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Fires, toxicity, and plastics

The only uniform features in the toxicology of burning plastics are those of the toxicology of fire: heat, carbon monoxide, deficiency of oxygen, other combustion gases, and smoke. The hazard from combustion or thermal decomposition of plastics should be compared under equivalent conditions with that of wood or other appropriate materials. This comparison provides a basis for present assessment of hazard pending a more standardized evaluation anticipated in the future.

A technical feature
Gordon M. Kline, technical editor

In considering the toxicity of the combustion products of plastics, we must consider the toxicology of fire, since this is common to all fires, regardless of the material being consumed. In any real fire situation, the toxicology of fire assumes primary importance. Broadly speaking, toxicity refers to the potential for harm arising from the action of specific chemicals or other agents on living tissue.

The major causes of death or incapacitation in fires have been identified by several investigators (1-3)[1]. In a given fire, more than one or even all of these factors may be involved: 1) heat, by destruction of tissue (direct burns), or thermal shock; 2) carbon monoxide; 3) deficiency of oxygen; 4) other gases; 5) smoke; 6) panic or emotional shock (indirect). This last factor can be more serious than the actual fire, as in a recent evacuation where 31 people were injured, most of them from landing on top of one another (4). The physiologic stress of panic or shock can also aggravate any injuries from other causes. However, panic or fear is not an intrinsic part of the fire situation, thus it is not primarily involved in the toxicology of fire.

Direct burns. Heat that destroys tissue is obvious as a cause of immediate death. Burns of over 50% of the body surface are frequently fatal, especially in children and older people (5), and deep burns of only 10% of the body can be disabling (6). However, "it is generally recognized . . . that many, if not a majority, of those who succumb in building fires are not seriously burned and that death or trauma must be due to other factors" (3).

Thermal shock. Heat disseminated beyond the area of the actual flames is considered the primary cause of death in well-ventilated fires where there is a good supply of oxygen. Combustion in excess oxygen generates carbon dioxide (CO_2), water, and more heat, which in turn promotes more combustion. The amount of heat that develops during a fire is a function of the caloric or heat-yielding value of a given substance, the amount of a combustible material, and the rapidity with which the reaction takes place (3). Petroleum products, for example, have a high caloric value that can readily result in a lethal generation of heat. Wood has a relatively high level of combustion but is low in comparison with kerosene or coal.

Temperatures in ordinary building fires can quickly climb beyond the usual tolerable limit of 150 to 160° F. In a series of experimental fires started on the first floor, the heat in a second floor bedroom was intolerable within about 2 min. when the bedroom door was open and within 9 to 12 min. when the door was closed (3). In high-rise buildings, where a self-contained fire can reach massive proportions, fires have been reported to reach temperatures of 1500° F. (7). Available protective equipment is grossly inadequate under such circumstances, and heat is perhaps the most uncontrollable factor in fires today.

Carbon monoxide (CO). In poorly ventilated fires, where the supply of oxygen is not plentiful, combustion is incomplete and the end products are CO, water, and less heat. Also, other toxic gases can be formed depending on the nature of the material being burned. Of all the gases generated from natural or synthetic materials, CO produces the most deaths in real fire situations (1). CO is insidiously toxic; it is a colorless, odorless gas primarily absorbed through the respiratory tract, although absorption through uncovered skin has been demonstrated experimentally. In-

Table I: Physiological response to carbon monoxide

CO in atm., %	Response
0.01	Allowable exposure for several hours
0.04–0.05	No appreciable effect after 1 hr.
0.06–0.07	Just appreciable effect after 1 hr.
0.1–0.12	Unpleasant after 1 hr.
0.15–0.2	Dangerous when inhaled for 1 hr.
0.4	Fatal when inhaled for less than 1 hr.
1	Fatal when inhaled for 1 min.

Table II: Physiological effects of reduced atmospheric oxygen levels

O_2 in atm., %	Response
21	None
17	Impaired muscular coordination; increased respiratory rate
12	Dizziness, headache, rapid fatigue
9	Unconsciousness
6	Death in 6 to 8 min.

