

Toxicity of the Pyrolysis and Combustion Products of Poly(Vinyl Chlorides): A Literature Assessment

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Poly(vinyl chlorides) (PVC) constitute a major class of synthetic plastics. Many surveys of the voluminous literature have been performed. This report reviews the literature published in English from 1969 through 1984 and endeavors to be more interpretive than comprehensive. PVC compounds, in general, are among the more fire resistant common organic polymers, natural or synthetic. The major products of thermal decomposition include hydrogen chloride, benzene and unsaturated hydrocarbons. In the presence of oxygen, carbon monoxide, carbon dioxide and water are included among the common combustion products. The main toxic products from PVC fires are hydrogen chloride (a sensory and pulmonary irritant) and carbon monoxide (an asphyxiant). The LC_{50} values calculated for a series of natural and synthetic materials thermally decomposed according to the NBS toxicity test method ranged from 0.045 to 57 mg l^{-1} in the flaming mode and from 0.045 to $> 40 \text{ mg l}^{-1}$ in the non-flaming mode. The LC_{50} results for a PVC resin decomposed under the same conditions were 17 mg l^{-1} in the flaming mode and 20 mg l^{-1} in the non-flaming mode. These results indicate that PVC decomposition products are not extremely toxic when compared with those from other common building materials. When the combustion toxicity (based on their HCl content) of PVC materials is compared with pure HCl experiments, it appears that much of the post-exposure toxicity can be explained by the HCl that is generated.

Keywords: carbon monoxide, combustion products, hydrochloric acid, large-scale fire tests, polyvinyl chloride, pyrolysis products, small-scale fire tests, toxicity.

INTRODUCTION

Poly(vinyl chlorides) (PVC) constitute a major class of synthetic plastics and are used in a wide variety of industrial and household products. Approximately seven billion pounds of PVC resins were produced in the United States in 1984.¹ More than half of this amount, which corresponds to an average of about 30 lb per person, is used in building products, including pipe and fittings, flooring, siding, and a wide variety of other construction products.² Much of this goes into residential construction. Other major uses include packaging, electrical insulation for wire and cable, interior furnishings and a host of miscellaneous household products. Because of its ubiquitous presence in the built environment, PVC is a possible source of fuel in unwanted fires. In a number of fires, injuries to firemen and building occupants have been attributed to its thermal decomposition or combustion products.³⁻⁵ This, together with PVC's wide distribution, has led to numerous studies of the nature of the products, their occurrence in fires and their physiological effects on living organisms.

A number of surveys of this voluminous literature have been performed. One of the early reviews was performed at the Underwriter's Laboratories in 1963.⁶ An extensive survey was made by Tewarson at Factory Mutual in 1975-6, in which he cited 262 references.⁷⁻⁹ In a supplement prepared in 1979, he cites an additional 56 references.¹⁰ The literature has increased in volume at an accelerated pace since that time. Barrow, in his PhD

thesis, provides an excellent review of the toxicity of the thermal decomposition products of PVC, with emphasis on experimental methods and physiological effects.¹¹ Boettner and Ball reviewed work on the composition of the volatile combustion products of PVC in 1981,¹² Kent and van der Voort described the behavior of PVC in fires in 1981.¹³ Recently, Hinderer has reviewed the combustion product toxicity of PVC.¹⁴

Despite this volume of publications, it is difficult to obtain a clear picture of the role of PVC in fires. Reported data are difficult to compare and sometimes contradictory. A number of reasons may be cited for this difficulty:

- (1) Pure PVC homopolymer (PVC resin) is almost never encountered outside the research laboratory. Most useful products are made from compositions compounded with a variety of additives designed to improve their properties. These additives include polymerization catalysts, plasticizers, lubricants, heat and light stabilizers, fire and smoke retardants, fillers and reinforcing agents.¹⁵ The amount of plasticizer may vary from 10 parts per hundred of resin (phr) in semi-rigid PVCs to 100 phr in very flexible PVCs. Any of these additives can affect the fire properties of the material and the composition of its combustion products. It is rare that two investigators use what can be identified as the same formulation. Often the samples are not adequately identified and, in some cases, the formulation may not be known to the investigators.
- (2) Methods of thermal decomposition or combustion of the samples vary widely from one study to another, particularly with respect to the thermal and atmospher-

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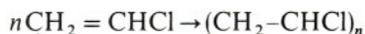
eric environment. These differences will affect the rate of product formation as well as the composition and concentrations of the combustion products.

- (3) In those cases where animals have been used to assess the physiological effects of the thermal degradation products a variety of species, which may differ in their response to this exposure, have been employed. Even when the same species and strain is used in different studies, variations in the conditions of exposure can lead to differences in response.
- (4) A plethora of methods for measuring responses to exposure have been employed. Different endpoints have been used, different parameters to characterize the experimental system are reported and the results may be given in different and frequently non-comparable units.

Despite these difficulties a fairly coherent picture of the fire behavior of PVC emerges from this mass of material. Minor inconsistencies may be attributed to one or more of the factors listed above. The present review concentrates on the more recent work (since 1969) and endeavors to be interpretative rather than comprehensive.

PROPERTIES OF PVC

Poly(vinyl chlorides) are high molecular weight polymers formed by the free radical polymerization of vinyl chloride monomers:



The homopolymer contains 56.7% chlorine by weight. The structure is primarily the linear head-to-tail configuration but various irregularities can occur in the chain structure. The ends of the polymer chain may be occupied by a number of different catalyst fragments and chain transfer agents. Typical number average molecular weights lie in the range of 50 000 to 120 000.

The PVC homopolymer (PVC resin) is a hard, tough material that has little practical application. It has poor stability when exposed to heat and light and must be compounded with stabilizers to make it useful. These stabilizers are often compounds of heavy metals, e.g. barium, tin, cadmium and lead. Rigid PVC, with a minimum of additives, may contain of the order of 90% PVC homopolymer. It is used for pipes, ducts, building panels, siding, floor coverings and other building applications.

