point the smoke may contain so little CO that the major injuries from smoke inhalation may be caused by irritants that create lung conditions favoring the onset of complications such as pneumonia. The corrosive vapors also produce local inflammation, which causes fluid accumulation in the lungs. This edema may in itself cause death by asphyxiation (refs. 1 and 10).

Finally, atmospheric contaminant hazards associated with the use of plastics can exist without any thermal degradation. This was demonstrated in the manned environmental system assessment experiment conducted for NASA and the Air Force (ref. 11). Materials within the cabin include coatings, adhesives, films, fabrics, elastomers,

gaskets and seals, foams, thermoplastic sheets, thermal insulation material, potting electrical insulations, moldings, laminates, lubricants, greases, fluids, tubing, containers, and clothing. Five men were to live in a closed, self-sustained environment simulating an Apollo moon flight for 30 days. Contaminants evolved at ambient temperatures, for the most part, built up quite rapidly in the air as evidenced by the sweet pungent odors. The crew members developed nausea, cold sores, and loss of appetite. The test had to be terminated at the end of $4\frac{1}{2}$ days. Contaminants, identified by analysis of the atmosphere, and their presumed sources were halogenated compounds from cleaning solvent degradation and from neoprene in ducts carrying air at temperatures as high as 175° C; phosgene from partial oxidation of halogenated compounds; Freon 12 from a leaking air conditioner system; paracresols from degradation of tricresyl phosphate, a plasticizer; CO from pyrolysis of organic material and from carbon black, a plastic reinforcement; sulfur compounds from vulcanizing agents and accelerators; hydrocarbons from resin binders; and methyl ethyl ketone from adhesive solvent (ref. 11).

PLASTICS AS A FIRE RISK

Synthetic polymers are being increasingly used as textiles, furnishings, and construction materials and in vehicles and aerospace applications. Thus, the fire problem has taken on yet another dimension – that of the possible toxic effects from the gaseous degradation and combustion products of these new man-made materials.

Plastics, being organic polymers, are combustible. As such they represent a fire risk, like any common organic material, if not properly used. When a polymeric material is heated, sufficient energy can be introduced into the polymer system to cause thermal degradation by breaking the bonds among the polymer chains. Gas molecules are released. If these gases are combustible, and if there is an oxidizing agent present, the gases will ignite and produce a flame. Other gases may also be released that are not combustible. Particles, primarily carbon, may also be emitted, leading to smoke. These three components – unburned gases, burned gases, and smoke – will for the most part be responsible for the direct toxic effects generated in a real fire situation.

The pyrolysis products of wood can be equally hazardous. In spite of this, many building codes contain the requirement that interior finishes that produce smoke or toxic gases greater than those produced by wood burned under similar circumstances shall not be permitted. This gives the false impression that wood is a relatively safe material in a fire situation. One should not, of course, assume that all synthetic plastics and resins will be as safe as any natural material they might replace. But neither

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should one assume that the natural materials give off harmless pyrolysis products. In judging the safety of a synthetic resin for a proposed use, the hazards from combustion or thermal degradation should be compared under equivalent conditions with the hazards of alternative materials that have, if possible, a history of similar use (refs. 12 and 13).

The National Fire Protection Association (NFPA) Committee on Fire Gases has stated (ref. 12): "The large number of fire casualties from the inhalation of noxious products of combustion, as distinguished from burns sustained in fires, has long been of most serious concern to the fire-protection fraternity."

Various investigators have shown that inhalation of heated air, oxygen-deficient air, and toxic gases, particularly carbon monoxide, can be fatal. Also, the inability of fire victims to escape the fire because of smoke obscuration can fatally prolong the exposure. Often death occurs some time after the exposure to the toxic gases from the aftereffects of the exposure, usually from lung injury complications.

It is generally recognized that many fire casualties have suffered or died from exposure to gaseous combustion products rather than from heat or external burns. Materials involved in these fires are known to decompose under fire conditions and emit fatal quantities of smoke and toxic gases. Authorities estimate that 55 to 80 percent of fire deaths can be traced to smoke inhalation (refs. 12, 14, 15, and 16).

The toxicity hazard presented by fires involving plastic materials is common to all fires regardless of the materials being consumed. This common hazard, the toxicity of fire, is a major factor contributing to death or incapacitation. In a given fire situation one, several, or all of the following factors may be involved: (1) heat destruction of tissue; (2) thermal shock; (3) carbon monoxide; (4) carbon dioxide; (5) deficiency of oxygen; (6) lung edema due to irritant gases such as acid anhydrides, aldehydes, and acids; (7) other toxic gases; (8) ventricular fibrillation due to inhalation of hydrycarbon vapors; (9) smoke; and (10) emotional shock. (These factors are not necessarily listed in their order of toxicity or hazard since more than one cause may operate in a single case.) The toxicity potential of the total fire hazard is determined by the complex resultant of these factors. Combinations of effects can arise that can be additive, antagonistic, or synergistic (refs. 17 and 18).

Plastics based on carbon, hydrogen, and oxygen are unlikely to evolve gases that are much more toxic than the gases from cellulosic materials such as wood. But certain plastics may also contain nitrogen, chlorine, fluorine, bromine, sulfur, and many other elements. Under fire exposure these can be released to combine with other constituent elements and with oxygen and nitrogen in the air to form a wide variety of gases, many of which can be toxic.

Plastics containing nitrogen produce, on complete combustion, molecular nitrogen and small amounts of the oxides of nitrogen as well as CO_2 and water. On incomplete

combustion, HCN, cyanogen, nitriles, and ammonia (NH_3) may be formed in addition to hydrocarbon gases, presenting a significant health hazard in fire situations. Faster heating rates minimize HCN formation, and in real fire situations only trace amounts are generally found. Decomposition and combustion tests on such plastics as nylon and polyurethane have disclosed that the amount of these gases is less than that produced by combustion of wool or silk and that, in all of these tests, the toxic hazard of the CO probably outweighs that of the HCN (ref. 19).

Plastics containing sulfur form acid gases, in addition to CO_2 and water, on complete combustion and organic sulfur compounds on incomplete combustion (ref. 20). The situation is different for plastics containing halogens. Decomposition tests suggest that the bulk of the halogens will be evolved as the hydrogen halide either in combustion or in thermal degradation. These gases are substantially more toxic than CO, and the amount that can be evolved may be considerable. In addition, some plastics, such as natural rubber, may produce heavy smoke. For any given material, the nature of the combustion gases and smoke depends largely on the amount of oxygen available (refs. 12 and 21).

Under combustion conditions, CO and CO_2 should always be expected and at some stage there will probably be oxygen deficiency. Where nitrogen is present, one might expect the oxides of nitrogen (NO_x), NH_3, and the cyanides. Chlorinated plastics will produce HCl, but the presence of carbonyl chloride ($COCl_2$), or phosgene, in hazardous concentrations is doubtful. Fluorinated plastics should behave like chlorinated plastics but with greater stability and therefore with the emission of gaseous fluorocarbon compounds in addition to HF (ref. 22).

The proportions of gases will vary with fire conditions. In dwellings, the combustibles will normally be mainly cellulose, and the major toxic hazards will be oxygen deficiency and CO. In factories and stores, where larger quantities of plastic materials may be concentrated, gases other than CO may be significant. Some of these (e.g., HCl and NH_3) are exceedingly irritating at concentrations below the dangerous level and thus give a warning of their presence. Although many plastics are not combustible, they can be heated to decomposition by other combustibles present in the fire. The resultant gases will then approximate pyrolysis products, among which will be dense smoke (ref. 22).

As the fire progresses, combustible gases are burned, oxygen concentration decreases, and CO and CO_2 levels increase. The ratio of CO to CO_2 produced by a fire depends on ventilation. Generally, the better the ventilation, the less CO is present. At flashover (when all combustible gases ignite almost simultaneously) the oxygen concentration decreases sharply and CO and CO_2 levels show marked increases. Simultaneous high concentrations of CO and CO_2 and the presence of certain irritant gases such as HCl, nitrogen dioxide (NO_2), and sulfur dioxide (SO_2) are thus usually associated

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with low oxygen concentrations. It is probably this combination of factors, rather than CO alone, that is responsible for most fire casualties from toxic gases. A fire atmosphere containing a nonlethal concentration of CO in itself could cause a fatality from either the additive or synergistic effects of low oxygen concentration or the presence of other toxic gases. Since there may be little physiological evidence of the action of such conditions, the fatality could be mistakenly attributed entirely to CO poisoning (ref. 23).

Smoke is the airborne mixture of heated gases, liquid droplets, and solid particles evolved from combustion. It can include acids, alcohols, aldehydes, and hydrocarbons. Organic acids and aldehydes in some cases appear to condense on the surface of the smoke particles, thus making the particles more irritating. Reduction of vision by smoke obscuration and irritation to the eyes is a definite hazard that plays a significant role in fire situations by impeding or preventing escape. The visible density of smoke is not necessarily an index of its toxicity.

The Fire Gas Research Report (ref. 18) states that where the oxygen content is reduced to 12 to 15 percent of normal levels under fire conditions, muscular coordination for skilled movements is lost; at between 10 and 14 percent oxygen, consciousness continues but judgment is faulty and muscular effort leads to rapid fatigue. Breathing ceases when the oxygen content falls below 6 percent. Concentrations below 6 percent will result in death at ambient temperatures in 6 to 8 minutes (ref. 1).

Another cause of fatalities in fires is the production of heated air that if inhaled interferes with the function of the respiratory system. The temperature of the smoke and fumes from burning foamed polyethylene, for example, was found to be in excess of 1000° C; with self-extinguishing polyethylene foam, temperatures in excess of 1200° C were measured at ceiling height.

BEHAVIOR OF PLASTICS IN FIRES

The detailed behavior of a specific plastic material subjected to fire situations is extremely complex and thus difficult to analyze experimentally. A review by Saunders and Backus (ref. 24) outlines the major features of the behavior of plastics in a fire. A qualitative model representing these features is illustrated in figure 1 (ref. 25). The model emphasizes that pyrolysis or thermal degradation to yield combustible gases precedes and is independent of combustion, apart from the feedback of heat. Significant features of this model include flame, heat, mechanical collapse, smoke, toxic gases, and oxygen deficiency. The overall assessment of the hazards is complex because these features are interdependent. Many quantitative aspects become determining factors as to whether one particular hazard will be important in an actual fire. The mass
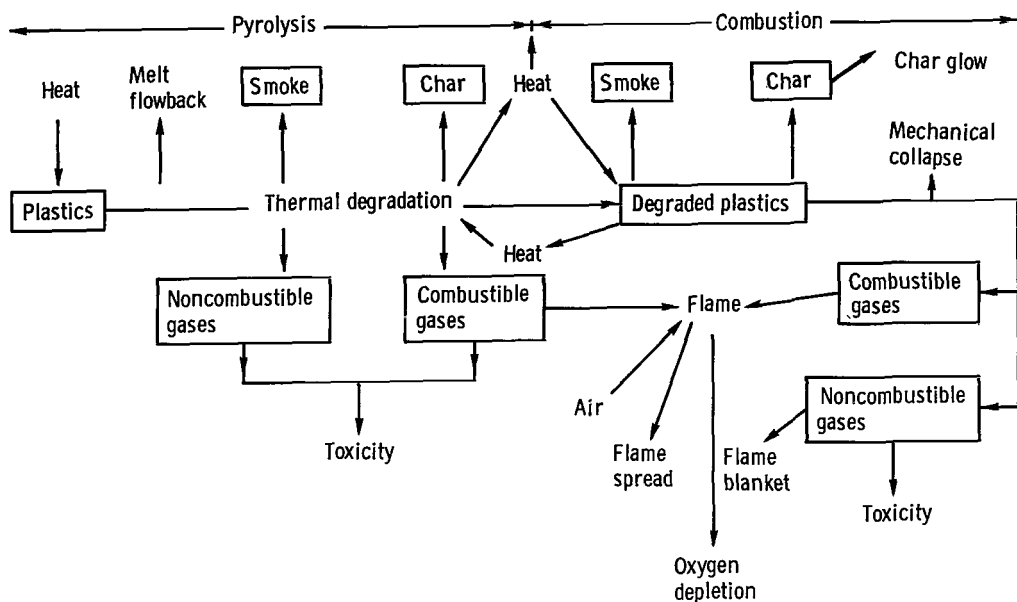
Figure 1. - Schematic representation of major features of the behavior of plastics in a fire.

of the combustible, the surface area exposed, and the orientation are particularly important in evaluating the hazard.