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1 - Numbers in parentheses designate references at end of article.

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halation of 0.1% concentrations usually produces a warning dizziness or headache, but 1% concentrations do not produce any sensory warning before escape is too late (8). The general response that can be expected from specific atmospheric levels of CO is shown in Table I (8, 9).

Physiological response is influenced by such factors as rate of breathing and individual susceptibility. The rate of breathing will obviously be increased in strenuous physical exertion. Age, health, smoking habits, and previous exposure to CO all have some influence on the total effect produced by any specific concentration of CO.

When inhaled, CO combines with the hemoglobin of the blood to form carboxyhemoglobin rather than the oxyhemoglobin which transports oxygen to the tissues. Additionally, CO may decrease oxygen delivery to the tissues and hinder removal of CO_2 from the blood stream (8).

Deficiency of oxygen (O_2). This situation occurs as a natural result of combustion. A summary of the physiologic effects that may be expected at various atmospheric O_2 levels is given in Table II. Although atmospheric O_2 concentration dips of 3% or less have been recorded in various experimental poorly-ventilated fires (8, 10), a 15% O_2 level is usually required to support combustion of most burnable materials. Thus, it is possible that man could survive where fire could not, if O_2 deficiency by itself were the only serious factor in building fires. However, in a fire situation, as the O_2 supply decreases, CO will increase and the O_2 supply in the blood can then be under a double strain. In the presence of these combined effects and heat, smoke, and other combustion gases, O_2 deficiency may produce serious and possibly irreversible effects.

Other combustion gases. CO_2 and many other organic and inorganic materials also result from fires (Table III).

Smoke. Smoke is the airborne mixture of heated gases, liquid droplets, and solid particles evolved from combustion. It includes acids, alcohols, aldehydes, and miscellaneous hydrocarbons. Smoke from wood and fat contains the irritant aldehyde acrolein. In some cases, organic acids and aldehydes that are liquid at ordinary temperatures appear to condense on the surface of the smoke particles and cause more irritation than the actual particles, which are mostly carbon. The heat in smoke, which can cause tissue injury in itself (11), may enhance the toxic effects of any of the complex products contained in smoke.

Smoke can also reduce vision and lead to panic. Smoke obscuration is a definite hazard in itself since exits cannot be located. Relative smoke obscuration time must be considered in the selection of building materials.

Plastics

Chemically, plastics consist of chain-like substances called polymers, as illustrated below:

Polyethylene	*Polystyrene*	*Cellulose (natural polymer—more than 90% of cotton, 50% of dried wood)*
$\{CH_2\text{-}CH_2\}_n$	$\{CH_2\text{-}CH\}$ with C_6H_5	$\{C_6H_{10}O_5\}_n$

where n = the number of units in the chain.

The significance of n is more easily visualized when the

Table III: Physiolog effects of combustion gases (exclusive of CO)