The PVC resin can be compounded with a variety of plasticizers, usually high molecular weight organic esters, to give products the improved flexibility needed for use in films, tubing, wiring insulation, etc.

Di-2-ethylhexyl phthalate (di-octyl phthalate, DOP) is perhaps the most widely used plasticizer, but a great variety of other compounds are also used to impart special properties. Phosphate esters, such as tri-cresyl phosphate, are sometimes used as plasticizers to avoid the increase in flammability caused by phthalate and other purely organic plasticizers.¹⁶

Rigid PVC has an oxygen index of greater than 40.¹⁶ The addition of large amounts of plasticizer may lower this value to about 20 or 25. Fire retardants containing

bromine, antimony or phosphorus compounds may be added to counteract this effect. PVC compounds in general are among the more fire resistant common organic polymers, natural or synthetic.

In addition to PVC composites, a number of other chlorine containing polymers can be expected to show some similarity to PVC in their thermal decomposition properties and the toxicological properties of their combustion products. These materials will include vinyl chloride copolymers, poly-(vinylidene chloride), polychloroprene (neoprene), chlorinated polyethylene and chlorinated PVC.

THERMAL DECOMPOSITION OF PVC

It is to be expected that the thermal decomposition or combustion properties and the composition of the products from commercial items identified as 'PVC' will vary widely, depending on the nature and amount of additives contained in the formulation. Nevertheless, a certain consistency of behavior can be discerned if one focuses on the properties of the PVC homopolymer and considers the further effects of additives on this basic behavior.

PVC homopolymer has relatively poor thermal stability, beginning to lose hydrogen chloride (HCl) slowly in the neighbourhood of 100°C. The reaction is believed to start at imperfections in the polymer chain. Tertiary chlorine atoms, allylic chlorides and various oxygenated structures have been suggested.¹⁷ The reaction appears to be weakly autocatalytic. Thermal stabilizers react preferentially with the weak points in the polymer chain, preventing development of the autocatalytic process. Through the use of stabilizers, useful service temperatures can be achieved.

The pyrolysis and oxidation of PVC have been studied by a number of investigators. Woolley¹⁸ and O'Mara¹⁹ have given the most detailed accounts and have summarized earlier work. The reported results depend on the particular formulation used, and close agreement is not to be expected between investigators. However, a fairly consistent pattern of behavior emerges. Stabilized PVC resins begin to lose HCl slowly when heated to about 200°C. The rate of HCl evolution increases with temperature, becoming fairly rapid at 230°C. By 300°C, the dehydrochlorination is very rapid and results in an almost quantitative evolution of HCl. Woolley reports activation energies for the dehydrochlorination reaction of 174 kJ mol⁻¹ and 151 kJ mol⁻¹ in nitrogen and air, respectively, indicating the rapid increase of reaction rate with temperature.

The evolution of HCl results in unsaturation in the polymer chain. The dehydrochlorination appears to progress in stepwise fashion along the polymer chain to produce conjugated unsaturation. This leads to color formation in the residue and cyclization reactions producing benzene and related compounds. Both Michal²⁰ and Woolley²¹ found about 70 compounds among the thermal decomposition products of PVC resin. Table I lists those products identified by Michal from PVC and some vinyl copolymers. Among those identified were aromatic hydrocarbons, unsaturated hydrocarbons and chlorine-containing compounds. Benzene was the most

Table 1. Compounds identified in pyrolysis and thermo-oxidation products of poly(vinyl chloride) and some vinyl copolymers²⁰

Compound	Pyrolysis	Thermo-oxidation
Carbon dioxide	+	+
Chloromethane	++	-
Cyclopentane	+	-
Cyclopentadiene	+	-
Cyclohexadiene	+	-
Benzene	++	++
Toluene	++	++
Dioxane	++	-
Xylene	++	+
Styrene	+	-
Methyl styrene	+	-
Indene	++	-
Naphthalene	++	+
Butadiene	+	-
Vinyl chloride	+	-
Acetaldehyde	+	-
Methylcyclopentene	+	-
Chlorobenzene	++	++
Divinylbenzene	++	++
Cyclopentene	+	-
Trichloroethylene	+	-
Chloroethane	+	-
Chloropropene	+	-
Propanal	+	-
Methyl ethyl cyclopentane	++	-
Trimethyl cyclopentane	+	-
Methyl cyclohexene	+	-
Methyl indane	+	-
Cyclohexene	+	-
Trimethylbenzene	+	-
Dichloroethylene	+	+
Acrylonitrile	+	-
Hydrogen cyanide	+	-
Acetonitrile	+	-
Dichlorobutadiene	+	-
Dichloropentene	+	-
Trichloropropane	+	-
Dichlorobenzene	+	+
Trichlorobenzene	+	+
p-Chlorobenzonitrile	+	-
Dichlorobenzonitrile	+	-
Dichloropropene	-	+
Methylmethacrylate	-	+
Trimethylpentene	+	-
Dichlorobutylene	-	+
Dichloropentadiene	-	+
Dichlorocyclopentene	-	+
Benzaldehyde	-	+
Trichlorobutylene	-	+
Chloropyridine	-	+
n-Propylbenzene	-	+
Chlorobenzonitrile	-	+
Dichlorotoulene	-	+
p-Dichlorobenzonitrile	-	+
Methylnaphthalene	-	+
Chloronaphthalene	-	+
Tertiary butyl methyl phenol	-	+
Chlorostyrene	-	+
Diphenyl	-	+
Tetradecylene	-	+
Pentadecylene	-	+
Dichloroethylbenzene	-	+
Diphenylethane	-	+
Di-tert-butyl methyl phenol	-	+

Compound	Pyrolysis	Thermo-oxidation
Hexadecylene	-	+
Diphenylbutylene	-	+
Hydrogen chloride	++	++

++: Main components.

+: Other products present in amounts less than 2% of total products.

-: Not detected.

prevalent organic product, amounting to several per cent of the original sample weight.^{19,21} Others were present in much smaller amounts.

