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Behavior of PVC in Fires

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ABSTRACT

Methods used to study the behavior of PVC in fire are described. At the Fire Research Station both laboratory and full-scale tests are carried out; appropriate results are given.

INTRODUCTION

At the Fire Research Station, Borehamwood, considerable effort is now being directed to the study of the behavior of combustible materials in fires. An important part of this effort concerns the production of smoke and toxic gases which is becoming an increasingly important factor in causing fire fatalities. They now account for over one half of all the fire deaths in the U. K. [1].

The approaches being adopted at the Fire Research Station involve: (1) laboratory experiments [2] which are carried out to study the general decomposition mechanisms of materials and to gain an insight into the types and quantities of products formed at various temperature regimes in air and oxygen depleted atmospheres and (2) full-scale fires [3] which are carried out in a special compartment-corridor facility designed to represent a room attached to a corridor. This

work provides information about the general burning characteristics of materials and gives an indication of the hazard of the fire atmosphere under real fire situations.

Both of the above techniques rely on analytical measurements of smoke and toxic gases which can provide useful data about the combustion hazards of materials but care is needed in interpreting the results. Supporting work is currently being carried out at the Huntingdon Research Centre and the Chemical Defence Establishment using animals exposed to fire and pedigree gases to provide relevant toxicological information.

This paper outlines the general procedures and methods being adopted at the Borehamwood Laboratories of the Fire Research Station to study the hazards of fire atmospheres. A summary of results obtained with PVC involving both laboratory studies and full-scale fire tests is given.

METHODS AND PROCEDURES

Laboratory Studies

In the laboratory experiments, small samples of PVC (15 mg) were decomposed [2] in a furnace system in a flow of air or nitrogen and the general products analyzed by gas chromatography and mass spectrometry. In the dehydrochlorination studies [3], the released hydrogen chloride was monitored by titration after absorption into aqueous solution.

Full-Scale Fires

The full-scale fire tests [4] described in this report were carried out in a compartment (3 m × 3 m and 2.5 m high) coupled with a variable ventilation slit of between 200 and 700 mm (doorway) to a long corridor (12 m long and 1.3 m wide) with an open end. The sole means of ventilation of the compartment was effectively the open end of the corridor. In this way, fresh air entered the compartment via the lower part of the corridor and the smoke and hot gases were discharged from the upper part.

Thermocouples in the compartment and corridor were used to measure the temperature of the fire gases. The rate of air input to the rig was measured and the optical density of the emerging smoke monitored with a photocell-lamp device.

The production of carbon monoxide and carbon dioxide and the extent of oxygen vitiation in the room and corridor were measured by standard gas chromatographic techniques. Hydrogen chloride was sampled through lacquered stainless steel tubes, collected in bicarbonate solution, and measured with a selective ion electrode.

Materials

The laboratory experiments and fire tests in which the compartment was fitted with a thick PVC wall lining were carried out using a commercially available rigid PVC sheet (unplasticized). Other wall linings examined were decorative PVC papers and cloth.

RESULTS OF LABORATORY TESTS

Dehydrochlorination Studies

The release of hydrogen chloride from PVC was studied at constant temperature over the range 200-300°C in nitrogen and air and can be represented approximately by an equation based on a 3/2-order decomposition where

$$(100 - P)^{-1/2} = 0.1 + (1/2) kt \quad (1)$$

where P is the released hydrogen chloride as a percentage of the theoretical, k is the rate constant, and t the time in minutes.

For a nitrogen atmosphere

$$\log k = 15.27 - 9.13 \times 10^3 (1/T) \quad (2)$$

and in air

$$\log k = 12.93 - 7.86 \times 10^3 (1/T) \quad (3)$$

where T is the decomposition temperature in degrees Kelvin.

Table 1 shows the calculated times for 20, 40, and 60% dehydrochlorination at temperatures between 200 and 300°C. It is important to note that the dehydrochlorination is very rapid once a temperature of 300°C

TABLE 1. Calculated Time for 20-60% of Theoretical Dehydrochlorination of PVC in Nitrogen and Air

Temperature (°C)	Dehydrochlorination time (min)					
	20% Dehydrochlorination		40% Dehydrochlorination		60% Dehydrochlorination	
	Nitrogen	Air	Nitrogen	Air	Nitrogen	Air
200	251.4	114.9	619.8	283.3	1237.8	565.8
220	41.4	24.3	102.1	60.0	204.0	119.8
240	7.9	5.8	19.4	14.3	38.7	28.6
260	1.69	1.55	4.16	3.82	8.31	7.62
280	0.41	0.45	1.00	1.12	2.00	2.23
300	0.11	0.14	0.27	0.36	0.53	0.71

has been reached. If decomposed for a sufficient length of time at an adequate temperature, the release of hydrogen chloride from PVC appears to be an almost quantitative decomposition.