There are several factors that decide the nature and the quantity of the end products in a plastics fire. Depending on the temperature at which the degradation proceeds, very different substances are released. The primary fragments of the macromolecules are usually so active chemically that they immediately start a secondary reaction. Also, a decisive role is played by the oxygen content of the fire environment. Generally, the more complete the combustion, the less toxic are the end products. Any consideration of the problem must also not ignore the fact that thermal degradation of most materials starts prior to any visible burning and may be a slow process.

In any specific case of thermal degradation, the following factors can affect the gaseous products: (1) type and quantity of material; (2) type of combustion (or fire); (3) size of fire enclosure; (4) rate of ventilation (oxygen content); (5) temperature; (6) duration and rate of heat application; (7) ignition source; and (8) physical configuration (sheet, foam, powder, etc.) (refs. 26 and 27). Thus, it is difficult to accurately predict the composition of a fire atmosphere. Since there is a large and increasing usage of plastics and since the usage of natural materials also changes with changes in technology, the "average" fire atmosphere of today will be different from that of the past or future.

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Analysis of decomposition products also has indicated major changes in the nature of the products from condensation, recombination, or cross reactions when the temperatures of combustion are changed (ref. 1). The pyrolysis products, which are produced by heat in the absence of air, also differ from the combustion products, which are emitted from a fire in oxygen. As indicated previously, where ample oxygen is present, the air temperatures may reach or exceed 1000° C. These temperatures are above the ignition temperatures of hydrogen sulfide (H_2S), formaldehyde (CH_2O), HCN, and CO. Thus, a clean-burning, hot fire may be safer from a toxicity standpoint than a cooler, smoldering fire. It should be kept in mind, however, that some gases (e.g., SO_2, which is highly toxic) will not burn (ref. 12).

PHYSIOLOGY OF COMBUSTION/PYROLYSIS GASES

The gaseous combustion products of polymers are generally well known and have been thoroughly studied by toxicologists. There are, however, gaps in the knowledge of the effects of both combined gases and brief exposures to high concentrations such as might be encountered in fire situations. Also to be considered is the combustion process itself. Under any set of test conditions the gases and smoke given off may change with time, ventilation, and the form of the burning material. High ambient temperatures may in fact "burn up" some of the noxious gases to less toxic forms.

Whether the fire victim is "poisoned" or not depends both on the properties of the material and on the quantities absorbed. No substance is so toxic that there is not a tolerable dose, and none is so harmless that unlimited absorption is safe. The extent to which damaging doses can enter the body through the respiratory passages or by skin adsorption during a fire situation is finite. For some toxic gases, sufficient concentration or time of exposure is so limited that a damaging dose is improbable. Among these gases is CO_2, which must be present for at least 10 to 20 minutes in a concentration as high as 4 to 5 percent by volume. Many aliphatic and aromatic hydrocarbons fall in this category, as do ketones and the organic acids – except formic and acetic acid (ref. 28).

Bieberdorf and Yuill (ref. 12) reviewed the hazards of gaseous combustion products and pointed out the numerous ways in which these products are injurious to humans. Briefly, the effects fall into three categories: irritation to the eyes and respiratory tract, systemic poisoning, and alteration of respiration. As irritants, the gases may cause extreme discomfort and result in panic, even though in themselves they may not be very toxic. They may serve as lachrymators or be so irritating as to affect the victim's ability to escape. Little attention has been given to these products because, as might be expected in a fire investigation, primary attention is given to the most hazardous toxic gases. As a rough guide we may assume that water-soluble irritants such as

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HCl and CH_2O warn the victim at the first inhalation or contact and that less soluble ones such as phosgene and toluene diisocyanate penetrate into the lungs in large quantities and have a more serious effect there. The lungs are the principal site of action for the irritants, but corrosive vapors such as acids and aldehydes will also affect the skin. The most common irritants encountered in fires are acetic acid, acetic anhydride, acrolein, formic acid, NH_3, CH_2O, furfural, H_2S, SO_2, the hydrocarbons, and tar (refs. 18, 28, and 29).

The toxic gases that act as systemic poisons are often more subtle in their effect. They must generally be absorbed into the blood stream before leading to toxic symptoms. In effect, these symptoms can be almost immediate or may become evident only at a later time. Another consequence of exposure to even small amounts of toxic gases has not received much attention; the gas may act as a sensitizing agent, producing antibodies that on repeated exposure may produce increasingly serious effects. And finally, in low concentrations there may be no specific symptoms of toxicity, but the mental functions may be affected sufficiently to lead to erratic behavior (refs. 12 and 30).

Some gases, such as CO_2, accelerate respiration and thereby increase the intake of poisonous gases. Others, such as some highly irritating compounds, decrease the respiration frequency. Acetaldehyde is reported to reduce respiration frequency to as few as 5 inhalations per minute in humans under certain circumstances (refs. 16 and 18). The physical, chemical, and psychological state of the individual to a great extent affects the toxiocological response.

It is also important to remember that especially with newer plastics and additives, toxicity considerations must be extended to include possible health effects from lower concentrations of gases and exposures over longer periods of time. Further extension of knowledge to the environmental effects of industrial processes and incineration of plastics trash is desired (refs. 27 and 30).

CHARACTERISTICS OF TOXIC GASES

Fires, almost without exception, involve the rapid oxidation of organic materials, which are composed chiefly of carbon, hydrogen, and oxygen with usually lesser amounts of other elements. Combustion in the ideal situation results in production of the highest oxidized form of the elements present. The real fire situation, however, is never ideal and intermediate states of oxidation occur. In some cases, compounds are formed in which an element other than oxygen is substituted.

Carbon Monoxide

The most important fire hazard, from the standpoint of toxicity, is considered to be carbon monoxide (CO), which represents an intermediate stage of oxidation. Carbon monoxide is an almost universal product of combustion. And in any situation in which heat, flame, and smoke are produced, CO is sure to be present. The incomplete or inefficient combustion of any carbonaceous material will result in greater production of CO than does efficient and complete combustion. Depletion of oxygen in a fire, as well as water and low temperature, will result in the production of increasing amounts of CO as the fire progresses.

Of all the gases generated in fires, CO is reported to produce the most deaths. Carbon monoxide is insidiously toxic; it is a colorless, odorless, nonirritating, flammable gas that is primarily absorbed through the respiratory tract. The presence of 3500 parts of CO per million parts of air (ppm) is immediately hazardous to life. It is poisonous because the hemoglobin in the blood combines with it in preference to oxygen. Then carboxyhemoglobin is formed, which cannot carry oxygen to the tissues, and chemical asphyxia results. Poisoning severe enough to cause unconsciousness can result in damage to the central nervous system. Physiological response is influenced by such factors as rate of breathing and individual susceptibility. Age, health, and smoking habits all have some influence on the total effect produced by exposure. In addition, CO stimulates the respiratory center in the brain and can cause an abnormally high respiratory intake of other gases present in the fire environment. Thus, toxic or lethal concentrations are inhaled that might otherwise have been avoided (refs. 12, 17, 18, and 23).

Carbon Dioxide

Carbon dioxide (CO_2) is a heavy, colorless, nonflammable, odorless gas that has a sharp taste in high concentrations. It is the end product of the complete combustion of carbonaceous material and thus must be considered in any fire situation. Normally, air contains about 300 ppm. Since it is an important constituent of the physiological processes, it is not ordinarily considered to be a toxic gas. When an atmosphere containing higher than normal CO_2 levels is respired, the CO_2 concentration in the blood increases, stimulating respiration and leading to abnormal, labored breathing. These symptoms are initiated at about 20 000 ppm; a concentration of 30 000 ppm doubles the lung ventilation rate. Conversely, concentrations of 10 to 12 percent are fatal within a few minutes because of paralysis of the central-nervous-system respiratory center. As

is the case in CO poisoning, initial increased breathing results is increased inhalation of other toxic gases present (refs. 12, 23, and 30).

Hydrogen Cyanide

Hydrogen cyanide (HCN) is a colorless, flammable gas with a faint odor of bitter almonds. It is slightly lighter than air so that air currents may sweep it away from the fire area. When inhaled, it is absorbed by the blood and carried to the tissues, where it deactivates catalysts needed for oxidative processes in the body. It is thus a chemical asphyxiant. The odor of HCN warns of its presence, but it may be obscured by other odors or the olefactory sense may be quickly paralyzed. Also absorption may take place through the intact skin. Exposure to 20 ppm produces slight symptoms in several hours; 200 to 480 ppm is fatal within 30 minutes; 2000 ppm is rapidly fatal even with prompt medical treatment. Inhalation of low concentrations will lead to a reflex action that stimulates breathing and thus increases inhalation of additional toxic gases (refs. 12, 18, 23, 30, and 31).

Hydrogen cyanide was measured in an FAA study on burning aircraft interior materials (ref. 32) and was generally found in much smaller quantities than CO. Nearly all the materials tested yielded HCN in concentrations from a few ppm to 40 ppm. Urethane, ABS, acrylic, and polyamide materials produced the highest concentrations. Other plastics that can emit HCN under fire conditions include melamine (urea-formaldehyde), polyimides, and nitrocellulose. Under the usual fire conditions the quantity of HCN emitted would probably not present a hazard by itself. However, relatively low concentrations of HCN in combination with other toxic gases may produce toxic effects not otherwise anticipated (refs. 16, 17, and 32).

Ammonia

Gaseous ammonia (NH_3) is colorless and has a characteristic sharp, extremely pungent odor. It is extremely irritating to the eyes, skin, and respiratory system and so provides ample warning of its presence. As much as 100 ppm for 8 hours is tolerable; 1700 ppm for 30 minutes may be fatal because of the corrosive effects on the lungs (refs. 17, 23, 33, and 34). From the data available it is difficult to postulate how much NH_3 might be found in a real fire situation. It is produced on combustion of a variety of nitrogen-containing materials. It has been found in the pyrolysis products of nylon, phenolic and melamine resins combined with fillers, polyacrylonitrile foamed with certain agents, and polyurethane (refs. 16, 27, 33, and 34).

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Oxides of Nitrogen

The oxides of nitrogen (NO_x) are much more toxic than is commonly realized since in the water vapor of the lungs they form nitrous acid or nitric acid. Injury from this group may often be sustained without marked discomfort at the time of exposure. Nitrogen dioxide (NO_2) is the most toxic oxide of nitrogen encountered in a fire situation. Ten to 40 ppm is the minimum concentration tolerable for a prolonged period of exposure; 100 to 150 ppm is dangerous for exposures of 30 minutes to 1 hour; 200 to 700 ppm is rapidly fatal after a short exposure. The irritating effect on the nose and throat of high concentrations may be tolerated even though a lethal concentration is being breathed. Oxides of nitrogen tend to anesthetize the throat, and the appearance of lung damage and edema is often delayed (refs. 18, 23, and 30).

In Gross' work (ref. 32) oxides of nitrogen were evolved by several of the aircraft materials tested. Some of the materials were ABS, polyamides, cotton, polyether urethane, and wool/polyester. The highest concentration measured under the test conditions was 50 ppm from a polyamide. Other materials that may emit NO_x under fire conditions include nitrocellulose and polyurethane. The tests suggest that the NO_x gases by themselves would pose no real threat in an ordinary fire. Small amounts, however, may give rise to synergistic effects in combination with other toxic gases (refs. 16, 23, and 32).