Lattimer and Kroenke²² have shown by isotopic labeling experiments that the benzene and other conjugated species result from intramolecular cyclization, while the mixed aromatic-aliphatic compounds such as toluene involve intermolecular reactions. Only small amounts of the vinyl chloride monomer and other chlorine-containing organic compounds are found.

In the presence of oxygen the decomposition is somewhat accelerated but primary products are little affected. Carbon dioxide (CO₂), carbon monoxide (CO) and water are formed from the dehydrochlorinated residue, particularly at high temperatures, thus decreasing the yield of organic products. Oxygenated organics are not found in significant amounts.²¹

The presence of plasticizers and other additives will give additional products characteristic of the additives. There appears to be little interaction between the PVC and the plasticizers. O'Mara suggests that gas chromatography-mass spectrometry (GC-MS) 'finger prints' of plastisols can be used to identify the plasticizers.¹⁹ Inorganic fillers capable of reacting with HCl, such as CaCO₃, can reduce the amount of HCl evolved.²³ Other inorganic additives, such as molybdenum compounds, have been promoted as smoke-reducing compounds. Presumably, they catalyze the oxidation of particulates.

The presence of phosgene among the combustion products of PVC has been investigated because of its well-known toxic properties. Woolley²¹ was unable to confirm the presence of the compound among the thermal decomposition products of PVC in air. Brown and Bitensky²⁴ conducted a careful search for phosgene using a variety of decomposition conditions. Under most conditions, only trace amounts (0.01 to 0.16 mg g⁻¹) of phosgene were detected. However, greater quantities (up to 1.6 mg g⁻¹) were formed when decomposition occurred as a result of electrical arcing.

Burning PVC can produce large amounts of particulate matter, and the actual amount will depend on the conditions of combustion, particularly the oxygen supply, and the presence of other fuels. HCl may be adsorbed on the particulates and be transported in that manner.²⁵ HCl may also be condensed by moist air to form a corrosive hydrochloric acid mist. This mist and smoke can obscure vision, thus interfering with escape and rescue. The pulmonary damage from PVC smoke inhalation has been shown to be more severe than that from HCl alone, probably because the particulates may be drawn into and deposited in the lungs, where the adsorbed or dissolved HCl enhances the toxic effect.⁵⁴ On the other hand, the potential exists that a water spray applied to the fire gases may remove some of the HCl.²⁶

TOXICITY OF PVC PYROLYSIS AND COMBUSTION PRODUCTS

Many studies of the toxicity of PVC combustion products have been performed. A recent review by Hinderer¹⁴ presents a summary of the findings. Again, the drawing of quantitative conclusions is made difficult by variations and uncertainties in the materials tested, differences in procedure and dissimilar ways of presenting the results. Nevertheless, it is possible to form a useful qualitative picture of the toxicological behavior of PVC in fires.

According to the literature discussed in detail below, the acute inhalation toxicity during and following exposures to PVC thermal degradation products appears to be due almost entirely to the presence of CO and HCl. The chronic effects of multiple exposures to PVC thermal decomposition products have only been examined in a few cases and are not well understood.²⁷ Additives contained in PVC compositions and other fuels that accompany PVC may produce other toxic products. For example, an experimental PVC composition containing zinc ferrocyanide was shown to produce a rapidly acting toxic combustion atmosphere.²⁸ This effect was probably due to hydrogen cyanide (HCN) which formed by a reaction of HCl with the ferrocyanide (Table 9).

Since carbon monoxide and hydrogen chloride exert their physiological effects through different mechanisms, direct interaction between them is not expected and the assessment of their individual roles in casualty production is difficult. Carbon monoxide is an asphyxiant causing incapacitation and death primarily during exposure. HCl, on the other hand, is both a sensory and a pulmonary irritant. As a sensory irritant in the upper respiratory tract, HCl can depress the respiration rate, thus slowing the ingestion of CO. The sensory effect is rapid and concentration-dependent.^{11,54} HCl can also act as a pulmonary irritant, causing severe damage to the lower respiratory tract and post-exposure death.⁵⁴

Hydrogen chloride is extremely soluble in aqueous body fluids. Therefore much HCl is removed from the inhaled gases in the nose and upper respiratory passages. This occurrence affords some protection against pulmonary damage. Rats and mice, used in most experiments, are obligatory nose breathers. Humans, on the other hand, when confronted with a sensory irritant, tend to bypass the nasal passages by breathing through the mouth. Some investigators have thus predicted that pulmonary damage from HCl would be much more severe in humans than in rodents.²⁹

Alarie and his coworkers examined the effects in mice exposed to HCl or PVC decomposition products both by normal breathing and through a tracheal cannula that delivered the gases directly to the lungs. They found the PVC LL_{50}^a (30 min exposure plus 3 h post-exposure period) to be about seven times greater for the nose-breathing mice than for the cannulated mice.³⁰ The HCl LC_{50} (10 min exposure plus 3 h post-exposure period) values for mice with and without tracheal cannulas were 1100 and 10100 ppm, respectively. From these results, they postulate that the acute lethality of materials that produce water-soluble acid gases will be underestimated by experiments with small rodents and that the actual toxicity to humans will be underestimated by this ratio.

Work by Kaplan *et al.*³¹ using juvenile baboons, which, like humans, may breathe through their mouths, does not support this conjecture. They showed the lethal amount of HCl to be about the same for baboons (5 min at 16 600 ppm) and nose-breathing rats (5 min at 15 200 ppm). These deaths were post-exposure. Moreover, exposure to high concentrations (baboon: 17 300 ppm; rat: 77 000 ppm) of this sensory irritant for 5 min did not incapacitate either animal, as measured by an escape task.