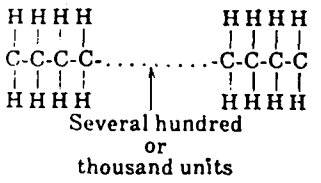
Combustion gases[a]	Highlights of toxic hazard
Carbon dioxide (CO_2)	
Produced in all fires	Toxic by itself only in high concentrations, but stimulates respiration; 3% concentration doubles lung ventilation
Nitrogen compounds	
Nitrogen dioxide (NO_2) and other oxides of nitrogen	
Produced in small quantities from fabrics and in large quantities from cellulose nitrate and Celluloid (prepared from cellulose nitrate and camphor). Decreasing use of Celluloid in consumer products today	Strong pulmonary irritant capable of causing immediate death as well as delayed injury
Ammonia (NH_3)	
Produced in combustion of wool, silk, nylon, and melamine. Concentrations generally low in ordinary building fires	'Characteristic odor and unbearable irritating effects at sublethal concentrations would probably give adequate evidence of its presence' (8)
Hydrogen cyanide (HCN)	
From combustion of various products such as wool, silk, polyacrylonitrile, nylon, polyurethane, and paper, in varying amounts	A rapidly fatal but flammable asphyxiant poison. No known toxicity in real fire situations
Halides	
Hydrogen chloride (HCl)	
From pyrolysis of some wire insulation materials such as polyvinyl chloride (PVC), also chlorinated acrylics and retardant-treated materials	Over-all, 'the HCl generated in fires is probably not a serious threat to life unless one is unable to move from the area of generation' although in one reported instance fire injuries were attributed to exposure to HCl (8)
Phosgene ($COCl_2$)	
From pyrolysis of carbon tetrachloride used as fire extinguisher and, in small amounts, from other chlorinated materials	Deaths reported in connection with fire use of carbon tetrachloride. No known effects from small amounts generated from combustion of other sources
Fluorine and bromine compounds	
From combustion of fluorinated resins or films and some fire-retardant materials	'In most cases, warning of the presence of a toxic halide would be given by the sharp odor and noticeable irritating action on the respiratory tract' (8)
Sulfur compounds	
From pyrolysis of certain high-temperature mechanical parts, rubber, wool, upholstery materials, and some natural polymers. Sulfur compounds are usually not abundant in total combustion sources present at a given site in building fires	
Sulfur dioxide (SO_2)	A strong irritant intolerable well below lethal levels
Hydrogen sulfide (H_2S)	An irritant capable of causing systemic poisoning. Flammable. Characteristic rotten-egg odor at very low concentrations, olfactory fatigue possible at higher concentrations

a—All these gases can be lethal in sufficient concentration. However, in most fire situations, combustion gases except for carbon monoxide would be expected to act as a contributory rather than a primary cause of death or incapacitation.

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chain is extended, as shown in the case of polyethylene:



Combustion of polymers causes the molecular chain to break and decompose into oxidized fragments as illustrated in Table IV. In real fire situations, the fire often includes a combination of well-ventilated and poorly-ventilated areas of different temperatures, and the combustion products vary accordingly. Although the toxicology of polymer combustion products is extremely complex, one practical approach is based on experimental animal data, which include comparable testing of natural and synthetic polymers. Data from several of these studies (12-14) are tabulated in Table V.

From a flammability standpoint, the most hazardous plastic is cellulose nitrate (15), which thermally degrades into oxides of nitrogen and carbon monoxide. In the case of Celluloid, another toxic factor may be the camphor plasticizer. Consumer use of Celluloid is generally regulated today in recognition of the fire hazard.

Analytical determinations of pyrolysis products provide another means of comparing the combustion hazards from synthetic and natural polymers. An understanding of the toxic mechanism involved can be achieved when these data are coordinated with biological data. Also, it may be possible to assess the hazard from a particular pyrolysis product in terms of both familiar and new parent polymers. Table VI lists the results obtained when 20-mg. samples of various materials were pyrolyzed in a liter flask containing air or nitrogen and the resultant products analyzed for HCN (16). The authors comment that "apparently polyurethane foam does not produce more hydrogen cyanide than do many other natural and synthetic consumer products. . .(and) that it is difficult to understand why cotton and paper produce HCN on pyrolysis unless nitrogen fixation is assumed. If this be the case, apparently some oxidation is necessary for nitrogen fixation, since less cyanide is produced in atmospheres consisting originally entirely of nitrogen."

In another investigation, experiments were conducted with the combustion products generated from the burning of various building materials and also with varying combinations of O_2, CO, and CO_2 at different temperature levels (17). When mice were exposed in this experiment, the in-

Table IV: Polymer fires

Type of fire	Combustion products
Well ventilated	Heat + carbon dioxide + water + varying complex of oxidized fragments
Poorly ventilated	**Carbon monoxide** + heat + water + varying complex of semi-oxidized fragments

Table V: Toxicity results from thermodegradation products of polymers

Part 1: Series of 15-min. exposures using 3 g. of foamed materials, 30 g. of all other materials. Pyrolysis temperatures up to 1364° F. (12).