Halides and Halogens

The halogens and halides (HCl, HBr, HF, Cl_2, Br_2, F_2) all act as pulmonary irritants, and some act as systemic poisons when inhaled. Mild exposures respond to treatment, but heavy doses may have serious effects. Sharp odor and irritation to the respiratory tract ordinarily give adequate warning of their presence. One hundred ppm of HCl causes lung edema and laryngeal spasm; over 1000 ppm of HCl or HF causes lung injury and is dangerous to life for even brief exposures. Under real fire situations the halides and halogens are generally not a serious threat to life unless the victim is unable to flee the area of high concentration (refs. 12, 16, 17, 23, and 30). The source of the halides and halogens in a real fire situation would be halogenated plastics such as polychlorotrifluoroethylene, polyvinylidene, PVC, polytetrafluoroethylene (PTFE), and fluorinated polyethylene-propylene. Several studies have been made of the pyrolysis products of PTFE. The major product of pyrolysis in air at $500°$ to $600°$ C was COF_2; above $650°$ C, PTFE yielded mostly CF_4 and CO_2. Fluorinated polymers, if heated sufficiently, release HF and a group of low-molecular-weight, saturated and unsaturated fluorinated hydrocarbons.

In an investigation of burning aircraft interior materials (ref. 32), HF was found for nearly every fluorine-containing material, and PTFE seals yielded 90-ppm HF under nonflaming conditions, a hazardous situation. Toxicity studies in which rats were exposed to PTFE combustion products suggest that the particulate matter, rather than the gaseous toxic byproducts, may cause death (ref. 35). Generally, the small amount of fluoroplastics found in real fire situations and their sharp odor and irritating action minimize their toxicity contribution (refs. 16, 23, 36, and 37).

Coleman and Thomas (ref. 38) heated PVC, vinyl and vinylidene copolymers, and chlorinated polymethyl methacrylate to various temperatures and found that copious quantities of HCl were liberated, the amount generally increasing with temperature. The authors estimated that three pounds of any of these plastics heated in an unventilated room of 1000 cubic feet could produce a toxic hazard from the CO and HCl generated. In reference 32, Gross and Loftus measured HCl and several other gases. Hydrogen chloride was released rapidly during combustion or pyrolysis of PVC, modified acrylics, and fire-retardant-treated materials. Flaming conditions produced higher HCl concentrations, probably because of the higher temperature. Concentrations of HCl in the test systems changed rapidly as a result of the high reactivity and absorptivity of the HCl (refs. 23, 32, and 38).

Phosgene, or Carbonyl Chloride

Phosgene ($COCl_2$) is a colorless, irritating, suffocating gas with an odor of musty hay. It is perceptible by odor at about 5 ppm, though a lesser concentration causes irritation. It is dangerous at 25 ppm after 30 to 60 minutes of exposure; 50 ppm is lethal for this duration; 250 ppm is lethal in a few minutes (refs. 18 and 23). Phosgene is used in the synthesis of isocyanates, polyurethane, polycarbamates, and other materials. Coleman and Thomas, in their work on chlorinated plastics (ref. 38), found the largest concentration of phosgene to be 1/1700th the amount of HCl produced. Underwriters' Laboratory cites several unpublished reports of studies in which phosgene has been found (refs. 20, 23, 38, and 39).

Hydrogen Sulfide

Hydrogen sulfide (H_2S) may be present if sulfur-containing materials are involved in the fire. It is a colorless, flammable gas readily identified by its rotten-egg odor, which is detectable at less than 1 ppm. It may act as both an irritant and an asphyxiant. Twenty to 150 ppm causes eye irritation; 800 to 1000 ppm can be fatal due to

rapid loss of consciousness accompanied by paralysis of the respiratory control center of the brain. In the usual fire, H_2S would not generally be of much concern because relatively small amounts would be present (refs. 17 and 23).

Sulfur Dioxide

Sulfur dioxide (SO_2) is a pungent, heavy gas that is extremely toxic. It is highly irritating to the eyes and respiratory system. In contact with the water vapor in the lungs it forms sulfurous acid. The concentration detectable by odor is 3 to 5 ppm; greater than 20 ppm causes injury after 1 hour. Lethal concentrations of SO_2 are not respirable because of the intense irritation it causes, unless the victim is unconscious or cannot escape the fire situation because of incapacitation. Death most likely results from asphyxiation caused by swelling of the respiratory tract (refs. 17, 18, 23, 30, and 31).

Sulfur dioxide is formed by the incomplete combustion of sulfur-containing compounds. Reference 32 showed that sulfur-containing plastics could produce SO_2 when combusted. Polysulfones produce as much as 150 ppm. Materials commonly emitting SO_2 on combustion include chlorosulfonated polyethylene, polysulfone, and certain rubber formulations (refs. 23 and 31).

Organic Compounds

A few generalizations relative to the toxicity of fire off-gases involving aliphatics are pertinent. In a homologous series of hydrocarbons, the greater the number of carbon atoms, the greater is the toxicity. As the number of hydroxyl groups increases, the toxic action decreases. The substitution of a carboxyl (-COOH) group for a hydrogen atom prevents anesthetic action. The substitution of a halogen for a hydrogen atom increases anesthetic action (ref. 18).

The thermal degradation of organic, natural, and synthetic polymers will produce a variety of saturated and unsaturated aliphatic hydrocarbons with a range of molecular weights. The lower molecular weights tend to produce narcosis. As the molecular weight increases, the biologically toxic effects tend to decrease. Unsaturated hydrocarbons will generally have a greater toxic effect than saturated compounds.

The aromatic hydrocarbons, starting with benzene, have both irritating qualities and systemic toxicity. Several of the hydrocarbons can be absorbed not only by inhalation but also by direct absorption through the intact skin. Levels of 100 ppm and greater are considered dangerous to the health. Among these compounds are benzene,

toluene, and styrene from the degradation of such plastics as polystyrene and polyphenylene oxide (refs. 1, 16, 18, and 30).

A number of organic compounds formed in the combustion processes are classified as irritants. These substances generally fall into the class of oxygen-containing compounds such as aldehydes, ketones, and acids (formaldehyde, acetic anhydride, acetaldehyde, acetic acid, formic acid, acrolein, and furfural). The threshold limit values (TVL), or concentrations normally permitted for occupational exposures for a period of 8 hours in any 1 day, range from 0.1 ppm for acrolein to 200 ppm for acetaldehyde. Madorsky (ref. 34) presents a compilation of the many degradation products of organic polymers when they are pyrolyzed in air, inert atmospheres, or vacuum. In real fire situations these irritants may be adsorbed on particulate matter in smoke and should be expected in the early, smoky stages of fires (ref. 23).

Other Gases and Their Toxic Effects

Many other gases may be encountered in dangerous concentrations under special circumstances (e.g., where large quantities of specific plastics are stored in one location). It is possible that under ordinary fire conditions these gases would not comprise a serious hazard. What synergisms may exist to complicate the toxicity picture are not yet known in great enough detail.

There are also a number of gases that are best described as irritants or lachrymators. Under severe conditions their irritant qualities can effectively interfere with reasoned judgment and normal vision, increase respiratory resistance, and induce panic.

Gases with anesthetic properties may be evolved in small quantities in the thermal degradation of plastics. Generally such gases as benzene and the higher paraffins and olefins must be present in relatively high concentrations to exert any appreciable effect and would not usually be of any consequence as an anesthetic in a fire situation (ref. 23).

Smoke comprises the nongaseous airborne products of combustion, which are predominantly carbon and on which may be adsorbed irritants such as organic acids, aldehydes, HCl, and other combustion products, including SO_2 and NH_3. In addition to particulates, smoke may also contain droplets of condensed combustion products. A major hazard of smoke is the obscuration of vision which, coupled with its irritating effects, causes fear and panic (ref. 23).

Oxygen deficiency occurs as a natural result of combustion of polymers in air. The decrease in oxygen concentrations depends on the material combusted and the physical conditions in the fire situation (e.g., ventilation). A 15 percent oxygen level in air is usually required to support combustion of most burnable materials - although

some plastics provide the necessary oxygen because of their chemical makeup. As previously stated, breathing ceases when the oxygen content falls below 6 percent. Thus, it is possible that man could survive when fire could not, if oxygen deficiency by itself were the only hazardous factor in the fire situation. However, as the oxygen supply decreases, the levels of CO and other toxic gases increase.

Denial of sufficient oxygen to brain tissue can produce irreversible brain damage or death. Lower oxygen concentrations can produce behavioral changes with erratic behavior and faulty judgment under the stress of the fire situation. In the presence of heat, smoke, and toxic gases, lower degrees of oxygen deficiency may produce serious, irreversible effects not usually found with those degrees of oxygen deficiency. Serious oxygen deficiency is probably not as great a threat to life in fires as CO. However, a certain degree of oxygen-deficiency hazard can be expected in any fire situation (refs. 23, 26, 30, and 34).

Other gases produced in the fire situation also can contribute to the oxygen-deficiency problem. Such gases, although not toxic themselves, displace oxygen from the breathing air. Such asphyxiants include nitrogen, hydrogen, and methane. Irritant gases such as SO_2 can also displace oxygen. Certain asphyxiants may be produced as intermediate products of combustion, for example, the hydrocarbons.

This summary of the most important hazardous compounds and conditions produced in fires is, of course, incomplete. The polymeric materials contain many other chemical agents that contribute to the emitted gases. Also, chemical composition, physical structure, surface area, geometry, fuel configuration, rate of heating, and environmental factors are but a few of the parameters governing the combustion of plastics. Any single factor or combination of factors can affect the degree of toxicity of the combustion products (refs. 1, 16, and 40).

Thus, thermal degradation products can lead to extremely toxic responses when inhaled. However, dose (concentration and duration of exposure to that concentration) is the governing factor as to the degree of toxic effect produced.

COMPARATIVE TOXICOLOGY OF THE GASES

A review by Dufour of the Underwriters' Laboratories (ref. 20) of the toxicity of the gaseous products from the thermal degradation of plastics generally presents the view that plastics do not contribute a greater hazard than conventional cellulosic materials (e.g., wood and furnishings). Certain very toxic gases were reported from some plastics, but concentrations were low. And CO was considered to be the most hazardous product. Some other toxic gases were acrid, readily detected, and thus considered less dangerous despite the fact that they could impair vision. Such conclu-

sions were made with caution because the effects of all the factors known to influence fires had not been investigated and the available data were mostly from laboratory studies and difficult to assess.

Dufour in another paper (ref. 41) refers to published conclusions of several studies that point to the principal inhalation hazard in fires as either the presence of CO or oxygen deficiency. Other toxic products may also be present but in lower concentrations than CO. Thus, the other products may present a hazard to life, but the chief hazard is judged to be either the presence of CO or the lack of oxygen.

There is other support in the open literature for the contention that CO is produced at such a rate that the presence of other toxic gases becomes academic – that they do not present a life hazard. There is also support to the contrary – that the other toxic gases either alone or in concert with CO, heat, and oxygen deficiency generate a life-hazard environment. Additional research is needed to define and resolve the question. The data produced to date are far from complete or conclusive (ref. 12).

In real fire situations it becomes nearly impossible to ascertain which one of two or more agents or combinations of agents caused death, excluding oxygen deficiency and CO. At the present time the simplest approach used is to have some knowledge of what gases are formed and to seek information on the toxicity of these individual compounds. However, the combination of products being inhaled generally does not produce the same biological effects as singly administered products. (See the section SYNERGISTIC EFFECTS.)

Higgins, et al. (ref. 42) of the FAA Civil Aeromedical Institute conducted experiments with animals to determine the toxic effect of short-term exposures to HF, HCl, NO_2, and HCN singly and in combination with CO. These studies showed the toxicity rankings of the four materials when present in equal concentrations to be HCN, NO_2, HF, and HCl in decreasing order of toxicity. Carbon monoxide concentrations that alone are not hazardous to life did not enhance the toxic response to these substances (refs. 42 and 43).

Kishitani (ref. 44) developed a CO toxicity profile for mice wherein he reports that he was able to determine whether the toxic and lethal effects of effluent gases were due to CO or to the presence of other gases. This investigation also demonstrated that the generation of gas precedes that of smoke and that considerable toxic effects can occur before smoke becomes sufficiently dense to obliterate vision (ref. 45). Seader, et al. (ref. 46) found that CO was the primary cause of death in laboratory animals when they were exposed to burning polyisocyanurate foam (refs. 43 and 44).