In fires, the temperature of PVC is likely to increase in a non-uniform manner. This temperature time profile can be regarded as a series of small intervals with a fixed temperature over each interval. In this way the dechlorination can be represented by a summation process where

$$(100 - P_n)^{-1/2} = 0.1 + (1/2)\Delta t \sum_{i=1}^{i=n} k_{mi}$$

where P_n is the total hydrogen chloride released after the n -th interval, Δt is the time interval in minutes, and k_{mi} is the rate constant of the mean temperature of the i -th interval.

In this way the extent of dehydrochlorination can be estimated for almost any temperature/time profile and has been shown experimentally to give representative results [3].

General Product Studies

The general release of products from PVC has been studied by GC-MS over the temperature range 300-600°C. This work has shown that the decomposition proceeds in two parts. First, there is a period of dehydrochlorination (defined as the primary decomposition region) where loss of hydrogen chloride takes place, leaving a type of residual polyene structure. Second, there is the decomposition of the residual material during the secondary decomposition region.

The many organic products which have been detected during the thermal degradation of PVC are formed predominantly during the primary (or dehydrochlorination region) and appear to be associated in some way with the release of hydrogen chloride. These organic species are mainly hydrocarbons (both saturated and unsaturated) with aromatic materials predominating. An air atmosphere tends to increase the yields of certain products but without altering their general nature.

During the secondary decomposition region in a nitrogen atmosphere the products are again hydrocarbon species but without the predominant aromatic species. The presence of air converts the residue to inorganic products (carbon monoxide, carbon dioxide and water) but no oxygenated organic species are formed. Contrary to certain beliefs, no phosgene has been detected, and only traces of organic halides appear to be present.

RESULTS OF FIRE TESTS WITH PVC

General Results

Full-scale fires have been carried out with fire loads of wood (120-240 kg) in the form of a crib in the compartment with various PVC wall linings in the compartment or corridor giving loads from 0.63 to 115 kg. The work was carried out to study the general contribution of these linings to the overall fire behavior and the production of smoke and toxic gases and to examine the feasibility of predicting the production of toxic gas (particularly hydrogen chloride) from laboratory data.

The main fuel loading in all tests consisted of a wooden crib made of sticks 50 mm square and 1.5 m long with 200-mm spacings. The cribs were chosen to represent typical fire loads of 13.5 and 27 kg/m² (3-6 lb/ft²).

It is not possible in this report to include the detailed results of these tests, but some broad generalizations will be given.

In the tests, temperatures of 900-1000°C were attained rapidly in the compartment even with wood alone and this steady state burning condition under ventilation control remained until most of the fuel was consumed. The large loads of PVC did not substantially increase the maximum temperatures but tended to give longer burn periods. The time taken by the gases to exceed a temperature of 300°C, particularly within the compartment, was very short indeed. However, it is to be expected that the temperature of PVC linings would have a substantial lag behind the gas temperature, and estimates of the dehydrochlorination on the basis of gas temperatures alone would not be valid.

Relatively dense smoke was formed during the combustion of the wooden cribs alone, and the presence of PVC did not necessarily increase the density of the smoke but a greater volume of smoke was produced with PVC linings because of the extended burning period.

Even at the corridor end of the test rig, the temperature of the fire gases in all tests exceeded a bearable temperature within a few minutes after ignition. During the steady-state burning conditions, inhalation of the hot gases would be likely to prove fatal by temperature effects alone.

The carbon monoxide concentrations in the undiluted fire gases rapidly increased to hazardous levels with wood alone. Although some variation in the carbon monoxide yields was observed between tests there was little evidence of a major increase in carbon monoxide concentrations even with large amounts of PVC.

Hydrogen chloride was released relatively quickly with the large loads of PVC, particularly at the high ventilations and with the PVC present in the compartment.

Some typical results of the maximum concentrations of carbon monoxide and hydrogen chloride obtained with 240 kg wood fuel and 95 kg PVC wall lining are given in Table 2.

An assessment of the hazard arising from the presence of the two toxic gases in the fire gases is difficult because of the very high temperature of the undiluted gases. In practical situations it is often necessary to consider the dilution of the gases as would occur during the discharge of fire gases into an enclosed space within a building. Table 3 shows the maximum concentrations of hydrogen chloride and carbon monoxide formed when the compartment and corridor gases are diluted with clean air to a bearable temperature taken as 120°C.

When diluted in this way the carbon monoxide levels could in

TABLE 2. Typical Summary of Results for Full-Scale Fire Test with Wood and PVC Wall Lining^{a,b}

	Compartment	Corridor
Temperature (max) (°C)	1020	550
Oxygen (min) (%)	4.5	12.8
Carbon dioxide (max) (%)	14.5	7.3
Carbon monoxide (max) (%)	1.9	1.8
Hydrogen chloride (max) (%)	4.0	1.0
Optical density (max) (OD/m)	-	2.6

^aWood, 240 kg (crib); PVC, 95 kg (wall lining); vent width, 700 mm; time of burning, 30 min.

