

## **SMOKE AND TOXICITY HAZARDS OF PLASTICS IN FIRES\***

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### **Summary**

Plastics are now used widely in a variety of applications both within the general structure of buildings and in furnishings and fittings and there is concern that the widespread use of these materials may increase the fire hazard because of the possible production of large amounts of smoke and toxic gases.

Smoke and toxic gases are generated in a number of different ways in fires, involving particularly the thermal and thermal oxidative decomposition of the polymeric material and the gas phase pyrolysis or combustion of volatiles. In some instances these routes can also lead to destruction of smoke and gases.

The problems of smoke and toxicity hazards are being studied at the Fire Research Station, Borehamwood using laboratory decomposition techniques with gas chromatography and mass spectrometry, and fire tests in a full scale compartment-corridor facility.

Animal experiments carried out under contract provide the link between the analytical results and the physiological response of fire gases.

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### **1. Introduction**

Opinion is often expressed that present day fires show rapid growth and release larger quantities of dense and toxic smoke than was observed some ten to twenty years ago.

Over this period a number of changes have taken place within buildings which may have contributed either partly or wholly to this observation. For example, in domestic premises (where the majority of fire fatalities occur), furniture now tends to be relatively lightweight in construction and is housed in areas where the thermal insulation properties are being improved to assist both the comfort of occupants and the conservation of energy. Also over the period there has been a change in the types of materials, with plastics tending to replace more traditional materials both within the structure and furnishings of buildings.

A recent survey of the statistics of fatal and non-fatal casualties within the United Kingdom has been carried out by Bowes [1] using data from the Annual tables [2] for the 17 years from 1955 to 1971.

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\*This paper is based on a lecture given at the International Symposium on "The Fire Safety of Combustible Materials" in Edinburgh, 15–17 October 1975.

For the purposes of this exercise the two main areas of consideration were casualties due to (a) smoke and toxic gases and (b) burns and scalds, which together comprise some 90 per cent of total casualties. Further for the period covered, some 85 to 90 per cent of all casualties occurred in buildings with the majority of these within private dwellings.

Figure 1 shows the numbers of fatal casualties overcome by smoke and toxic gases, the total fatal and non fatal\* casualties by this cause and the total fatal casualties for all causes. It will be seen that fatal casualties due to smoke and toxic gases are becoming an increasingly important factor in fire and now account for nearly one half of all fire deaths. The proportion of deaths due to burns and scalds has in fact decreased slightly over the period examined.

An interesting observation from Fig. 1 is the relative numbers of fatal and non-fatal casualties. Over the period examined the probability of a casualty surviving an exposure to smoke and toxic gases has remained almost constant at about 60 per cent. This may suggest that the nature of the main toxic gases in fires has not changed significantly during this period and may direct attention towards the behavioural and obscuration effects of smoke.

## 2. Effects of fire atmospheres

There are many factors which need careful consideration in assessing the overall hazard of a fire atmosphere. It is helpful to identify these factors:

- (i) Heat: By the very nature of fire the combustion gases are hot. Inhalation of gases at elevated temperature can cause serious injury and death [2].

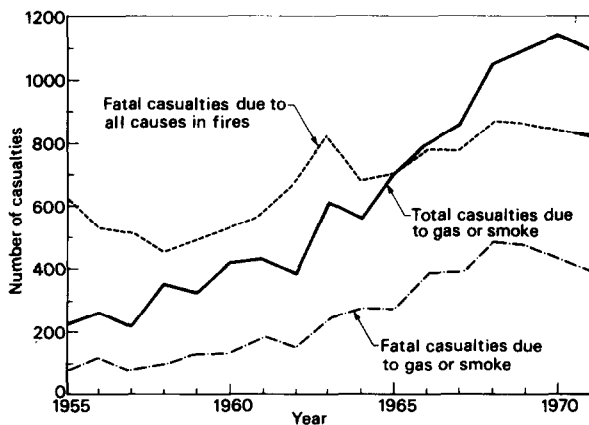


Fig. 1. Casualties "overcome by smoke or gas" in fires.

\*A non fatal casualty is a person requiring more than first aid treatment.

- (ii) **Vitiation:** Fire gases are normally vitiated because of the oxygen uptake by the fire. Low levels of oxygen (less than 6 per cent) can cause rapid unconsciousness and death [3].
- (iii) **Smoke:** Smoke (defined here as the particulate matter of the atmosphere) can reduce visibility and impede escape either directly or by inducing panic.
- (iv) **Toxic products:** Toxic products (gas or particulate matter) of the fire atmosphere may bring about unconsciousness and death [4]. Low levels of toxic products may induce behavioural effects.
- (v) **Irritants:** Irritants present both in gaseous or particulate form may impair vision by affecting the eyes, or induce panic when breathing is hindered.

It is difficult to generalise about the relative importance of these factors because of the many different fire situations which can arise. For example, with personnel involved in the room of origin of the fire, the rate of build up of heat may be a more predominant factor than at sites remote to the fire where the smoke has had a time to cool to a breathable temperature. In these 'remote' situations smoke obscuration and the overall behavioural effect of toxic gases are important.