There has been concern as to whether carbonyl fluoride (COF_2) is the principal toxic product resulting from the pyrolysis/combustion of Teflon. Its presence has been confirmed by a number of investigators including Coleman, Scheel, and Birnbaum (refs. 35, 36, 37, 47, and 48). The remaining major gaseous products are HF and CF_4. Of

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these, HF is extremely toxic and CF_4 is less toxic than carbon tetrachloride (CCl_4).

Wagner of Johns Hopkins University wrote a paper (ref. 27) reviewing in some detail the toxic species evolved over a wide range of pyrolysis/combustion conditions. He also described the physiological responses to the common fire-produced gases and liquids. Of interest are not only the extremely toxic materials (e.g., CO and NO_2) but also the moderately toxic ones since they include materials that may produce irreversible as well as reversible changes in the human body. However, these changes may not result in serious physical damage unless the dose is massive.

In addition to the gaseous phase of pyrolysis products (e.g., CO, CO_2, and acetic acid vapor) the liquid aerosol or mist phase also contributes to the overall toxicity whenever the toxic acids or the aldehydes undergo condensation due to cooling (to less than about 100° C). A further complication occurs when the liquid phase condenses out in contact with the particulates in smoke. Particles in the size range of 0.005 to 1.0 micrometer readily penetrate deeply into the lungs (ref. 27).

In summary, most investigators agree that CO is the major hazard in gas inhalation in fire situations. There is less agreement as to the role played by other toxic gases. A great deal of research is needed in this area to evaluate the role played by gases other than CO in the toxicology of fires.

THE ROLE OF ADDITIVES

Commercial polymers contain additives to impart such desirable properties as flexibility, weatherability, thermal stability, and low flammability to the basic polymer structure. Additives include fillers, plasticizers, antioxidants, colorants, flame retardants, and stabilizers. Such additives often have a marked tendency to increase toxic emission problems by chemically changing the composition of the gases or particulates released in fire situations. Information on these interactions, including catalytic reactions, is scanty and not well documented. The flame retardants are a case in point. In 1971, over 80 million kilograms (179 million lb) of flame-retardant agents were used (ref. 49). The gases that are evolved because of the incorporation of flame retardants may show a completely different type of emission profile – with the evolution of new toxic compounds. Many additives are themselves toxic under normal conditions and are not expected to lose their toxicity at elevated temperatures. In addition, even some of the more inert fillers may degrade to toxic species in such a chemically reactive environment.

To date, the major concern of those engaged in the development of fire-retardant materials has been the reduction of the ease of ignition and of flame propagation. There has been less concern for other fire-induced characteristics such as smoke emission

and increased toxicity of combustion products. Few, if any, of the flame-spread retardants are also smoke suppressants; the mechanisms employed in retardants tend to actually increase smoke production in many situations. For example, smoke generation is usually greatest at the thermal degradation stage just prior to ignition. Flame retardants do not alter the thermal degradation but simply delay ignition of the gas phase; and the longer ignition is retarded, the more smoke is produced.

In a toxicology study by Petajan, et al. (ref. 50) the physiological and toxicological effects of the combustion products of a fire-retarded rigid-foam polyurethane were fatal to exposed rats in a matter of minutes. The same foam without the fire retardant produced only elevated carboxyhemoglobin blood levels, which were nondebilitating. A bicyclic phosphate compound was believed to have caused the deaths by affecting the central nervous system. Compounds exhibiting such extreme toxicity could be present in biologically hazardous concentrations in a complex mixture (i.e., smoke) and go undetected by conventional fire-study analytical techniques such as gas chromatography and mass spectrometry. Petajan used this example to illustrate the necessity for a biological testing program to parallel chemical analytical methods during evaluation of a material's combustion products.

SYNERGISTIC EFFECTS

There is a fallacy in accepting an absolute threshold concentration value for the degree of toxicity of a gas. It is a misleading value since the minimum toxic concentrations are usually determined for a single gas in air. Yet, in an actual fire, a single gas or vapor is seldom encountered. There is ample evidence that the sum of the toxicity potential of two or more gases or vapors is more than additive at times. It is possible that individual gases, each of which is present at a tolerable level, may be fatal when combined with other gases that are also present at individually tolerable levels. The toxicity of such a mixture may be further increased by low oxygen concentration and high temperature. This phenomenon of a mixture of two or more gases having a greater physiological effect than the sum of the individual effects is known as synergism (refs. 18 and 51).

One of the oldest known examples of synergism is the combined action of oxygen and small amounts of CO_2. In this case a medically beneficial action results wherein CO_2 increases the breathing rate to stimulate the oxygenation of the blood.

In no combustion process is it likely that a single product is formed. Therefore, what should be considered in judging the toxicity of a fire atmosphere is the effect of a combination of gases, both those that are individually toxic and those that might otherwise be innocuous by themselves but adversely affect health in the presence of other,

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toxic materials. If the physiological effects of a combination simply represent the sum of the effects of the gases present, the effect is termed "additive." When one substance counteracts or tends to cancel the effect of the other the relation is termed "antagonistic."

In regard to synergistic effects, the NFPA Fire Gas Research Report (ref. 18) illustrates possible synergisms with a specific example:

"For example, a mixture of CO and H_2S in air, containing of each, respectively, 50 and 4 parts per 10,000 parts of air is fatal to animals when breathed, but neither gas in these concentrations is fatal when breathed alone." (ref. 12)

Publications examining synergistic effects are limited. The effects of combinations of various liquid aerosols or particulates with toxic gases on human response are largely unknown (ref. 27). Very little data are available on the critical time needed for individuals to escape fire situations before being incapacitated by toxic gases. Gaume, et al. (ref. 52) exposed mice to each of the gases CO, CO_2, and NH_3, which represent both asphyxiant and irritant categories, and to various combinations of these gases. Single-gas exposures were completed first to establish baseline data. Next, mixtures of CO/CO_2 and CO/NH_3 were used at several concentrations. Finally exposures were made at various concentrations of mixtures of all three gases. The time of exposure required for the mice to collapse was noted. It was found that compared with single-gas exposures, using CO as a baseline, double-gas exposures involving CO extended the time to collapse and triple-gas exposures extended it even further (antagonistic effects). Interacting physiological mechanisms and the development of mechanical (lung fluid) barriers may be involved in this time extension phenomenon. According to Gaume these results are considered preliminary and must be substantiated by additional studies.

A series of animal-exposure experiments were made by Pryor, et al. (refs. 51 and 53) to evaluate the significance of exposure to combinations of combustion gases. Initially, groups of 10 mice were exposed to various levels of four variables (CO, temperature, oxygen, and CO_2) individually and in combinations of two and three variables. The number of fatalities served as an index of toxicity. The exposures to combined variables revealed that levels that were not lethal in uncombined form became lethal when combined. When three variables were used, a further increase in deaths was noted. An exception, however, occurred with CO_2. When combined with CO, carbon dioxide exerted an antagonistic effect. Additional tests then incorporated SO_2, NO_2, and HCN with the initial variables. The results confirmed the definite synergistic effect exerted by the extreme toxicity of these variables even in trace quantities, when they were superimposed on the initial variables. Later addition of Douglas fir fire products to the previous variables showed a further increase in overall toxicity. Autopsies on the animals that died showed only congestion of the lungs and the vascular system. No

lesions or irritation of the upper respiratory tract were noted. The congestion was of equal degree regardless of the toxic variables or the length of survival time. This suggested to Pryor, et al., that the combined variables in all exposures disrupted the thermoregulatory center in the brain, resulting in body temperature elevation and circulatory collapse at time of death. Examination of animals that survived 10 days after exposure also showed no lesions or congestion. It may be concluded from the relatively few studies available that the hazards of combinations of toxic gases are greater than might be expected from the toxicity of individual components of a combination. More work is necessary to better define the problems associated with combinations of toxic gases and to elucidate the mechanisms of this action (refs. 23, 51, 53, and 54).

Tsuchiya and Sumi examined Pryor's data by using statistical techniques whereby synergistic or antagonistic effects are detected as an interaction of factors, for example, toxic gases, oxygen deficiency, and heat. In their paper (ref. 55) they state that the effect of combinations of such factors is generally additive. They assert that some of Pryor's data (ref. 53) involving combinations of oxygen deficiency and CO, oxygen deficiency and heat, CO and heat, and CO_2 and heat did indeed indicate possible synergism (in general agreement with the conclusions of Pryor, et al.). Antogonism of the combination of CO and CO_2 was found once out of four analyses. The synergism of the oxygen deficiency/CO_2 combination reported by Pryor was not considered significant in the Tsuchiya and Sumi analysis. They claim that even when synergism is found the contribution from interaction is much smaller than the main effects of the factors.

It might be concluded from the relatively few available studies that combinations of toxic gases do not simply act additively one on another but rather that the effect is not predictable from the action of the individual substances. More work is obviously needed to better define the physiological response to the many combinations that are likely to be encountered in a real fire situation.

In general, it has been concluded that CO, oxygen deficiency (anoxia), and excessive heat (hyperthermia) are the factors of primary importance in exposures to single variables. Which variables are important in exposures to combinations of the constituents is not known (ref. 53).

LABORATORY STUDIES

Laboratory tests for determining the identity and toxicity of the decomposition products of plastics generally fall into two types: those concerned with identification and analysis of the chemical compounds in the gaseous combustion products, and those concerned with studying the physiological effects of these gases on test animals – usually rats or mice. These tests have common shortcomings in that there can be interference

because of the mixture of compounds and there can be a loss or change in composition between the fire source and the test location. Losses may result from condensation or adsorption. Thus, a laboratory study could produce results that may have little relation to a real fire situation. For instance, high temperature might be required to keep readily condensible gases in the gas phase, but high temperature would present a hazard to life and then toxicity would be irrelevant to the fire victim.

Animal Toxicology Studies

In any given fire situation involving loss of life, there is a temptation to place the blame on one specific factor. Much publicity was given a Chicago coroner's statement that enough HCN was found in the blood of 10 victims of an airplane accident to have caused death. Later reports indicated that lethal amounts of CO were also present. Which factor caused death is not really known. Also, it is generally recognized by medical authorities that body chemistry changes after death and that the development of acids is characteristic of such change. Thus autopsies, to be meaningful, must be performed as soon as possible after death and must be thorough (ref. 56).

The techniques for using animals to determine the physiological effects of gases are well established. These have been the basis for determining the allowable concentrations or threshold limit values (TLV) of many of the gases found in industry. The method requires considerable knowledge of ths history, growth, physical condition, and susceptibility of the animals used. The test animals must be carefully maintained for a healthy state to be assumed at the time of the test.

Leong and MacFarland (ref. 57) reported the results of several toxicity studies of specific epoxy resins. The lethal concentration to kill 50 percent of the test rats was calculated[1] and histological studies of lung tissue and other organs were performed. Under the conditions of the study, the toxicity of the gases under combustion conditions was insignificant, but the toxicity of the gases under pyrolysis conditions was significant.

In this study (ref. 57), deaths caused by the pyrolysis products of the electric motor potting epoxy were attributed to respiratory failure from pulmonary edema or

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[1]In experimental toxicology it is a common practice to determine the quantity of poison (often expressed per unit of body weight of the animal) that will produce a lethal effect. A commonly used measure is the amount of toxic material that is required to kill one-half of a group of exposed test animals within a specified period of time. This is known as the LD-50 test (lethal dose - 50 percent). The survival period is usually established, such as a 30-day period (ref. 46).

histoxic anoxia, possibly complicated by cardiac, renal, or hepatic involvement. Excessive heat stress and oxygen deficiency exerted no significant effect. The authors calculated that a man confined to a 42.5-cubic-meter (1500-ft^3) volume for 1 hour with no appreciable air change would receive a lethal inhalation exposure from the pyrolysis products derived from 0.45 kilogram (1 lb) of epoxy resin. However, in overt fires where combustion with flames occurs, the hazard appears to be greatly reduced.

It has been suggested that in the practice of cooling gases prior to exposing animals the potency of some component gases might be lost, such as by condensation on cool surfaces. Yet if the gases were not cooled, the results might be affected by thermal injury to the test animal, particularly to the lungs (ref. 12).