Material	Mortality for mice[a]
Polystyrene rigid foam (A or B)	0/10
Phenolic rigid foam	0/5
Wood-wool cement board	1/5
Acrylic rigid sheet	4/5
Wood (cedar)	5/5
Fire-retardant plywood	5/5
Melamine laminate	5/5
Polyvinyl chloride rigid sheet	5/5
Polyurethane rigid foam	5/5

Part 2: Series of exposures (13):
No. 1. 6-hr. exposure, 4.7 to 5.5-g. sample.
No. 2. 6-hr. exposure, 5.7 to 6.8-g. sample.
No. 3. 10-min. exposure, 2.0-g. sample.

	Mortality for rats[a]		
	No. 1, 392° F.	No. 2, 482° F.	No. 3, 1040° F.
Polyurethane A	0/4	1/4	0/2
Polyurethane B	0/4	1/4	0/2
Polyurethane C	0/4	0/4	0/2
Neoprene	0/4	1/4	0/2
Rubber latex	0/4	4/4	0/2
Polyvinyl chloride	2/4		1/2

Part 3: Series of 30-min. exposures, 5-g. samples (14).

	Mortality for rats[a]			
	572° F.	752° F.	932° F.	1112° F.
Polystyrene A	0/12	0/12	0/18	11/12
Polystyrene B or C	0/24	0/24	25/42	24/24
4 other PS	0/48	0/48	48/48	48/48
Expanded cork	0/12	5/18	12/12	12/12
Rubber	0/12	12/12	12/12	12/12
Wool	2/12	12/12	12/12	12/12
Pine wood	3/12	12/12	12/12	12/12
Felt	6/12	12/12	12/12	12/12
Leather	12/12	12/12	17/18	11/12

Part 4: Series of 30-min. exposures, 5-g. samples (14).

	Mortality for rats[a]				
	392° F.	572° F.	752° F.	932° F.	1112° F.
Polyethylene	0/12	0/12	12/12	12/12	12/12
Fir	0/12	13/18	12/12	12/12	12/12
PVC	0/12	10/12	11/12	12/12	12/12
Celluloid	12/12	12/12	12/12	12/12	12/12

a—Mice or rats exposed to products resulting from pyrolysis temperatures indicated. Figures in table show ratio of number of mortalities to number exposed. All temperatures have been converted to °F.

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dication was an increase in over-all toxicity from the combustion products compared to the combinations of the previously studied variables (O_2, CO, CO_2, and heat). A number of qualitative and quantitative analyses were done in order to define and control exposure conditions, and selected data are shown in Table VII.

To be realistic, the toxicology of polymer combustion must be based on biological data obtained from combustion of the actual polymer. Extrapolation of data generated elsewhere may result in either an under- or overestimate of toxic potential. In a real fire situation, the toxic potential is the sum, either additive or synergistic, of all the various causes of death or incapacitation that may be present.

Thermal degradation of polymers probably dates from the first wood fire when obvious benefits overshadowed potential harm. The toxicology of thermal degradation developed slowly, but recent years, particularly the last decade, have seen an increasing awareness of the need for research support, generation of valid data, and a meaningful estimate of toxicity (18-20). The concept that no one test is adequate to characterize the fire hazard of a given material has now been recognized. Unfortunately, standardized tests that include biological evaluation of combustion products are not available at present, although a multitude of tests exist (21). Procedures and criteria have been proposed (19-21). Future work on standard tests must include evaluation, formal acceptance, and practical experience.