Barrow *et al.*³² have made extensive studies of the irritant effects of inhaled gases including HCl and the total thermal decomposition products of PVC. Both caused a reduction in respiration rate. The maximum percentage decrease in the respiration rate was found to be a linear function of the log of the concentration over a considerable range of concentrations of the irritant gas. They define the RD_{50} as the concentration of gas necessary to cause a 50% decrease in the respiratory rate from that of the animal prior to exposure. Since pulmonary irritants, in contrast to sensory irritants, increase the respiratory rate while decreasing the tidal volume, it can be judged that PVC products act more like sensory than like pulmonary irritants. The decomposition products of PVC were reported to be somewhat more potent than pure HCl. Unfortunately, the method of exposure in the two cases was different so no quantitative comparison is possible. The RD_{50} depends on the maximum concentration of products in a flowing air stream rather than the total amount. The PVC samples were decomposed in a ramp-heated furnace where the concentration of decomposition products varied with time and no determination of the maximum concentration was made. Experimental details, including extensive observations of physiological and pathological effects, are given in a thesis by Barrow.¹¹ Mice and rabbits were used; some of the rabbits had tracheal cannulas to study pulmonary irritants. The extensive damage noted in the upper and lower respiratory tract 24 h following exposures was similar for both HCl and the PVC decomposition products. At high concentrations, eye damage resulted.

Wong *et al.*³³ have examined the long-term pulmonary performance of guinea pigs following 30 min acute inhalation exposures to different concentrations of PVC thermal decomposition products. They used a non-intrusive and non-invasive method in which the animals are exposed to the toxic combustion products and then challenged with a mixture of 10% CO₂, 20% O₂ and 70% N₂. In control animals, this mixture will increase both tidal volume and respiratory rate. In the exposed animals, these responses are depressed—an indication of pulmonary damage. The gradual return to normal indicates the recovery of the animals. Wong *et al.* found that only the group exposed to the greatest amount of combustion products from PVC (10 g or ~16 mg l⁻¹) still showed lowered pulmonary performance 57 days following the exposure. Animals exposed to lower concentrations recovered prior to that time.

Laboratory measurements of PVC decomposition product toxicity

Cornish and Abar³⁴ were among the first to investigate the toxicity of PVC decomposition products. They used a

Table 2. Toxicity measurements of various PVC materials and PVC-containing products³⁴

Sample	Description	Max CO (ppm)	Average COHb ^a (%)	LC ₅₀ ^b (mg l ⁻¹)
A	Homopolymer	> 3000	72	3.1
B	Homopolymer	> 3000	69	3.3
C	Homopolymer	> 3000	51	5.1
E	Electrical wire insulation	2000	20	> 10.3 and < 15.3
G	Wire insulation	800	—	> 15.3
D	Vinyl chloride: vinyl acetate—85:15	8000	36	> 5.1
F	Floor tile	> 3000	—	> 15.3

^aBlood taken from dead animals.^bRats were exposed for 115–140 min, under ramped heating conditions. Lethalities include a 24 h post-exposure period.

flow system with a temperature slowly rising (3°C min⁻¹) to a maximum of 550°C. The airflow was 2.8 l min⁻¹ and the exposure chamber (a dessicator) volume was 7 l, so the products were quickly swept through and out of the chamber where four rats were exposed for approximately 140 min or until death. They were observed for 24 h following the exposure. The results of these studies on seven different PVC samples are shown in Table 2. The samples identified as pure homopolymers of PVC were more toxic on a sample mass basis. Carbon monoxide appeared to be a factor in causing lethality, but the data were inconsistent.

In a later study, Cornish *et al.*³⁵ compared results obtained in their dynamic system (rising temperature of 3°C min⁻¹ until a maximum of 800°C was reached; five animals were exposed for 140 min and observed for 7 days; airflow was 3 l min⁻¹) to those obtained in a 1500 l static system during a 4 h exposure of 15 rats (temperature reached in 1–2 min; material exposed for 6–10 min). The observed LC₅₀ values were 4 mg l⁻¹ in the dynamic system and 36 mg l⁻¹ in the static system.

At about the same time, Hofmann and Oettel³⁶ and later Hofmann and Sand³⁷ studied the toxicity of PVC decomposition products. They subjected rats to the products from a rigid PVC (5 g samples) decomposed in the DIN toxicity test furnace at a series of fixed temperatures. This apparatus supplies an approximately constant concentration of decomposition products to a flowing air stream (100 l h⁻¹) during a 30 min exposure period. The mass loading density was 50 mg l⁻¹, and in the later experiments 20 mg l⁻¹ and 10 mg l⁻¹ due to subsequent air dilutions. The expected variation of toxicity with temperature (Table 3) was observed and correlated with the decomposition temperature of the polymer. For a mass loading of 50 mg l⁻¹, no fatalities occurred from exposure to the products generated at 200°C, but 10 of 12 animals died when PVC was decomposed at 300°C. Deaths were reported during the 30 min exposure, but no post-exposure observations were taken. Since PVC decomposition products have been found, in other methods, to produce many post-exposure deaths of animals that survive the exposure, we can assume that the specimens would have been found to be much more toxic if the animals that survived the exposure had been observed post-exposure. The carboxyhemoglobin content of the blood in the dead animals was below the lethal level

Table 3. Dependence of PVC smoldering toxicity on temperature of decomposition in the DIN toxicity test method^{36,37}

Air dilution ^a (l h ⁻¹)	Effective specimen charge (mg l ⁻¹)	Temperature (°C)	COHb (%)	# Deaths/# Animals tested
100 ^b	50	200	< 15	0/12
		300	25	10/12
		400	45	11/12
		500	70	12/12
		600	76	12/12
400 ^c	20	300	< 10	2/12
		400	< 10	4/12
		500	25	3/12
		600	40	8/12
900 ^d	10	300	< 10	0/12
		400	< 10	0/12
		500	16	0/12
		600	26	0/12

^aIn all cases, 100 l h⁻¹ of air passed through the furnace containing 5 g samples.^bAn additional 100 l h⁻¹ of air was added prior to animal exposures resulting in 50 mg l⁻¹ specimen charges.^cSpecimen charge reduced to 20 mg l⁻¹ by an additional 400 l h⁻¹ of air.^dSpecimen charge reduced to 10 mg l⁻¹ by an additional 900 l h⁻¹ of air.

expected for pure CO, an indication of the presence of toxicants in addition to CO.