Sumi and Tsuchiya (ref. 58) measured the toxic gases produced from the combustion of untreated polystyrene and evaluated the toxic hazard created by the combustion products. They found that the maximum toxicity index obtained (see ref. 59 for details of their proposed maximum toxicity index) was of the same order of magnitude as from wood on a weight-for-weight basis. Carbon monoxide, rather than styrene gas, was the main toxic product.

Hoffman and Oettel in their studies (refs. 60 and 61) show the thermal degradation products of cellular polystyrene to be decidedly less toxic than the gases from wood and other conventional building materials. The only toxic components of the fire off-gases, primarily CO, were not fatal until the styrofoam burned, and even then death was solely due to CO.

MacFarland and Leong (ref. 62) exposed rats to a single 60-minute inhalation exposure to both the pyrolysis and combustion products of polyurethane foam and a nylon fabric coated with polyurethane. The pyrolysis products of each material proved to be of about equal toxicity and much more toxic than the combustion products. They calculated that the LD-50 for the pyrolysis products was about 2000 gram-minute per cubic meter of air. The sample weight had a marked influence on the survival time of the animals. No deaths were observed when rats were exposed to similar doses of the combustion products of the two plastics. The authors estimated that gases emitted from the pyrolysis of 0.45 kilogram (1 lb) of polyurethane foam distributed in 7.1 cubic meters (250 ft^3) of air would be likely to prove lethal after 30 minutes of exposure without an appreciable air change. This hazard is not greatly different from that of PVC. It may be that pyrolysis products were more toxic since under combustion conditions such toxic products as isocyanates dissociate to less toxic products. Histological studies of the lung tissue of the rats killed indicated that death was due to acute asphyxia from occlusion of the upper respiratory tract in the case of pyrolysis of the polyurethane foam; death in the case of pyrolysis of the polyurethane-coated nylon resulted from pulmonary edema (refs. 25, 27, 62, and 63).

Barrell (ref. 64) on the other hand, reports that in large-scale fire tests involving

polyurethane, a distinguishing characteristic was the production of HCN and isocyanates in quantities fully comparable in toxicity to the CO. The British Fire Research Station burned bulk quantities of polyurethane foam in air. Large quantities of thick smoke at least twice as dense as that from wood were generated. Also much larger quantities of CO were formed than from a wood fire. Even with good natural circulation of air the oxygen concentration fell very rapidly to a level well below that needed to support life.

Kishitani (ref. 44) conducted animal tests in which mice were exposed to the gaseous combustion products of a number of materials, including urethane. Pathological examination showed that the carboxyhemoglobin content of the blood was much lower than that required to kill the animals. The deaths were probably due to the combined effect of CO and other toxic products (ref. 65).

Seader, et al. (ref. 46) studied the toxicological characteristics of uncoated and coated polyisocyanurate foams. The coatings were fluorinated copolymers and an intumescent material. Smoke generation was substantial in the coated specimens. The LD-50 values for rats, based on a 2-week survival period, were about 71 grams per cubic meter (2 g/ft^3) for all materials. Autopsy findings indicated the absence of any significant cause of death except CO poisoning. Considering the incidence of paralysis, etched eyes, and so forth, LD-50 values are probably not the only standard by which the harmful effects of these materials should be judged. Obvious loss of physical coordination was noted early in the exposures (ref. 12).

Zapp (ref. 66) compared the effects of polyurethane foam with those of neoprene and PVC foams when they are heated in air to 560° C. Test rats were exposed to the gases emitted. He concluded that all the toxic foams tested yield toxic products if the temperature is sufficiently high and that the polyurethane foam plastics are not more hazardous than other foam plastics in common use.

Sumi and Tsuchiya (ref. 65) burned five nitrogen-containing polymers at 800° C and measured the amounts of HCN, CO, and CO$_2$ produced. The harmful effects of these products were then evaluated. The experimental data were translated into concentration of gas for 1 gram of specimen burned in 1 cubic meter of volume. Toxicity index values were as follows: acrylic fiber, 1.21; nylon-6, 0.52; wool, 0.38; urea-formaldehyde, 0.27; and rigid urethane foam, 0.10.

Cornish and Abar (ref. 63) studied the toxicity of the pyrolysis products of PVC on rats. They heated PVC in air to 600° C and exposed the rats to this air diluted to twice its volume with additional air. The major cause of death was CO, and there was little evidence of lung damage. In additional tests, when enough oxygen was added to the stream of off-gases to prevent death from CO, pulmonary edema and interstitial hemorrhage developed. Those PVC formulations that contained additives and inert materials were generally less toxic per gram of sample pyrolysed. Ives, et al., of the National Bureau of Standards (NBS) (ref. 23) in their study of toxic atmospheres asso-

ciated with real fire situations concluded that the HCl emitted from PVC in fires is probably not a serious threat to life unless one is unable to move from its area of generation. The sharp odor and physically unbearable nature of a lethal concentration serve to warn of its presence.

Coleman, et al. (ref. 48) heated polytetrafluoroethylene (PTFE) in air at temperatures varying from 500° to 700° C. At temperatures to 650° C the predominant decomposition product was COF_2. Above 650° C the major products were CF_4 and CO_2; other fluorocarbons were present in lesser amounts but did not enhance the toxicity of the off-gases. When PTFE was heated in the presence of silicon dioxide, silicon tetrafluoride was also detected. Evidence indicated that the COF_2 could chemically enter into reaction to form CO_2 and CF_4. Experimental exposure of rats showed COF_2 to be the most toxic component of the gases emitted. Four samples of PTFE from four major manufacturers were investigated, and no major differences in products were observed.

In a separate paper, Coleman, et al. (ref. 36) showed that the particulate products from the pyrolysis of PTFE in air are not particles of PTFE but are composed of a complex mixture of fluorinated acids and olefins. The particles are of respirable size. The yield of particles proved to be a function of the humidity of the pyrolysis chamber. Thus, the composition of the mixtures of compounds in the particles may change with changes in the pyrolysis atmosphere.

Scheel, et al. (ref. 67) investigated the toxicity of the pyrolysis products of PTFE at 550° C by exposure of test animals. Carbonyl fluoride was identified as the principal toxic component. One-hour exposures of rats showed a 24-hour LD-50 of 370 ppm for the other pyrolysis products and 360 ppm for the COF_2. Pathology studies revealed changes in the lungs and livers of exposed animals. Irritation of the lungs persisted for some days following exposure.

Waritz and Kwon (ref. 68) conducted experiments on the pyrolysis products of Teflon at temperatures below 500° C. They were also interested in the possible toxic effects of particulates. Their results further supported the conclusion that particulate matter from Teflon thermal degradation contains toxic constituents that are lethal to animals by inhalation and that the quantity and nature of the pyrolysis products of Teflon depends on degradation temperature. They reported no adverse effects on rats exposed to the products emitted at temperatures to 400° C. However, pyrolysis at 450° C produced acute pulmonary hemorrhage and edema.

Treon, et al. (ref. 69) found that the larger the quantity of Teflon heated and the higher the temperature, the more lethal the gaseous emissions. Fumes from Teflon heated to 500° C appeared to be equally as toxic as those formed at 800° C, but those formed at less than 400° C were much less toxic. No deaths occurred among animals exposed to fumes of Teflon heated to 300° C.

The toxicity of the pyrolysis products of polychlorotrifluoroethylene (CTFE) was studied by Birnbaum, et al. (ref. 35). The concentration of gases to which rats were exposed was controlled by the rate of pyrolysis. The higher the temperature, the smaller the quantity of plastic required to be lethal. The greater toxicity was not accompanied by an increase in hydrolyzable fluoride. It appears that the toxicity may be associated with the particulate products of pyrolysis.

Scheel, et al. (ref. 47) performed toxicity studies on five polychlorotrifluoroethylene-ethylene copolymer samples (Halar resin). Thermal degradation began at 350° C and was complete at 600° C. The principal gaseous products formed at 600° C in air were HF, CO_2, CO, HCl, and CH_2O. Fatalities could be correlated only with the HF concentration. The toxic effects were characterized by primary irritation of the respiratory tract, pulmonary edema, and hemorrhage.

Smith and Kuchta (ref. 70) studied toxic gases produced by burning elastic conveyor belts composed of neoprene, PVC, styrene butadiene, rubber, and other fire-resistant materials. Generally, the CO level was noticeably higher than the NO_2 and HCl levels. No phosgene was detected. They concluded that in assessing the toxicity hazard from the combustion of fire-resistant materials it is necessary to consider the concentration and relative toxicity of the fire products, the exposure times to the products, the combustible loading conditions, and such environmental conditions as air ventilation rates.

Honma and Kawasaki (ref. 71) analyzed some of the gasous pyrolyzates evolving from the thermal degradation of an epoxy polysulfide polymer – primarily EPON 828. They assessed the toxicity hazard posed by these products. Many gases were evolved and 21 components were separated by gas chromatography; 13 were positively identified, including CO_2, CO, carbonyl sulfide, H_2S, SO_2, and methyl mercaptan. For H_2S, a toxic situation developed at temperatures above 250° C; for CO_2, air dilution was necessary only at 450° C and above to keep it below human toxicity tolerance levels; for SO_2, the toxic hazard developed in the 350° to 450° C range.

Studies were conducted for NASA (ref. 72) to determine the relative toxicity of pyrolysis products from selected spacecraft materials. Animal deaths occurred hours or even days after exposure, suggesting that neither CO nor HCN was likely to have been the sole cause of death since they exert their lethal action quite rapidly. Ten materials were studied, including Fluorel, Nomex, Kevlar-29, asbestos foam, Viton, and urethane foam. The LD-50's ranged from 1 gram for urethane to 7.3 grams for Nomex.

Hofmann and Sand (ref. 37) studied the toxicity of decomposition products under smoldering conditions for PVC, polyethylene, and polyurethane. Mortality rates of rats exposed to the off-gases of these plastics heated to a range of 300° to 600° C were noted. They found that PVC and polyethylene degradation products are not more toxic

than wood products under smoldering conditions. However, off-gases from unsaturated polyester resins containing halogen-based flame retardants can be more hazardous than wood off-gases, and expanded polyurethane products have varying toxicity. The authors concluded that PVC, polyethylene, and polyurethane do not present any greater toxicological hazard than conventional organic materials such as wood, felt, and leather under smoldering fire conditions.

For the purpose of evaluating and comparing the potential danger from toxic gases produced by the combustion of material, Tsuchiya and Sumi (ref. 59) proposed a "maximum toxicity index." Their index is calculated from data on the quantity of toxic combustion products and the lethal concentration of these products.

Epstein and Heicklen (ref. 74) also proposed a thermal-decomposition toxicity index. This index includes the rate and temperature of degradation and the quantity and toxicity of the degradation products. By using this index they rated the following polymeric materials in the order of increasing toxicity when heated from 260° to 370° C: carboxy nitroso rubber, perfluoropropylene, Viton, Kapton polyimide film, Teflon FEP, and Teflon TFE.

Laboratory (In-Vitro) Emission Studies

A representative sampling is given here of publications dealing with the study of the toxicity of pyrolysis and combustion products of various types of polymers without animal exposures. Some of the studies looked at the effects of additives on the emission gases.

It must be recognized that the various laboratory test conditions and procedures vary widely and that the data frequently cannot be directly compared. Nor is a classification of the comparative hazard of gases and vapors derived from the various materials always possible. In fires, every conceivable condition is possible, ranging from complete to partial combustion or smoldering and destructive pyrolysis. Hence, it can be readily appreciated that the wide variety of test conditions and of plastics and their additives can bring about an extensive series of noxious and toxic byproducts of varying concentrations.

Coleman (ref. 33) reviewed the published results of toxic-combustion-product studies of many different materials. He concluded that in the majority of fires, the toxic product of principal concern is CO. Although other more-toxic gases may also be present, he felt the volume of CO would be so much greater that it would constitute the major hazard.

Grimaldi (ref. 30) in a discussion of the toxicity of the thermal degradation and

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combustion products of some plastics states that the burning process takes place in three stages:

(1) Destructive distillation of the material occurs, which produces gases whose nature depends on the composition of the plastic.