### 3. Product formation routes

#### (1) *Toxic gases*

The primary step in the formation of products in fires involves the decomposition of the fuel and release of volatile species. This decomposition may take place under oxidative conditions (as might exist during the early stages of fire) or under inert (pyrolytic) conditions and at temperatures up to and sometimes in excess of 1000°C.

The primary products are released into the relatively mobile atmosphere of the fire and may be discharged unchanged from the fire zone. Alternatively, the primary products may enter a very hot but inert zone where further gas-phase pyrolysis takes place or a hot oxidative zone where combustion or gas-phase oxidation occurs.

The primary products of pyrolytic degradation are usually small molecular fragments of the original polymeric material\*. For example polymers containing carbon and hydrogen (polyethylene, polystyrene, polypropylene) yield hydrocarbon species during degradation [5, 6, 7]. If nitrogen is also present (polyurethane, polyacrylonitrile, wool, nylon, urea-formaldehyde) then nitrogen containing products such as ammonia and cyanides can result [8]. If an inorganic element is present (PVC, rubber), inorganic decomposition products (HCl and oxides of sulphur respectively) occur [8]. Polymeric

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\*For the purposes of this report, polymeric materials refer to all synthetic or natural materials which have a repetitive molecular structure.

materials containing oxygen (polyurethane, polyesters, wood) produce inorganic and inorganic oxygenated species during degradation.

A further complication arises when oxidative degradation occurs since oxygen from the atmosphere can be incorporated into the thermal decomposition products of non oxygen-containing polymers. For example, oxidation of polyethylene, polystyrene and PVC produces carbon monoxide, carbon dioxide and water but oxygenated organic species do not usually arise via these routes [9].

The primary products (pyrolytic or oxidative) can be modified further by gas phase pyrolysis or by combustion. A gas phase pyrolysis zone may destroy thermally unstable species such as isocyanates [10] whereas a combustion zone can lead to destruction of toxic species (such as cyanides) with the generation of other hazardous species such as oxides of nitrogen [11].

Carbon monoxide which is usually the most important toxic product from fires can be generated in a number of ways, firstly as a pyrolysis product of oxygen containing fuels, secondly as a thermal-oxidative product of all organic fuels and thirdly as a combustion product of all flammable volatiles.

### *(2) Smoke*

Particulate matter of smoke can also be generated in a number of ways in fire. Smoke is generated (without flame) during the thermal or thermal oxidative degradation of fuels along with the production of primary products. A further, and very important route, is the smoke generated during the incomplete burning of volatiles during gas phase combustion. In this respect, fuels such as polystyrene which release aromatic volatiles usually give high smoke densities. An interesting point to note is that smoke released with a fuel-rich but vitiated fire atmosphere can be effectively destroyed when air entrainment allows flaming to occur some distance from the main fire zone.

### *(3) Flame retardants*

Flame retardants often interact in a complicated way to modify the production of or suppress the flammability of the primary degradation products [12]. Modern flame retardants are based widely on phosphorus and antimony (with halogen donor) compounds [4] and may need to be given careful consideration to ensure that the measures to suppress the ignitability and flammability of fuels do not also give rise to extreme toxicity products as has been the case with certain polyurethane foams [13]. In addition, the interaction between flame retardancy and smoke production needs to be firmly established.

## **4. Experimental methods and results**

At the Fire Research Station, the problems of the smoke and toxic hazards of fire atmospheres are being studied in a number of different ways. In-house work is of an 'analytical' nature and is linked to physiological data

by work carried out under contract at the Chemical Defence Establishment at Porton Down.

### (10) Analytical approach

For studies of the primary products, small samples of polymeric materials are decomposed in a furnace under inert (pyrolysis) or oxidative conditions at temperatures up to  $1000^{\circ}\text{C}$  and the products analysed by gas-chromatography-mass spectrometry [9, 14].

Additional decomposition apparatus and a special burner system are being used to study further pyrolysis and combustion of the primary volatile species [11].

In this way, information about the types and quantities of possible toxic species which may be present in fire gases in various situations can be ascertained [9, 14, 15]. This information is vital for the effective design of realistic full-scale fire tests.

Full-scale fire tests are carried out in a special compartment-corridor [15, 16], as shown diagrammatically in Fig. 2, which is designed to represent a fire situation in a room coupled with an open doorway to an escape route (corridor). The rig is fully instrumented for measurements of temperature, smoke release and toxic gases.