Kishitani³⁸ studied the toxicity of smoke from 30 g of a rigid PVC board to mice. The material was decomposed at temperatures rising from ambient to 740°C in 15 min. Two liters per minute of the smoke flowed through the 56 l exposure chamber in which one mouse was exposed for 15 min. Five tests were run on each material. It is difficult to make a quantitative interpretation of his data. All the animals died during or immediately following the 15 min exposure. COHb levels ranged from 13% to 30%. Kishitani and Nakamura³⁹ made a more detailed study in 1974, but, again, quantitative evaluation of their results is difficult. They noted that all surviving animals died within 24 h following the exposures. Rapid decay of the HCl concentration was noted. However, they believed that at 350°C, the toxicity was mainly due to HCl and that at 500°C and above, it was due to CO and HCl. Kishitani

Table 4. Toxicity of PVC decomposition products in the presence and absence of water²⁶

Temperature (°C)	Mode	LC ₅₀ (mg l ⁻¹) ^a		HCl (ppm)	
		w/water	w/o water	w/water	w/o water
400	NF	166	33	0	10 000 ^b
850	F	145	25	0	7 500 ^c

NF: Non-flaming.

F: Flaming.

Airflow rate: 120 l h⁻¹

^aRabbits were exposed for 30 min and observed for 4 h post-exposure.

^bAt 33.3 mg l⁻¹ loading.

^cAt 25.0 mg l⁻¹ loading.

and Yusa⁴⁰ attempted to determine the relative toxicities of the thermal decomposition products of various building materials by observing the exposure time necessary to cause the collapse of mice placed in rotating cages. Post-exposure deaths were noted. Based on times-to-collapse, comparison of a series of materials, which included five different types of wood, two melamine-resin sheets, a polyacrylonitrile, a polyamide, a wool, a urea resin foam, a polystyrene foam and a polyurethane foam, showed a rigid PVC foam to be of medium toxicity and a PVC flexible sheet to be the least toxic.

Boudene *et al.*²⁶ determined the effects of water solubility on the toxicity of PVC decomposition products. They used a traveling furnace in a flow system similar to the DIN system but with the furnace travel cocurrent with the airflow (Table 4). Rabbits exposed for 30 min including a 4 h post-exposure period. When the products of PVC decomposition were passed through a water bubbler before entering the exposure chamber, the toxicity was decreased five to six times, presumably because the HCl was removed by dissolution in the water. Lethal concentration (LC₅₀ value) of HCl for rabbit was calculated to be 12 500 ppm for a 30 min exposure. HCl rarely caused the rabbits to die during the exposure; deaths were usually noted after very long delays, sometimes as long as a month. The thermal decomposition products of PVC, like

HCl, caused post-exposure deaths, sometimes after 15 days.

Hilado and Crane⁴¹ attempted to compare toxicity results obtained with the USF/NASA and FAA/CAMI methods for a variety of polymers. The USF/NASA method exposes four mice in a 4.2 l chamber to the decomposition products from 1 g samples heated at 40°C min⁻¹ from 200° to 800°C, while the CAMI method exposes three rats in a 12.6 l chamber to the decomposition products from 1 g samples heated at 600°C. If all the material decomposed, then the test animals would have been exposed to a nominal concentration of 240 mg l⁻¹ in the USF test and 80 mg l⁻¹ in the CAMI test. Time to death for a PVC specimen was 16.4 min in the USF/NASA test and 15.3 min in the FAA/CAMI test. Time to incapacitation was 6 min in the USF/NASA method and 11.9 min in the FAA/CAMI method. No post-exposure observations were made.

Alarie and Anderson⁴² give results for a 92% PVC resin which showed an LL₅₀ of 7.0 g for a 30 min exposure plus a 10 min post-exposure period. A plasticized formulation containing 46% homopolymer showed a correspondingly lower toxicity with an LL₅₀ of 15.2 g. A 92% PVC resin containing 5% zinc ferrocyanide produced an LL₅₀ of 2.3 g. Assuming all the material decomposed and the combustion products are diluted by 600 l of air in this flow-through dynamic system, the nominal 30 min LC₅₀ values would be 11.7, 25.3 and 3.8 mg l⁻¹ for the three formulations, respectively. In Alarie's classification scheme, the first two PVC materials fall into the more toxic than wood class, whereas PVC with zinc ferrocyanide is considered much more toxic than wood. The increased toxicity of the last material is presumably due to the high concentration of HCN that is generated.

In the process of comparing the University of Pittsburgh's test method and the NBS test method, Anderson *et al.*⁴³ examined a number of PVC materials. The Pittsburgh test method was modified to include a 14 day post-exposure period. The LC₅₀ values are given in Table 5.

Herpol⁴⁴ used the DIN method to compare a number

Table 5. Toxicity of some PVC materials⁴³

Material	Test Procedure	Animal species	Combustion mode	LC ₅₀ values
				30 min + 14 days (mg l ⁻¹)
Vinyl wall covering	NBS	Rats	NF	51.0
	NBS	Rats	F	39.3
	Pittsburgh ^a	Mice	M	14.0
Conduit	NBS	Rats	NF	37.0
	NBS	Rats	F	29.5
	Pittsburgh ^a	Mice	M	9.8
C-PVC pipe	NBS	Rats	NF	9.1
	NBS	Rats	F	16.0
	Pittsburgh ^a	Mice	M	4.7
Vinyl-coated wire	Pittsburgh ^a	Mice	M	16.5

NF: Non-flaming.

F: Flaming.

M: Mixed includes both non-flaming and flaming.