(2) Oxygen unites with free carbon to form CO and a dense smoke usually forms – if sufficient oxygen is present – combining with the flammable gases produced in the first stage.

(3) Carbon monoxide burns to CO_2 if sufficient oxygen is present to combine with all combustible materials.

Woolley, et al. (ref. 9) studied the products from the thermal and thermal-oxidative decomposition of PVC from $300°$ to $500°$ C by gas chromatography and mass spectrometry. Approximately 75 off-gas products were detected up to naphthalene. These products are generated mainly during dehydrochlorination. The products are modified slightly by the presence of oxygen, but no oxygenated organic materials (e.g., phosgene and CH_2O) were detected. The products, except for CO. were shown to have little toxicity when compared with HCl. At these temperatures the dehydrochlorination of PVC is a rapid and almost quantitative process in air and in nitrogen. The formation of the minor products is temperature dependent, and a marked increase in production takes place at about $425°$ C and above. The exception is benzene, which shows little temperature dependence at these temperatures. If synergistic effects are neglected, the minor products make little or no contribution to the overall toxicity of the decomposition products based on the toxicity of HCl.

Woolley (ref. 75), in studying the production of toxic gases when PVC and flexible polyurethane foam are heated, found that PVC would release HCl at temperatures as low as $190°$ C and that at $300°$ C the dehydrochlorination was rapid and quantitative. Woolley also conducted decomposition studies (ref. 76) of PVC in air to specifically monitor the production of phosgene. Phosgene was not detected.

Cornish and Abar (ref. 63) investigated seven PVC materials for their thermal degradation products. In completely pyrolyzing varying sample weights they were able to approximate an LD-50 expressed as the original weight of the specimen.

Tsuchiya and Sumi (ref. 77) proposed a method for evaluating the off-gas product hazards of pyrolyzing plastics analyzed by gas chromatography. The toxicity was presumed to be proportional to the concentration and relative toxicity of the specific gases. In evaluating PVC, HCl was found to be the main toxic degradation product. The total toxicity of the products of PVC was little changed in either the presence of air or an inert atmosphere at temperatures between $350°$ and $850°$ C. The authors suggested that oxidation is not important in the formation of products other than CO, CO_2, and H_2O. Almost all the chlorine in the PVC was converted to HCl. Neither chlorine nor phosgene was detected. Benzene was found, as well as CO and CO_2. The authors stated

that they realize the limitations of their method of evaluating toxicity, which are as follows: toxicities are not necessarily additive; the mechanics of the toxicity of HCl and CO are quite different; synergistic effects were neglected in this study because the present state of knowledge precludes consideration in a simple formula.

In two studies (refs. 78 and 79) Boettner, et al., heated standard commercial PVC materials under varying conditions of air supply, temperature, and heating rate. They identified about 50 gaseous products of combustion, including CO, CO_2, HCl, benzene, methyl chloride, vinyl chloride, olefins, aromatics, and alkanes. The amount of HCl emitted was little affected by air supply or heating rate and began to evolve between 250° and 280° C. It may be markedly reduced by inorganic components used in product formulation. Higher heating rates produced less CO and more of the hydrocarbons, especially benzene and the olefins. Benzene was the most abundant hydrocarbon and was produced at 250° to 280° C, with little production above 350° C. No phosgene was detected. Volatile combustion products accounted for 100 percent of the original specimen mass with no residue.

Coleman and Thomas (ref. 38) studied the products liberated when chlorinated plastics are burned in air. The plastics included PVC, chlorinated polymethyl methacrylate, and vinyl chloride/vinylidene chloride copolymer. In most instances the amount of HCl released was about proportional to the chloride content of the sample and corresponded to 30 percent of the total chlorine present at the comparatively low temperature of 300° C. Traces of phosgene were also evolved in some instances.

Woolley, et al. (ref. 80) studied the thermal degradation products of a polyester and a polyester urethane flexible foam in a nitrogen atmosphere. The decomposition behavior of the two foams was similar. At 200° to 300° C there was a rapid and complete loss of the toluene diisocyanate of each foam as a yellow volatile smoke. This smoke contained all the nitrogen of the original foams. The smoke was stable up to 750° C. The nitrogen-containing products of low molecular weight such as HCN, acetonitrile, acrylonitrile, pyridine, and benzonitrile observed during the high-temperature (500° C) degradation of the foams were derived from the decomposition of the yellow smoke. At 900° C, HCN and benzonitrile predominated; and at 1000° C, HCN was the only product, where about 70 percent of the available nitrogen had been recovered as HCN. In a similar study (ref. 75) Woolley determined that during the early stage of a fire involving polyurethane foam, the toxic hazard from HCN approached the toxic hazard of CO.

Napier and Wong (ref. 81) heated polyurethane foams to temperatures of 220° to 400° C in nitrogen, in 6 percent oxygen in nitrogen, and in air in order to determine under what conditions flame retardants or compounds derived from such additives are released. Some of the anticipated toxic gases were detected. Then when phosphorus inhibitors were added, phosphorus compounds were evolved under most conditions.

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Other products detected were HCN, isocyanate, urea, halogenated compounds, and alkenes. The three main routes for thermal degradation of urethane proposed by the authors were (1) dissociation of alcohol and isocyanate; (2) formation of a primary amine, alkene, and CO_2; and (3) formation of a secondary amine and CO_2. In the presence of oxygen the array of products is considerably increased.

Backus, et al. (ref. 82) state that with sufficient oxygen the urethanes do not dissociate to isocyanate but oxidize to less toxic amines, olefins, and CO_2.

Barrell (ref. 64) in his study of the fire behavior of flame-retarding foams found that, although such foams were more difficult to ignite, once ignited some of them burned even more rapidly than untreated foams. In every case the treated foams produced a more dense smoke and at least as much CO and HCN as the untreated foams.

Wagner, in studying a wide range of plastics pyrolysis conditions (ref. 27), found that for Teflon heated in air to 550° C, COF_2 was the dominant off-gas product. Above 650° C the major products were CO_2 and CF_4. Wagner, in agreement with Coleman's study cited previously (ref. 48) found that the presence of SiO_2 led to an increase in the product toxicity through the formation of SiF_4. The hydrolysis of the SiF_4 to HF could also enhance the toxicity.

One of the most common char-forming polymers is phenol-formaldehyde (e.g., Bakelite plastic resins and compounds). Studies by Woolley and Wadley (refs. 83 and 84) define some decomposition products. The conclusions resulting from this study were (1) the toxic hazards resulting from decomposition of phenol-formaldehyde laminates under the worst conditions of 460° C in an inert atmosphere could approach those of HCl from PVC; (2) three trial, large-scale fires produced much lower phenolic concentrations than expected. In the second part of this study (ref. 84) oxidative decomposition between 200° and 500° C was performed. Formaldehyde was detected between 400° and 500° C at much higher concentrations than in the inert atmosphere, but the toxic level was still smaller than that of CO and the phenolic products.

Cotter and Dine-Hart (ref. 85) studied the thermal degradation of aromatic imides and found that typically, when polyimides are pyrolyzed at 540° to 660° C, the gaseous products are predominantly CO_2 and CO with a small amount of methane at a 49:47:4 mole percent ratio.

Johnston and Gaulin (ref. 86) in decomposing a cured polyimide resin (Skybond 700) in vacuum found that the decomposition products were H_2, CO, CO_2, HCN, water, and minor quantities of benzonitrile, benzene, methane, and NH_3. At 500° to 700° C, CO_2 became a major product; and at 500° to 605° C, CO was also a major product.

Thrune (ref. 87) burned five formulations of halogenated epoxy resins to determine if any unusual or highly toxic gases were emitted. The concern was that a smoldering fire reignited many times by a recurring source of ignition might supply gases that would be more hazardous than the normal fire off-gases. Phosgene and phosgene-like

gases were not found. The free halogens and hydrogen halides were predominant and were considered or greatest importance relative to health and safety. The other halogenated organic gases that were detected were present at such a low level that they are not considered as important hazards.

Paciorek, et al. (ref. 88) performed oxidative studies of four representative plastics: PVC-nylon, neoprene, polyurethane, and fiberglass. The fiberglass composite was included to illustrate the unexpected toxic product formation (in this case CO) from what might appear to be a "safe" material. In burning the PVC and neoprene compositions, smoke was associated with HCl evolution. At the higher temperature, HCl was evolved at a faster rate. When the material was depleted of HCl, the specimen glowed and the relative concentration of CO significantly increased. In the case of neoprene, SO_2 was produced in sufficiently high concentration to be detected in highly diluted samples, but compared with HCl and CO, the SO_2 was not a major toxic hazard, although it was definitely a contributing factor. Other toxic sulfur-containing constituents also were detected, such as carbon disulfide, carbonyl sulfide, and H_2S. The sum of all sulfur-containing species in the decomposition products may represent a considerable danger in the case of highly cured compositions since the threshold limit values are very low for some of these and the effects are at least additive, if not synergistic. Four different polyurethane foam specimens were investigated. Fluorocarbon-11 was the blowing agent and was found in the off-gases. It is also a potential phosgene precursor. Dichloroethylene and HCl were unexpected constituents of the off-gases in significant quantities.

The Kelly Air Force Base Environmental Health Laboratory (ref. 5) analyzed some of the thermal degradation products of five types of commercially available carpet:

(1) Nylon-II pile (40 percent) with PVC (plasticized with dioctyl phthalate) backing (60 percent)

(2) Acrilan pile (42 percent) with jute/polypropylene backing (58 percent)

(3) Nylon-66 pile (35 percent) with jute/paper backing (65 percent)

(4) Wool pile (48 percent) with cotton fiber backing (52 percent)

(5) Nylon-6 pile (25 percent) with foam rubber (polyisoprene) backing (75 percent)

All data reported in table II are calculated on the basis of the levels of gases that would be attained if 0.0929 square meter (1 ft^2) of carpet were thermally decomposed in 1 cubic meter volume of air.

Burland and Parsons (ref. 89) pyrolyzed polyacrylonitrile of 130 000 molecular weight under nitrogen between 200° and 320° C. The predominant gaseous products were HCN and NH_3. At 270° C after 300 minutes of heating, 10 percent of the available nitrogen had been lost. Below 210° C, only NH_3 was detected. The rates of emission were not significantly different when the plastic was heated in air.

TABLE II. - DECOMPOSITION PRODUCTS OF CARPET MATERIAL

$[0.0929 \text{ m}^3 \text{ (1 ft}^3\text{) per m}^3 \text{ of air.}]$

Carpet/backing	Oxygen content, percent	Carbon dioxide content, percent	Carbon monoxide content, ppm	Hydro-carbon content, ppm	Formaldehyde content, ppm	Condensable content, mg	Hydrochloride content, mg
Nylon/PVC	11.8	7.4	17 500	9 380	167	60 941	31 513
Acrilan/jute	15.4	3.7	3 400	1 200	93	54 723	593
Nylon-66/jute paper	16.8	3.1	12 400	20 400	197	52 267	------
Wool/cotton[a]	15.9	3.6	7 080	14 900	186	70 909	1 038
Nylon/rubber	16.4	4.0	2 800	15 500	154	159 866	------

[a]Other decomposition products of wool/cotton, NH_3, 1136 ppm; COS, 500 ppm.

Four neoprene compositions were subjected to thermal-oxidative degradation by Paciorek, et al. (ref. 90). Under static environmental conditions of no airflow, oxidation was low with as much as 84 percent of the chlorine content evolving as HCl and the sulfur released largely as carbon disulfide. Under flowing-air conditions and higher temperatures there was increased production of CO_2, carbonyl sulfide, SO_2, formic acid, and acetic acid.

The Naval Ordnance Laboratory (ref. 91) in studying the rate and mechanism of polybenzyl pyrolysis found that the gaseous degradation products constituted 4 percent of the total mass and were a mixture of benzene, toluene, and xylene. The toluene content predominated, being four times that of benzene.