Table VI: Hydrogen cyanide (HCN) measured in pyrolysis products

Material	HCN, μg./g. sample	
	Air	Nitrogen
Paper	1100	182
Cotton	93; 130	85
Wool	6500	5900
Nylon	780	280
Polyurethane foam	1200	134

Table VII: Analysis of combustion products generated by burning building materials[a]

Materials	Gas component, parts/million					
	CO	CO_2	HCN	NO_2	$COCl_2$	HCl
Red oak	13,600	93,000	35	10		0
Douglas fir	9,400	56,000	30	Trace	4	0
Red oak	11,000	100,000	55	Trace	0.5	0
Douglas fir	—	9,000	1	0	0	
Douglas fir	—	—	0.5	Trace	0	
Douglas fir	1,850	20,000	5	0	0	0
Douglas fir		12,000	2	0	0	0
PVC rigid pipe	1,500					100
Vinyl asbestos tile	900	10,000	10	0	0	0

a—Materials were burned in an ASTM E-84 tunnel furnace under varying conditions of ventilation. Samples from the combustion products stream were collected and then analyzed by colorimetric tubes, or with infrared analyzers when CO or CO_2 levels were beyond the range of the available indicator tubes.

References

1) J. Autian, J. Fire and Flammability 1, 239 (July 1970).

2) I.N. Einhorn, "An overview of the flammability characteristics of materials," 1971 Polymers and Materials Conference Series, College of Engr., Univ. of Utah, Salt Lake City.

3) F.W. Bieberdorf and C.H. Yuill, "An investigation of the hazards of combustion products in building fires," SwRI Project No. 3-1237-3, Final Report, USPHS Contract No. PH86-62-208, Southwest Research Institute, San Antonio, Tex. (1963).

4) Fire J. 64, No. 6, 45 (1970).

5) M.A. Krupp, M.J. Chatton, S. Margen, et al., "Current diagnosis and treatment," Lange Medical, Los Altos, Calif. (1971).

6) P. Reich and V.W. Sidel, New England J. Med. 277, No. 2, 86 (1967).

7) W.R. Powers, Fire J. 65, No. 1, 18 (1971).

8) J.M. Ives, E.E. Hughes, and J.K. Taylor, "Toxic atmospheres associated with real fire situations," NBS Report 10807, U.S. Dept. Comm., Washington, D.C. (1972).

9) F.A. Patty, ed., "Industrial hygiene and toxicology," 2nd ed., Vol. II, Wiley, New York (1963).

10) J.A. Zapp, Jr., "The toxicology of fire," Medical Division Special Report No. 4, Chemical Corps, Chemical Center, Md., PB143732 (1951).

11) B.A. Zikria, "Inhalation injuries in fires," Symposium on halogenated fire extinguishing agents, Apr. 1972, at NAS-NRC, Washington, D.C.

12) K. Kishitani, J. Fac. Engr., Univ. of Tokyo (B) 27, 1 (1971).

13) J.A. Zapp, Jr., Arch. Environ. Health 4, No. 3, 335 (1962).

14) H.Th. Hoffmann and H. Oettel, Modern Plastics 46, 94 (Oct. 1969).

15) C.J. Hilado, "Flammability handbook for plastics," Technomic, Stamford, Conn. (1969).

16) W.H. McDermott and F.E. Critchfield, "Thermal degradation of polyurethane to hydrogen cyanide," Union Carbide Plastics Co. (1961); cited in R.E. Dufour, "Survey of available information on the toxicity of the combustion and thermal decomposition products of certain building materials under fire conditions," Bull. Res. No. 53, Underwriters Laboratories, Chicago (1963).

17) A.J. Pryor, D.E. Johnson, and N.N. Jackson, "Hazards of smoke and toxic gases produced in urban fires," SwRI Project No. 03-2402, Final Report, OCD Contract No. DAHC20-70-C-0212, Southwest Research Institute, San Antonio, Tex., AD697839 (1969).

18) R.L. Dufour, reference 16.

19) C.H. Yuill, Fire J. 66, No. 3, 47 (1972).

20) J. Autian, "Toxicology considerations of man made materials due to fires," SPI 30th Antec, May 1972, Chicago.

21) S. Steingiser, J. Fire and Flammability 3, 238 (1972). END

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