^bRecoveries (vent): carbon monoxide, 34.7 kg; hydrogen chloride 40.2 kg (85% of theoretical).

TABLE 3. Production of Carbon Monoxide, Hydrogen Chloride, and Smoke from Full-Scale Fire Tests with PVC, after Dilution to a Bearable Temperature

Test no.	Fire load			Compartment		Corridor		
	Wood (kg)	PVC (kg)	Vent (mm)	CO (ppm)	HCl (ppm)	CO (ppm)	HCl (ppm)	Visibility (m)
2	120	95	240	4950	6020	8210	290	1.4
4	123	0.9	700	2750	3	4150	8	1.6
5	123	2.63	700	232	79	nm ^a	67	1.6
6	120	95	700	2080	3230	850	1460	2.4
7	120	115 ^b	700	526	360	nm	9690	1.2
10	240	95	240	1800	3800	nm	780	2.0
13	240	95	700	2350	3920	566	1890	2.4
14	240	115 ^b	700	6730	1800	3330	20500	2.0

^aNot measured.

^bCorridor lining.

many instances pose a hazard to life. An additional risk appears to be present with the high loads of PVC. A more detailed consideration of the hazard of these concentrations of gases, supported by results from animal experiments, is given in the next section of this report. The additional hazard from hydrogen chloride arising from PVC wall papers and cloths appears to be small.

Also given in Table 3 are the visibilities of the smoke after dilution, which in all tests were of the order of 1 to 3 m.

Dehydrochlorination Predictions

Some attempts have been made to predict the rate of dehydrochlorination of PVC in full-scale fire tests from a knowledge of the temperature of the fire gases. The main difficulty which arises is the estimation of the temperature profile through a thick PVC lining, particularly during the degradation of the PVC when the outer surface chars and so provides an insulating layer to the residual PVC.

An experimental finding is that the rate of dehydrochlorination can be estimated with some degree of approximation by introducing a kinetic "factor" into the thermal degradation equation where the temperature of the PVC is about $1/3$ of that of the gases within the room. This approach needs further consideration but may indicate that, in principle, the dehydrochlorination of PVC in a fire test may be predictable from laboratory data.

ADDITIONAL CONSIDERATIONS

The full-scale fire tests give carbon monoxide and hydrogen chloride levels approaching 10,000 and 20,000 ppm, respectively, in the fire gases following dilution with air to a bearable temperature.

Work has been carried out under contract with the Chemical Defence Establishment, Porton Down, to assess the toxicological effects of these gases with small animals [5]. In this work, groups of 15 animals (rats and guinea pigs) have been exposed to the fire gases for 30-min periods in a 10 m^3 chamber during experiments with PVC faced hardboard in an apparatus described in British Standard BS 476: Part 6. During this work it was found that serious loss of hydrogen chloride occurred within the chamber and additional hydrogen chloride was needed to restore the required levels.

In this way it has been possible to generate fire gases from wood or PVC giving hydrogen chloride at concentrations of 1300 to 13000 ppm with the appropriate carbon monoxide levels to simulate the

the range of concentrations encountered with the diluted fire gases of the full scale fires.

In general, the deaths of laboratory animals following exposure to hydrogen chloride occurred after a delayed period, whereas with carbon monoxide the animals which were not dead on withdrawal tended to recover.

At the high concentrations of hydrogen chloride, 100% mortality occurred within 24 hr whether carbon monoxide was present or not. Deaths due to exposure to the mixed gases in the high concentration ranges were generally associated with carbon monoxide poisoning.

It was observed that hydrogen chloride tended to enhance the response to the carbon monoxide but this effect was important only at concentrations of hydrogen chloride which would have produced high mortalities when present alone.

The presence of the hydrogen chloride caused damage to the internal and external tissues of the animals. It is important that additional consideration is given to the sublethal effects of hydrogen chloride because of the high irritancy of the material and the possibility of long-term permanent injury after exposure.

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The work described in this report forms part of a detailed program of work being carried out at the Fire Research Station Laboratories at Borehamwood to study the behavior of combustible materials in fires.

REFERENCES

- [1] P. C. Bowes, Ann. Occup. Hyg., **17**, 143 (1974).
- [2] W. D. Woolley, Brit. Polym. J., **3**, 186 (1971).
- [3] W. D. Woolley, Plastics and Polymers, **40**, 203 (1972).
- [4] G. W. V. Stark and P. Field, Fire Research Note 1030, Fire Research Station, Borehamwood, 1975.
- [5] P. C. Bowes, J. A. G. Edgington, and R. D. Lynch, Fire Research Note 1048, Fire Research Station, Borehamwood, 1976.