Gross, et al. (ref. 32) measured the smoke and gases produced by burning 141 different aircraft interior materials. These materials included a large variety of synthetics. A 7.6-cm by 7.6-cm (3-in. by 3-in.) sample of each material was thermally irradiated in an 1.67-cubic-meter (18-ft^3) chamber such that both smoldering and flaming conditions were observed. Gas analyses were made with commercial colorimetric detector tubes for CO, HCN, HCl, HF, SO_2, NO, NO_2, NH_3, Cl_2, and $COCl_2$. Carbon monoxide was produced in almost every case.

In a study of incinerator burning of plastics, Boettner, et al. (ref. 78) analyzed the combustion products of 19 polymers heated in air or in oxygen-enriched air. One- to 3-gram samples were heated at a controlled rate of 5° to 50° C per minute. In addition to CO_2 and water, straight-chain saturated and unsaturated hydrocarbons through hexane, aromatic hydrocarbons, HCl, SO_2, cyanides, NH_3, and NO_x were identified. A significant health hazard in open burning or accidental fire can occur, according to the authors. Generally, the more incomplete the combustion, the more NH_3 and cyanide will form.

STANDARDS FOR ANALYZING RESULTS

It is essential that a standardized test method be developed for studying the toxicity of thermal degradation products. Such a test method for specific gases must be capable of assessing the effects of combinations of gases, since there may be additive, synergistic, or antagonistic effects that make a mixture more or less toxic than any single gas. If sufficient research is done to establish a base upon which a formula could be developed for quantifying those effects, a simplified, standardized animal test might provide a more suitable answer to the problem. In such a test a given material could be pyrolyzed under standardized conditions, the gases condensed by cooling and filtered to remove particulate matter, and the residual used to expose a specified number and type of test animals (ref. 29).

It is of course well understood that laboratory conditions generally will not reflect all the possible fire conditions. The tests must be practical and must answer initially the immediate questions as to the life and death risks when a material is heated and burned. Information by which the hazard of smoke and toxic gases can be defined is of utmost importance. Without such toxicity data we cannot be sure how to use the results of tests, regardless of their reproducibility.

Several years ago, MacFarland (ref. 16) described the dilemma toxocologists face in attempting to define the toxicity of pyrolysis products of plastics. Determining the biological response of an animal to exposure to toxic substances is rather straightforward. The more difficult part of the dose-response situation is the definition of the dose. Without a knowledge of this, results are a mere qualitative description of biological changes. An adequate statement of dose is difficult with inhaled agents, but not impossible. The value of concentration times the time of exposure is not a statement of true dose but more properly a measure of the magnitude of exposure. More difficult is the determination of the concentration over the period of exposure, the particle size distribution, the particle shape, the surface characteristics, the physical state of the pyrolysis products, the physical and chemical changes continuing to occur in the products, the effects of dilution and cooling, and so forth. MacFarland suggests the method of simply stating the weight of plastic decomposed along with all the relevant circumstances surrounding the conditions of pyrolysis. The biological results are then related to the exposure to the degradation products yielded by a known weight of plastic under specific conditions. Some studies by MacFarland and by Leony (refs. 57 and 62) exemplify this technique. With the complexity of such studies, it is thus mandatory to provide some type of description of exposure conditions if the investigation purports to be a dose-response study.

This concept is reiterated by Nunez, et al. (ref. 45), who also affirm the urgent need to develop testing systems that can be used to rate the toxic liability of burning

plastics. They feel that the simplest approach would be to define lethal effects in terms of the original weight of the sample heated. Two separate heating tests are proposed: with and without the introduction of flame. Exact procedures should be clearly defined to ensure standardized testing. The procedures and equipment should be kept simple yet sufficiently sensitive to differentiate hazardous materials from those considered safe for intended use. Establishing these tests will provide a sound basis for working toward more meaningful toxicity tests that may have a closer relation to actual fire conditions.

Fire conditions vary widely, and there is no widely accepted norm that will permit sufficient uniformity in experimental work to assure the correlation of test results. Controlled room-burning tests probably most closely approach the real fire situation when used in conjunction with appropriate laboratory analytical techniques and animal effect tests.

NEED FOR TOXICOLOGY RESEARCH

The effects of the thermal degradation of polymers on man probably date back to the first wood fire used for heating, when the obvious benefits overshadowed the potential harm. The knowledge of the toxicology of thermal degradation developed slowly, but recent years have seen an increasing awareness of the need for research support, generation of valid data, and a meaningful estimate of toxicity (ref. 17). As early as 1940 the NEPA, in the Fire Gas Research Report (ref. 18) recognized that there has been a long-felt need for more exact technical information on fire off-gases, the condition of their formation in fires, their effects singly and in combination, and the most effective means for minimizing their hazard to life. In recognition of this need the NFPA initiated a project for research on fire off-gases. This project was interrupted by World War II.

Research on the toxicity aspects of pyrolysis products of man-made materials has lagged far behind the abilities to produce nearly unlimited polymer structures. Thus, even a fair assessment of the toxic hazards cannot be adequately made at this time except in great generalities. Within the coming decade, newer polymer materials will be increasingly used and will intensify the need for toxicological data when these materials are involved in fire situations (refs. 1 and 30).

The data accumulated to date relative to the composition and concentration of combustion and pyrolysis off-gases often have limited value because of (1) the lack of detailed information on testing, sampling, and analytical procedures and on the exact nature and condition of the test specimen; (2) the lack of information on the chronological history of the emission of each gaseous component; (3) the possibility of the synergistic

or antagonistic effect of two or more of the gases present; and (4) the lack of knowledge on how ambient temperature influences the physiological effect of the off-gases.

The toxicology of polymer combustion products is extremely complex. Boettner, et al. (ref. 30) in studying the volatile combustion products of PVC, for example, were able to detect 50 compounds. It is understandable that it becomes nearly impossible in a real fire situation to determine which agents may be responsible for hazards or deaths. At the present time, the method of hazard evaluation is often that the gases formed are analytically identified and the toxicity information available in the open literature is used to evaluate the toxicity. The true toxicity situation is then presumed to be the sum, either additive or synergistic, or all the various hazards causing incapacitation or death that may be present.

Research in the area of fire toxicology and material off-gassing has been proceeding uninterruptedly since the early 1940's. Most recently this type of research has been directed to the hazards inherent in confined locations such as mines, submarines, aircraft, and spacecraft. Nevertheless, there is insufficient information available. A great deal of research must be performed to permit sound and scientific information. The immediate toxic effects leading to death as well as the more subtle toxic effects, which can alter behavior, must be known for each material. Long-term effects of sub-toxic levels must also receive attention to help reduce the environmental pollution problem and its health consequences.

One practical approach to evaluating the toxicity of a specific polymer under fire conditions includes experimental animal exposures coupled with analytical determinations of the combustion products. An understanding of the toxic mechanisms involved can then be achieved when these biological and analytical data are correlated. Experimental efforts have largely been directed toward the burning of individual materials under controlled laboratory conditions. Very little has been done to define the actual hazard involved in terms of tolerable limits for life safety under real fire situations, where a multitude of materials may be present. In addition, the concept that no single test is adequate to characterize the fire hazard of a given material has been recognized (ref. 17). Also, because of the complexity of polymer degradation, many studies have been carried out only with pure polymers at low temperature in vacuum or inert atmosphere in order to avoid the difficulties associated with additives (ref. 27).

Standardized tests that include biological evaluation of combustion products are not presently available although there are a multitude of fire tests for flammability, smoke production, ignition, heat generation, flame propagation rate, and fire endurance (ref. 14). The concern of manufacturers with the ability of their polymeric material to pass a given flame-spread test should be extended to its ability to pass a toxicity test. No such tests or standards yet exist (ref. 27). At the moment, no general guidelines can be established for such studies other than insistence that exposure conditions and

pyrolysis methods be reported in some detail so that the data can be properly evaluated (ref. 12). Finally, the attainment of low flammability and other characteristics generally requires the use of potentially toxic additives. However, the relative toxicity of the combustion products of such modified materials as compared with those that are not modified by additives has not been widely investigated. A meaningful risk analysis that balances the benefit of reduced ignition and flame hazards with the possible increase in smoke-induced toxicity cannot be conducted until such studies are completed (ref. 50).

CONCLUSIONS

This review of the literature pertaining to the toxicological characteristics of the gaseous emissions from the pyrolytic and thermal-oxidative degradation of plastics leads to the following conclusions:

1. Some of the traditionally accepted notions concerning fire hazards are not as true as commonly believed. Consider the following facts that contradict traditional conceptions:

a. The heat developed in fires in enclosed areas is usually of secondary importance as a hazard to life. The development of combustion gases is of primary importance because of the more rapid spread of the gases. Many fire casualties suffer or die from exposure to gaseous combustion products rather than from heat.

b. Generally, humans can survive with less oxygen than that required by a fire to sustain itself, and therefore the development of toxic gases is of greater hazard significance than oxygen deficiency. However, an important toxicological effect of oxygen deficiency in the fire situation is the resultant incomplete combustion and accelerated production of dangerous gases. The pyrolysis products produced by heat in the absence of oxygen (i.e., air) differ from the combustion products emitted from a fire with oxygen.

c. A clean-burning, hot fire may be safer from a toxicity standpoint than a cooler, smoldering fire. The effect of elevated temperatures on the toxicity of combustion gases is not completely established. However, generally the more complete the combustion the less toxic are the gaseous products.

d. Although plastics emit toxic gases when involved in a fire situation, so do the common nonplastic materials such as wood. Wood is generally no safer than synthetic products when involved in a fire. Apart from extra smoke in some plastic fire cases, the total hazard is usually comparable.

e. The significant hazard of smoke is in obscuring vision. Secondary smoke hazards are induced panic and the physiological effect of smoke particles that may be swallowed or inhaled. The generation of toxic gases generally precedes that of smoke,

and considerable toxic effects can occur before smoke becomes sufficiently dense to obscure vision. The role of smoke in inducing panic and its physiological effect on motor coordination and sound judgment have not been studied sufficiently. Some of the authors believe smoke may indeed play a very serious role, but not necessarily toxicologically.

f. Little is known about the time in the fire sequence at which various gases develop. Even where we know such toxic gases as nitrogen dioxide, hydrogen cyanide, and hydrogen chloride are present, we do not know if these developed to lethal levels before or after the carbon monoxide levels, the oxygen deficiency, or the heat reached the danger point.

g. The incidence of paralysis, etched eyes, loss of coordination, and other physiological effects in animal exposure experiments shows that LD-50 values (lethal dose for 50 percent of test animal population) should not be the only criterion considered in fire toxicology studies.

2. In real fire situations - with some exceptions - the principal toxic combustion product will be carbon monoxide (CO). Other more lethal gases may also be present but generally in lesser volumes or concentrations. However, these gases may be more toxic than CO in lower concentrations. Carbon monoxide poisoning is the most commonly listed cause of fire deaths where severe external burns are not present. Usually, where there were clear indications of CO poisoning in the autopsy, determination of the presence of other toxic gases has not been made. There is no agreement in the literature to the effect that CO is the sole cause of incapacitation and death in toxic fire exposures. Many authors believe that other toxic gases either alone or in concert with CO, heat, and oxygen deficiency generate a life-hazard environment. The data produced to date are far from complete and conclusive. The toxicity of gases and smoke produced by polyvinyl chloride and polyurethane foams, for example, under most fire conditions and particularly in smoldering fires, appears to be due to constituents other than CO. Interrelations between CO, carbon dioxide, oxygen deficiency, and other gases, plus the possible existence of undetermined synergisms and antagonisms point to the difficulty of isolating any one gas as the primary hazard.

3. The interaction of two or more plastics in close proximity in the fire situation may produce an emission profile quite different than that predicted from the behavior of the same plastics independently subjected to the same conditions. The composition and concentration of the gases is not always simply additive. The effect may be greater than additive (chemical synergism) or less than additive (chemical antagonism).

4. Similarly, the relatively few available studies show that combinations of toxic off-gases do not physiologically act on the fire victim in a simple additive manner. Here again, synergism and antagonism phenomena are encountered, making physiological effects difficult indeed to predict.

5. Laboratory toxicology studies of the effects of fire off-gases on animals are often of limited value because detailed information is lacking on testing, sampling, and analytical procedures; the condition of the test specimens; and the chronological history of each gaseous component.