^aReported values converted to mg l⁻¹ as follows:

$$\frac{LL_{50} \text{ value (g)}}{600 \text{ l (volume of dilution air)}} \times 10^3 = \text{mg l}^{-1}$$

Table 6. Comparison of the toxicities of a fire retarded and non-fire retarded PVC floor covering and wall covering⁴⁴

Material	Fire retardant	Temp. (°C)	Mode	# Dead/ # tested	COHb ^a (%)	Mean CO (ppm)
Floor covering	—	500	NF	0/6	54	2190
		600	F	16/25	57	4000
		700	F	14/18	77	3460
	+ ^b	500	NF	18/18	76	6420
		600	NF, F ^d	4/27	77	1990
		700	F	16/18	74	3180
Wall covering	—	500	NF	5/6	78	3140
		600	F ^d	17/18	78	6880
		700	F	0/6	32	1520
	+ ^c	500	NF	15/17	84	3850
		600	F ^d	14/17	71	4670
		700	F	1/6	65	680

^aCOHb is the mean value of the dead animals unless there were no deaths, in which case, it is the mean of the live animals.

^bContains phosphate plasticizers and antimony trioxide.

^cContains phosphate and chlorine-containing plasticizers and antimony trioxide.

^dShort bursts of flames.

of fire retarded and non-fire retarded materials, including some containing PVC. Rats were exposed for 30 min to the decomposition products of a PVC floor covering and a wall covering heated at three different temperatures—500°, 600° and 700°C. In all cases, 10 g of material were placed in the furnace. The results for the fire retarded and non-fire retarded PVC materials are shown in Table 6. From these results, it appears that the fire retarded PVCs were more toxic than the non-fire retarded materials at 500°C (where the materials did not flame). At 600° and 700°C, the toxicities were about equal. In many cases, the CO and COHb levels seemed high enough to account for the deaths. Since there were no post-exposure observations, the toxicity due to the HCl from the PVC is probably underestimated.

Levin *et al.*²⁸ decomposed a PVC resin according to the NBS toxicity test method. They were not able to calculate within-exposure LC_{50} values since only one rat died during the 30 min exposures to either the flaming or non-flaming decomposition products at the highest concentrations tested. However, with a 14 day post-exposure observation period, LC_{50} values of 17.3 and 20.0 mg l⁻¹ were determined for flaming and non-flaming conditions, respectively. With this same PVC, they also examined the incapacitation times of the rats who were instrumented to perform the hind-limb flexion conditioned avoidance response. Exposures continued until all animals were incapacitated as indicated by no longer responding to an electrical shock (Table 7). At a concentration of 30.9 mg l⁻¹, the mean incapacitation time was 45 min (range from 9 to 86). At a higher concentration (46 mg l⁻¹), the mean incapacitation time was 36 min (range from 12 to 46).

Toxicological studies performed at NBS on CO in air indicated that 4600 ppm of CO were necessary to cause 50% of the rats to die during the 30 min exposures.⁵³ No deaths occurred following these CO exposures. In PVC experiments²⁸ the highest concentrations (averaged over 30 min) of CO were 900 ppm in the non-flaming mode and

Table 7. Incapacitation^a times after exposure to non-flaming PVC decomposed via the NBS toxicity test method²⁸

Mass loading/ Chamber volume (mg l ⁻¹)	Test duration (min)	Animal number	Incapacitation time	
			Actual (min:s)	Mean ± Standard deviation (min:s)
30.9	90	1	9:15	44:59 ± 32.31
		2	19:45	
		3	21:00	
		4	62:45	
		5	71:50	
		6	86:20	
46.4	60	1	12:15	36:39 ± 12:41
		2	33:50	
		3	40:40	
		4	42:30	
		5	44:40	
		6	46:00	

^aIncapacitation monitored by the hind-leg flexion avoidance response.

2300 ppm in the flaming mode. In both modes, these CO concentrations by themselves would not be sufficient to cause deaths. However, other studies at NBS have shown that in the presence of CO₂, the lethal CO level decreases such that at 5% CO₂, 2500 ppm of CO becomes lethal.⁵³ PVC, in the flaming mode at the highest concentration tested (30 mg l⁻¹), produced an average concentration of 2300 ppm of CO and 12 800 ppm of CO₂. This implies that at only slightly increased sample masses (~ 1.5 times), within-exposure deaths due to CO and CO₂ alone could have occurred. In the non-flaming mode, the levels of CO and CO₂ were not sufficient to produce within-exposure deaths. The sample loading would have had to be increased four-fold before the concentrations of CO and CO₂ would be lethal. HCl, on the other hand, produces post-exposure deaths and is probably largely responsible for those deaths. These data emphasize the importance of a post-test observation period for materials producing irritant gases.

These PVC results are compared to those from a variety of materials in Table 8.²⁸ According to the test

Table 8. Comparative toxicities of various materials using the NBS test method²⁸

Material	LC_{50} ^a (mg l ⁻¹)	
	Flaming	Non-flaming
ABS ^b	19	31
Douglas fir ^b	40	23
Douglas fir ^c	41	20
Flexible polyurethane foam ^{b,c}	> 40	27
Modacrylic ^c	4.4	5.3
Polyphenylsulfone ^b	20	9.5
Polystyrene ^b	39	> 40
Polytetrafluoroethylene ^c	0.045	0.045
PVC ^b	17	20
PVC plus zinc ferrocyanide ^b	15	11
Red oak ^c	57	30
Rigid polyurethane foam ^b	13	> 40
Wool ^c	28	25

^a30 min exposures plus a 14 day post-exposure observation period.

^bIn large cup furnace (1000 ml).

^cIn small cup furnace (300 ml).

Table 9. NBS 10 Min test for rapidly acting toxicants^{28a}

Material	Mode	Temp. (°C)	Percentage incapacitation	Percentage death			Maximum COHb (%)	Maximum HCN (ppm)
				10 min	10 min post-exp.	10 min + 14 days		
PVC-ZnFeCN	F	700	100	16.7	16.7	100	—	446
			100	0	16.7	100	46.3	330
	NF	650	100	50	16.7	100	—	858
			100	16.7	16.7	100	14.1	1095
PVC	F	625	0	0	0	0	27.5	
			0	0	0	20	22.8	
			0	0	0	0	14.4	
	NF	575	0	0	0	0	—	
			0	0	0	0	—	

PVC-ZNFeCN: PVC with zinc ferrocyanide.

F: Flaming.

NF: Non-flaming.