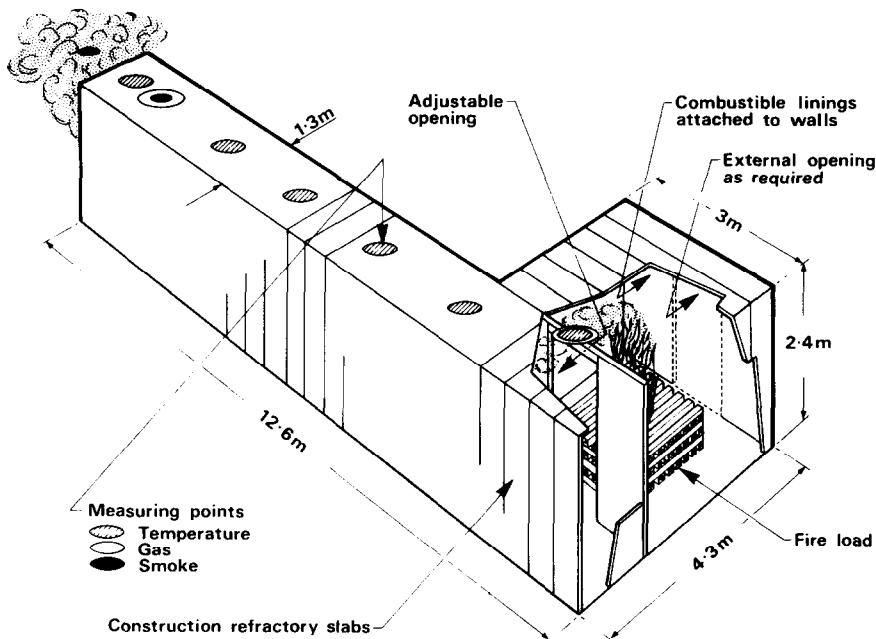


Fig. 2. Compartment-corridor.

### *(2) Behaviour of flexible polyurethane foams*

The initial decomposition process of flexible polyurethane foam involves the low temperature loss (200 to 300°C) of a nitrogen rich material [14] which has been termed 'yellow smoke', and appears to be a polymerised form of tolylene diisocyanate (TDI). This 'yellow smoke' is relatively stable but decomposes at temperatures in excess of 800°C to produce hydrogen cyanide and organic nitriles. The production of the 'yellow smoke' is accompanied by the release of a small proportion of free TDI [10].

Fire tests have shown that the hazard from hydrogen cyanide can be significant in the very high temperatures encountered during the burning of industrial loads of polyurethane foams [16]. The cyanide risk seems to be relatively low, in comparison with that of carbon monoxide, during fires involving domestic loads of these foams [17]. The hazard [17] from TDI during both industrial and domestic situations appears to be much lower than might be expected from decomposition data and may reflect the thermal instability of this product [17].

Because of the rapid rate of burning of polyurethane foams, particularly with industrial loads, there is a tendency for the smoke density to increase sharply to a high level which persists until the fuel has been consumed [1, 16].

### *(3) Behaviour of rigid polyurethane foams*

The initial decomposition processes of MDI rigid polyurethane foams and polyisocyanurates appear to be markedly different from the TDI flexible foams [18]. During degradation there is little or no preferential release of a nitrogen-rich polymer and the initial degradation products consist mainly of fragmented parts of the original polymers. These fragmented units decompose in excess of 800°C to produce a similar pattern of products (including hydrogen cyanide and organic nitriles) as observed with the flexible materials.

Further work to study the degradation of polyurethane and polyisocyanurate foams and their involvement in real fire situations is in progress. This work will include studies of polymers treated with organophosphorus flame retardants.

### *(4) Animal exposures*

The animal exposure studies involve rats and guinea pigs exposed to the fire gases from wood and a range of common plastics including PVC, flexible and rigid polyurethane foams. In this work, samples of material are burnt in a 10 m<sup>3</sup> chamber and the 50 per cent mortality rate compared with the expected value for the carbon monoxide alone to ascertain whether products, other than carbon monoxide contribute significantly to mortality. Experiments have been carried out with pure gases and combinations of gases to study synergistic effects [19].

Work to date with birch plywood (both with and without fire retardant)

shows that the fire gases are slightly more toxic than one would expect from carbon monoxide alone. This may be caused by the presence of irritants increasing the respiration rate of the animals during exposure.

With PVC—wood combinations, the released hydrogen chloride caused severe eye irritation and injury to the respiratory tracts and increased mortality, above that expected from carbon monoxide, was observed.

## 5. Discussion

An attempt has been made to present in this paper an overall view of the problems associated with fire atmosphere and particularly the production of toxic species.

Studies of fire properties such as temperature rise, heat release, rate of spread of flame and also smoke obscuration can be measured with physical instrumentation. There is no instrumentation available, or likely to be available, which can indicate the physiological or neurological action of fire gases and smokes.

Analytical studies, carried out over a wide range of decomposition conditions and real fire tests can give valuable information about the hazards of certain known toxic products but the ultimate assessment of toxic hazards of polymeric materials must involve experiments with live animals.

The Joint Fire Research Organisation is giving careful consideration to the problems of plastics in fires and currently about one tenth of the annual budget is involved in this way. This commitment includes the in-house and animal experiments (at Porton Down) and also considerable extramural research activity elsewhere. A detailed study of fundamental aspects of smoke production is being carried out under contract at Industrial Research Limited of Queen Mary College, London [20, 21] and the nature of smoke intermediates from polyurethane foams is being examined at King's College, London. In addition, the Rubber and Plastics Research Association at Shawbury are nearing the completion of a contract to study the fire behaviour of furniture and furnishings [22, 23].

## 6. Acknowledgement

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