6. Information on the off-gases of plastics containing additives and the effects of these additives on the thermal degradation products' toxicity is scanty and not well documented. The additives may result in the evolution of a different and more toxic type of emission profile.

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RECOMMENDATIONS AND RESEARCH NEEDS

1. There are needs for increased long-term study programs, both fundamental and applied, in many aspects of the pyrolysis/combustion of plastics. A few of these are as follows:

a. An area that has received very limited attention is the toxicology of additives. Because of the complexity of polymer degradation, pure polymers tend to be used in tests to avoid the difficulties associated with additives. Additional information must be developed on the degradation products associated with the use of additives and the effects of these additives on the toxicity of the off-gases.

b. There is support in the open literature for the contention that carbon monoxide is produced at such a rate in fires involving plastics that the presence of other toxic gases becomes academic – that they do not in themselves present a life hazard. There is also support to the contrary – that the other toxic gases either alone or in concert with carbon monoxide, heat, and oxygen deficiency generate a life-hazard environment. The data produced to date are far from complete or conclusive. Further research is needed to define and resolve the question.

c. Several studies show that small amounts of gases such as hydrogen chloride, nitrogen dioxide, hydrogen cyanide, and sulfur dioxide, when combined with toxic atmospheres containing carbon monoxide, carbon dioxide, and low oxygen concentrations, produce synergistic or antagonistic toxic effects. More work is needed to better define the physiological response to the many combinations that are likely to occur in a fire situation. Studies should also include the effects of smoke and the order of magnitude of the various relations.

d. A method of correlating small-scale laboratory results to some degree with full-scale real fire situations with a reasonable degree of certainty is needed.

e. Further studies of physiological response to fire situations are needed in such areas as identification of the relative effect of heated versus cool toxic gases, determination of reaction under both calm and emotionally excited conditions, and the

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physiological effects of smoke particles. Establishment of human tolerance limits to toxic gases for evacuation periods within a range of 1 to 5 minutes is needed.

2. Several areas in the study of the toxicity of burning plastics require standardization:

a. Although a multitude of fire tests exist for flammability, smoke production, heat generation, and so forth, none exists for biological evaluation of combustion products. Toxicity tests that can be applied in evaluating the safety of specific plastic formulations are needed. At the moment, no general guidelines have been established for such studies other than insistence that exposure conditions and methods of testing be reported in detail so that the data can be properly evaluated.

b. There is a substantial quantity of experimental data available pertinent to such toxicity studies. However, much of these data are of limited value because of variations in test methods and procedures. Criteria are needed that would serve as guides to the conduct of future experiments. There must be a degree of standardization of methods so that results obtained at different laboratories can be compared.

c. In affirming the need to develop testing systems that can be used to rate the toxic liability of burning plastics, some authors feel the simplest approach would be to define lethal effects in terms of the original weight of the sample tested. Two separate tests are proposed: heating with and without introduction of flame. Exact procedures should be clearly defined to ensure standardized testing. The biological results would then be related to the products yielded by the known weight of plastic under the specified conditions.

d. There is a need for improved and standardized methods for determining toxic gas concentrations generated by burning plastics.

3. Further study is required to establish and define the hazards from thermal degradation of plastics. This can be accomplished by

a. More thorough autopsy studies of fire victims to determine the cause of death

b. Continuing use of analytical techniques in conjunction with animal toxicity tests to define the degree of toxicity of the combustion products of specific fire situations

4. In describing fire casualties, the term "overcome by smoke" as generally used may cover several different causes of death or incapacitation, such as hypoxia due to oxygen deficiency or the presence of carbon monoxide, hyperventilation, or even heat exhaustion. The causes of casualties should be explicitly defined.

5. The attainment of low flammability and other desirable characteristics in plastics requires the use of potentially toxic additives. However, the relative toxicity of the combustion products of such modified materials as compared with those that are not modified by additives has not been widely investigated. A meaningful risk analysis that

balances the reduced ignition and flame hazards with the possible increase in smoke-induced toxicity cannot be conducted until such studies are made.

6. In laboratory toxicity studies, caution must be taken to give proper consideration to integrated dose when concentration varies with time; synergistic and antagonistic effects of several components; and the effects of heat, humidity, stratification, test-equipment scaling factors, absorption of gases on test-equipment surfaces, and physiological response factors.

Lewis Research Center,
    National Aeronautics and Space Administration,
        Cleveland, Ohio, July 1, 1976,
            505-08.

APPENDIX A

GLOSSARY OF TERMS

ABS	acrylonitrile-butadiene-styrene
Br_2	bromine gas
CAB	Civil Aeronautics Board
CCl_4	carbon tetrachloride
CF_4	carbon tetrafluoride
CH_2O	formaldehyde
Cl_2	chlorine gas
CO	carbon monoxide
CO_2	carbon dioxide
$COCl_2$	carbonyl chloride or phosgene
COF_2	carbonyl fluoride
CTFE	chlorotrifluoroethylene
FAA	Federal Aviation Administration
F_2	fluorine
HCl	hydrogen chloride gas
HCN	hydrogen cyanide gas
HF	hydrogen fluoride gas
H_2S	hydrogen sulfide gas
LD-50	lethal dose for 50 percent of a test animal population
NASA	National Aeronautics and Space Administration
NBS	National Bureau of Standards
NFPA	National Fire Protection Association
NH_3	ammonia gas
NO_2	nitrogen dioxide
NO_x	oxides of nitrogen not otherwise specified

O_2	oxygen
PTFE	polytetrafluoroethylene
PVC	polyvinyl chloride
SiO_2	silicon dioxide
SO_2	sulfur dioxide
TLV	threshold limit value

APPENDIX B

LIST OF PLASTICS, GASES EMITTED, AND REFERENCES

AND BIBLIOGRAPHICAL CITATIONS

Not all the many trace quantities or less-common gases are listed because of the large number involved. Where appropriate, the number of products or hydrocarbons that are not listed but are identified in the document cited in the reference or bibliography is indicated. Bibliographical citations are underlined.

Material	Gases emitted	References and bibliographical citations
Acrilan	CO, CO_2, HCN, NO_2, Br, HCl	4
Acrilan jute	CO, CO_2, CH_2O, HCl, HC's	4
Acrilic	CO, CO_2, HCN	2, 58
Acrilic carpet	7 products	4
Acrylonitrile	CO, CO_2, HCN, NO_2, HCl, NH_3, NO_x	22, 34, 60, 83
Acrylonitrile-ethyl acetate – butadiene (Barex)	CO, CO_2, cyanide, NH_3, HC's	57
Azo-bis-isobutyronitrile	HCl, methyl-succino-nitrile	83
Cellulose nitrate	CO, NO_x	12
Chlorotrifluoro-ethylene (CTFE)	COF_2, CCl_3F, $COFCl$	82
Durette	CO, HCN, Cl_2, HCl	10
Epoxy resin	17 products	4

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Material	Gases emitted	References and bibliographical citations
Epoxy-polysulfide (Epox)	CO, CO_2, COS, SO_2, H_2S, HC's	55
Florel	CO, HCN	10
Fluorinated copolymer	CO, HF, COF_2, O_2, N_2. HC's	9
Halar (CTFE/ ethylene)	CO, CO_2, HF, Fl^-, Cl^-, CH_2O	54
Isocyanurate	CCl_3F blowing agent, HC's	9
Kevlar-29	CO, CO_2, HCN, NO_x, NH_3, acetone	10
Melamine resins	CO, CO_2, HCN, NH_3	22, 34, 83
Methacrylate (chlorinated)	CO, CO_2, HCl, $COCl_3$, HC's, Cl_2, O_2	15, 22, 65
Methacrylate resin	CO, CO_2, HCl, $COCl_3$	83
Methacrylonitrile-styrene (Lopac)	CO, CO_2, cyanide, methacrylonitrile, styrene, HC's	57
Methylenedianilene	CO_2, HCl, HBr, Cl_2, Br_2, HC's, methyl chloride, methyl bromide	62
Methyl nadic anhydride	CO_2, HCl, HBr, Cl_2, Br_2, HC's (16)	62
Neoprene	CO, CO_2, NO_2, HCl, SO_2, HC's	32, 64
Neoprene compositions	CO, CO_2, HCl, CH_4, H_2S, SO_2, COS, CS_2, HC's (18)	87
Nomex (modified)	CO, CO_2, HCN, Cl_2	10
Nylon	HCN	12

Material	Gases emitted	References and bibliographical citations
Nylon-6	CO, CO_2, HCN	58
Nylon-66/jute	CO, CO_2, HCl, CH_2O, HC's	4
Phenol-formaldehyde	CO, CO_2, CH_3, NH_3, cyanide, phenol, cresol, xylenols, trimethyl phenol, formaldehyde	57, 90, 91
Phenolic resins	CO, CO_2, HCN, NH_3, 15 other products, phenol, cresols, xylenols, formaldehyde	4, 22
Phenoplastics	CO, CO_2, aldehydes, phenols	33
Piacryl	10 products	33
Polyamide	13 products	33
Polybenzimidazole	HCN	34
Polybenzyl	Benzene, toluene, xylene	89
Polycarbonate	CO, CO_2, aldehydes, etc., HC's (30)	9, 33, 39, 57
Polyester	CO, HCN, ClO_2, 29 products, CO_2, methanol, acetaldehyde, HC's	4, 33, 57
Polyester urethane flexible foam	HCN, acetonitrile, acrylonitrile, benzene, toluene, benzonitrile	61
Polyether	HCN, acetonitrile, acrylonitrile, pyridine, benzonitrile	2
Polyether urethane flexible foam	HCN, acetonitrile, acrylonitrile, benzene, toluene, benzonitrile	61
Polyethylene	CO, CO_2, CH_3, HC's (13), carbonyls	39, 57
Polyethylene/polypropylene	CO, CO_2, HC's	60

Material	Gases emitted	References and bibliographical citations
Polyimides	CO, CO_2, cyanides, HCN, NH_3, NO_x, HC's, H_2, H_2O	9, 34, 57, 71
Polyisobutylene	10 products	33
Polyphenylene	HCl	34
Polyphenylene oxide	CO, CO_2, CH_3, 19 other products, toluene, styrene, benzene	34, 57
Polypropylene	CO, CO_2, CH_3, HC's (13)	57
Polystyrene	CO, CO_2, O_2, HC's (15)	11, 31, 57, 59
Polystyrol	8 products	33
Polysulfone	CO, CO_2, SO_2, COS, styrene, HC's (23), etc.	9, 57
Polytetrafluoroethylene (PTFE)	CO_2, CF's (14), COF_2	63, 86
Polyurethane	CO, CO_2, HCN, unsaturated HC's (23), organics, aldehydes, 4-ethyl-1-phosph-2,6,7-trioxabicyclo $[2,2,2]$ octane 1-oxide, methanol, NH_3, NO_x, acetaldehyde, HCl, $CFCl_3$, $C_2H_4Cl_2$, acetonitrile, acrylonitrile, pyridine, benzonitrile, H_2O, N_2, alkene	2, 10, 12, 33, 38, 42, 51, 57, 58, 60, 64, 68, 74, 84
Polyvinoxaline	HCN	34
Polyvinyl chloride (PVC)	HCl, CO, CO_2, benzene, CH_4, 50 products, toluene, xylene, naphthalene, phosgene, HC's, vinyl chloride, acetic acid, $COCl_3$, HCN, NH_3, NO_2, H_2O, $COCl_2$, NO_x	2, 4, 7, 15, 17, 22, 32, 33, 34, 57, 60, 65, 66, 67, 73, 83

Material	Gases emitted	References and bibliographical citations
PVC–nylon	HCl, CO, CO_2, CH's	64
Silicone resin	10 products	4
Styrene–butadiene rubber	CO, HCl, NO_2	32
Teflon (PTFE)	CO_2, CF_4, COF_2, HF, SiF_4, CF's, TFE	34, 69, 80, 86
Urea-formaldehyde	CO, CO_2, HCN, CH_3, cyanide	57, 58
Vinyl foam	CO, CO_2, benzene, unsaturated HC's	2
Vinylidene	CO, CO_2, HCl, O_2	22, 83
Viton foam	CO, CO_2, HCN, organics	10

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