^a30 mg l⁻¹ decomposed; animals exposed for 10 min and observed for 14 days.

method developed at the National Bureau of Standards, the LC_{50} values of these natural and synthetic materials ranged from 0.045 to 57 mg l⁻¹ in the flaming mode and 0.045 to > 40 mg l⁻¹ in the non-flaming mode. Thus, PVC decomposition products do not appear to be extremely toxic compared with those from other common building materials.

According to Table 8, even PVC containing zinc ferrocyanide, a smoke suppressant, does not appear to be extremely toxic. However, in the NBS toxicity test method, materials with LC_{50} values between 2 mg l⁻¹ and 30 mg l⁻¹ should be tested to determine if they rapidly produce concentrations of combustion products that will cause death from very brief exposures (i.e. 10 min). Deaths that occur within a 14 day post-exposure period are counted. This test was performed for both the PVC and the same formulation with zinc ferrocyanide. The results are given in Table 9, and indicate that the PVC plus zinc ferrocyanide is a very rapidly acting toxicant. All of the animals were incapacitated in the 10 min and all died either during or post-exposure. The high concentrations of HCN that were generated from PVC with zinc ferrocyanide are also noted in Table 9.

Comparison of the post-exposure toxicity of PVC decomposition products with that of HCl

If HCl were the principal toxic product responsible for the deaths following exposure to PVC thermal decomposition products and if that decomposition gave a nearly quantitative yield of HCl, we would expect good agreement between the properly weighted toxicity of PVC decomposition products and that of pure HCl gas. To make this comparison, the toxicity data on HCl need to be examined first.

Higgins *et al.*⁴⁵ give data on the effects of 5 min exposures of rats and mice to HCl gas followed by a 7 day observation period. They also investigated the additional effect of exposures to CO (concentrations tested were calculated to produce 25% carboxyhemoglobin levels) on HCl toxicity. Their results are given in Table 10. The difference in LC_{50} values between exposure to HCl with and without CO at this sub-lethal level was not statisti-

Table 10. Toxicological results from HCl exposure with and without CO⁴⁵

Animal	Exposure time (min)	LC_{50} (ppm)	
		HCl	HCl + CO
Rat	5	41 000 (34 800–48 300) ^a	39 000 (35 100–43 400)
Mouse	5	13 700 (10 300–18 300)	10 700 (6 900–16 400)

^a95% confidence limits.

cally significant, supporting the position that HCl and CO react by independent physiological mechanisms.

In related work by Darmer *et al.*⁴⁶ rats and mice were exposed to HCl vapors and water saturated aerosols for periods of 5 and 30 min and observed for 7 days. Rats were found to be considerably more resistant to HCl vapors than mice. The 5 min LC_{50} values for the rats and mice were 41 000 and 13 700 ppm and the 30 min LC_{50} values were 4700 and 2600 ppm, respectively (Table 11). No rats died during the 5 min exposures, although some mice died at the two highest concentrations (26 000 and 30 000 ppm). In the 30 min exposures, deaths during the exposures were noted at 27 000 ppm and above. Exposures to the HCl aerosols did not significantly affect the toxicity. Rabbits and guinea pigs showed a degree of susceptibility to HCl similar to that of mice. In summary, the HCl LC_{50} value for 5 min exposures range from ~ 11 000 to 41 000 ppm and the 30 min LC_{50} values range from 2100 to 5700 ppm. These include post-exposure deaths.

Since the toxicity of HCl occurs primarily following exposures, data from some of the better characterized experiments on the toxicity of PVC decomposition products and which include post-exposure observations are

Table 11. Toxicological results from HCl exposures with and without a water mist⁴⁶

Animal	Exposure time (min)	LC_{50} (ppm)	
		Dry vapor	Moist aerosol
Rat	5	41 000 (34 800–48 300) ^a	31 000 (26 800–35 800)
	30	4 700 (4 100–5 400)	5 700 (4 900–6 600)
Mouse	5	13 700 (10 300–18 300)	11 200 (10 000–12 500)
	30	2 600 (2 300–3 100)	2 100 (1 800–2 600)

^a95% confidence limits.

Table 12. A comparison of HCl gas toxicity and PVC toxicity

Animal	Material	Exposure time (min)	Post-exposure time (days)	Mode	Conc. of HCl at the material LC_{50} (ppm)	Pure HCl LC_{50} (ppm)	References
Rat	HCl gas	30	7	—	—	4 700	46
	Rigid PVC	30	14	F	6 800		28
				NF	8 000		28
	Vinyl wall covering	30	14	F	15 800		43
				NF	20 500		43
	Conduit	30	14	F	12 000		43
				NF	14 900		43
	C-PVC pipe	30	14	F	6 400		43
NF				3 700	43		
Mouse	HCl gas	30	7	—	—	2 600	46
	Vinyl wall covering	30	14	M	5 600		43
	Conduit	30	14	M	3 900		43
	C-PVC pipe	30	14	M	1 900		43
	Vinyl coated wire	30	14	M	6 600		43

F: Flaming.

NF: Non-flaming.

M: Mixed flaming and non-flaming.

compared to those for HCl gas in Table 12. For this table it is assumed that PVC gives a quantitative yield of HCl (58.3% HCl by weight); additives and fillers are not considered. With the exception of C-PVC pipe, the results indicate that the post-exposure toxicity of the thermal decomposition products of PVC can be explained based largely on their HCl content. The agreement is close enough that there is no reason to hypothesize the need for other potent toxicants in significant quantities to explain the toxicological results.

LARGE-SCALE FIRE EXPERIMENTS

The problem of relating results obtained in a small-scale laboratory apparatus to conditions in a real fire is a universal one in fire research and particularly critical in combustion toxicology. The problem is particularly difficult in the case of PVC for two reasons. First, PVC is among the more fire resistant of commonly encountered fuels. It does not burn readily by itself and usually requires a vigorous fire involving more combustible fuels to bring about its thermal decomposition. The products from these combustible fuels, usually including substantial amounts of CO, mix with the products from the PVC and may be responsible for much of the toxic effects observed. Second, the HCl in the smoke can behave not as an inert mixture when the smoke moves away from the fire source, showing, instead, condensation on and settling out with particulate matter, adsorption on surfaces and dissolving in water droplets.⁴⁷ Consequently, the exposure to smoke that has traveled some distance in a building fire may be quite different from that received in a close-coupled laboratory system.

In an effort to obtain a better understanding of the problem, a number of investigators burned PVC in large-scale experiments simulating real fire scenarios. Stark *et al.*⁴⁸ were among the first to carry out such experiments at the Fire Research Station in 1969. They burned

cellulosic fuels in a small compartment with PVC wall lining or with strips of rigid PVC. With complete combustion of the PVC, the HCl was equivalent to the chlorine content. They concluded that the solid PVC would contribute a significant amount of HCl to the fire gases, but that PVC wallpaper would not be likely to contribute much to the toxicity due to the small quantity of PVC material compared with the amount of other furnishings.

Packham and Crawford⁴⁹ thermally decomposed electrical non-metallic tubing (ENT) made from rigid PVC and studied the toxicity in both small-scale and large-scale experimental conditions. In the small-scale tests, the NBS toxicity test method was utilized to decompose the materials in the non-flaming mode. The resultant LC_{50} value was 28.5 mg l^{-1} ; all lethalties were post-exposure. In the large-scale tests, samples were decomposed in a closed 21.7 m^3 room, using either a 2.2 kg wood crib or a radiant flux of 25 kW m^{-2} to decompose the ENT. In the experiments with wood cribs, they concluded that high temperatures and CO from the cribs posed a greater threat than the HCl. In the radiant heating experiments, significant concentrations of PVC decomposition products were found, but animal fatalities were still considered to result from heat stress rather than smoke inhalation. HCl recoveries ranged from 23% to 50% of the theoretical in the large-scale tests, whereas in the small-scale tests, 64–96% of the theoretical yield was generated.

In none of these tests was a quantitative full-scale/bench-scale correlation obtained.

PVC IN FIRES

Because of the wide occurrence of PVC in buildings and residences, it is to be expected that PVC will be present in many accidental fires. Since the decomposition products are usually accompanied by large quantities of combustion products from other fuels, it is difficult to judge their contribution to the toxic threat. Post-exposure analytical

studies of fire victims are of little help since chloride ion, the most characteristic PVC product, is a common constituent of all body fluids. Casualties attributed to 'Smoke inhalation' are frequently blamed on PVC, although there may be little direct evidence of its having played a significant role. For example, the Beverly Hills Supper Club fire is frequently cited as a fire where PVC contributed significantly to injury and loss of life, yet the amount of PVC involved was small compared with the amount of other fuels capable of producing toxic combustion products.³

Lowry *et al.*⁵⁰ analyzed gas samples from 72 residential fires in the Dallas area. Hydrogen chloride was found in 9% of the samples, with an average concentration of 1.1 ppm and a maximum concentration of 40 ppm. Of the gases examined, CO was the principal toxic gas found.

A small number of fires have occurred where PVC decomposition products appear to have played a significant role. These are fires involving electrical insulation and apparatus, although, in some of these cases, the origin of the toxic gases is not clearly established. Dyer and Esch⁵ describe a fire 'confined to an office copying machine constructed of plastic and Teflon parts' in which firefighters sustained respiratory injuries and one firefighter died 24 h later. The 'plastic' was not identified and the involvement of PVC was not demonstrated, although the article was entitled 'Polyvinyl Chloride Toxicity in Fires'.

Einhorn and Grunnet⁵¹ described a number of fires in the Salt Lake City area where PVC was specifically identified by analysis as a major fuel component. The fires resulted in respiratory and skin injuries to the firefighters and other exposed personnel.

Perhaps the prime example of a PVC fire was the New York Telephone Company fire of 1975.³ Fire burned through an eleven-storey switching center, fed largely by electrical insulation of wires and cables. A total of more than 700 firefighters were involved and many received varying degrees of respiratory injury. Follow-up studies⁵² suggest long-range health effects from exposure to PVC smoke. Other more limited studies suggest similar results.²⁷

CONCLUSIONS

When strongly heated or exposed to a fire environment, PVC-containing materials decompose at relatively low

temperatures to give a nearly quantitative yield of HCl, in addition to CO and a wide variety of minor organic products. At higher temperatures, the concentrations of CO₂ and its potentiating effect on CO should also be considered when assessing the toxicity of the combustion products.

HCl appears to be the major toxicant which is responsible for the deaths that occur following acute inhalation exposures to PVC decomposition products. HCl is both a sensory irritant and a pulmonary irritant. In the latter role, it can cause respiratory difficulties, permanent injury or death. In one case, however, a laboratory formulation containing the additive zinc ferrocyanide produced significant quantities of HCN that were probably the cause of the animal deaths that occurred from 10 min exposures.

PVC decomposition products are usually accompanied in fires by large amounts of products from other, more combustible, fuels. This, together with the rapid decay of HCl concentration presumed to occur in the fire environment, makes it difficult to determine the contribution of PVC to the toxicity of the atmosphere.

A few cases were noted, principally in fires involving electrical insulation or apparatus, where PVC decomposition products were probably the cause of the resultant injuries in firefighters and other personnel. However, long-term effects on firefighters of chronic exposure to PVC decomposition products are not well understood and should receive further investigation.

The toxicity of PVC thermal decomposition products based on LC₅₀ values falls within the range of values found for many other natural and synthetic materials. Its relatively low flammability is a positive factor in overall fire safety.

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NOTES

^aLC₅₀ is defined by Alarie as the mass of tested material which, when thermally decomposed via the University of Pittsburgh test method, causes 50% of the animals to die in the specified exposure time plus a short post-exposure observation period. However, in combustion studies, LC (which stands for lethal concentration, is usually defined

as the mass of tested material divided by the available volume of the combustion products or the concentration of a specific gas. Therefore, for the purposes of this report, the results of these experiments will be presented as LL₅₀, indicating that a lethal loading of material is the figure of merit.

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