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The effect of gas phase flame retardants on fire effluent toxicity

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ABSTRACT

Standard industry formulations of flame retarded aliphatic polyamides, meeting UL 94 V-0, have been burned under controlled conditions, and the yields of the major asphyxiants, carbon monoxide (CO) and hydrogen cyanide (HCN) have been quantified. Although both the combination of aluminium phosphinate and melamine polyphosphate, and the combination of brominated polystyrene and antimony oxide, inhibit combustion reactions in the gas phase, this study shows that the phosphorus causes a much smaller increase in the CO and HCN yields than antimony-bromine. The mechanisms of CO and HCN generation and destruction are related to the flame inhibition reactions. Both CO and HCN form early in the flame, and the OH radical is critical for their destruction. Crucial, in the context of the flame inhibition mechanism, is the observation that the phosphorus system reduces the H and O radical concentrations without a corresponding decrease in the OH radical concentration; conversely, the bromine system reduces all three of the key radical concentrations, H, O and OH, and thus increases the fire toxicity, by inhibiting decomposition of CO and HCN. Moreover, while the phosphorus flame retardant is effective as an ignition suppressant at lower temperatures (corresponding to early flaming), this is effect "switches off" at high temperatures, minimising the potential increase in fire toxicity, once the fire develops. Since flame retardants are most effective as ignition suppressants, and at the early stages of flaming combustion, while most fire deaths and injuries result from toxic gas inhalation from more developed fires, it is clearly advantageous to have an effective gas phase flame retardant which only causes a small increase in the toxic product yields.

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1. Introduction

1.1. Fire hazards

UK fire statistics [1] show that the main cause of death in fires, and the main cause of injury, arises from the inhalation of toxic effluents. To assess the contribution of a material, or a composite article (such as a chair or a fuse box) to the fire toxicity, it is necessary to know both the rate of fire growth and the yields of the different toxicants. The composition of these effluents depends on the chemical formulation of the burning material, oxygen supply, temperature and heating rate [2,3]. The most toxicologically significant products are asphyxiant gases and incapacitating irritants. The asphyxiants, carbon monoxide (CO) and hydrogen cyanide (HCN), decrease the oxygen supply to body tissue resulting in central-nervous-system depression, loss of consciousness and ultimately death. Irritant gases, such as acid gases, hydrogen chloride (HCl) and hydrogen bromide (HBr), certain hydrocarbons and their oxygenated decomposition products, cause immediate incapacitation, mainly by their effects on the eyes and upper respiratory tract, followed by longer term damage deeper in the lung [4].

Certain fire retardants inhibit the free radical reactions typical of flaming combustion. These gas phase "*flame* retardants" have been shown to increase the yield of carbon monoxide and hydrogen cyanide, both products of incomplete combustion [5,6].

Fires can be divided into a number of stages from smouldering combustion and early well-ventilated flaming, through to fully developed under-ventilated flaming (Table 1) [7]. A useful concept in characterising the gas phase flaming combustion conditions, and predicting the yields of products such as carbon monoxide (CO), carbon dioxide (CO_2), hydrogen cyanide (HCN) and hydrocarbons, is the equivalence ratio (ϕ), presented in Equation (1) [8].

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$$\phi = \frac{\text{actual fuel to air ratio}}{\text{stoichiometric fuel to air ratio}} \begin{matrix} \phi = 1 & \text{"stoichiometric" combustion} \\ \phi \ll 1 & \text{well} - \text{ventilated fires(fuel lean flames)} \\ \phi > & \text{under} - \text{ventilated fires(fuel rich flames)} \end{matrix} \quad (1)$$

When assessing fire toxicity, the toxic product yields show the greatest sensitivity to the combustion conditions. It is important to ensure that these are relevant to the full-scale fire scenario. It is therefore essential to the assessment of toxic hazard from fire that each fire stage can be adequately replicated, and preferably separating the individual fire stages. A number of different methods exist to assess fire toxicity [9], but most fail to relate the toxicity or toxic product yields to particular fire scenarios, or to replicate the most toxic under-ventilated conditions [3]. The steady state tube furnace (SSTF), ISO/DIS 19700 [10], was specifically designed to replicate individual fire stages. It is a bench scale tube furnace through which an 800 mm length of sample is driven at a fixed rate, inside a quartz boat. It is supplied with a fixed flow of primary air and the equivalence ratio, ϕ, can be controlled, in order to replicate different ventilation conditions. The heat fluxes in the SSTF have been reported [11]: at a furnace temperature of 650 °C the heat flux was 40 kW m^{-2}; at a furnace temperature of 825 °C the heat flux was 77 kW m^{-2}.

1.2. Fire toxicity

The contribution of individual toxicants to the overall toxicity can be expressed as a fractional effective dose (FED), described in an additive model of toxicity, as shown in Equation (2), based on rat lethality data to predict the toxicity of a fire effluent, ISO 13344 [12]. The concentration of each toxicant, X, is represented by [X] and each term is divided by the lethal concentration of that toxicant ($LC_{50,X}$); the individual contributions are summed to give the overall toxicity, described as the fractional effective dose (FED). When the sum exceeds 1.0, the effluent would be lethal to 50% of the exposed population. A more sophisticated approach recognises that incapacitation, rather than actual death, is the critical event in terms of fire safety. This has been defined in ISO 13571 [13] using consensus estimates of human response to toxicants. The measurements from the SSTF are suited to both approaches, but only the simpler rat lethality model is used here. Experimental toxic product yields can be normalised to a fixed mass/volume loading. In this work, a fuel mass-charge concentration of 20 g m^{-3} is used. This is equivalent to a fuel mass of 1 kg in a 50 m^3 room.

$$\text{FED} = \left\{ \frac{[CO]}{LC_{50,CO}} + \frac{[HCN]}{LC_{50,HCN}} + \frac{[HCl]}{LC_{50,HCl}} + \frac{[NO_2]}{LC_{50,NO_2}} + \ldots + \text{organics} \right\} \times V_{CO_2} + A + \frac{21-[O_2]}{21-5.4}$$
$$V_{CO_2} = 1 + \frac{\exp(0.14[CO_2])-1}{2} \quad (2)$$

A is an acidosis factor equal to $[CO_2] \times 0.05$.

1.3. Toxic product yields of polyamide 6.6

Previous reports [3,14] of the fire toxicity of polyamide 6 have shown that combustion is efficient at low equivalence ratios with low yields of CO, HCN and organics, all of which increase as the equivalence ratio exceeds 1. The yields for CO and HCN increase with decrease in ventilation, or increase in ϕ. In well-ventilated combustion conditions the CO yield was low, but increased steeply to a maximum of 0.32 g/g at $\phi = 2.3$. The yield of HCN, another product of incomplete combustion, also increases with increasing ϕ. The individual toxicant yields are shown in Fig. 1, as a function of equivalence ratio.

Equation (2) can be applied to toxic product yields, such as those shown in Fig. 1, in order to predict the toxicity of the effluent. This shows that for polyamide 6, the effluent toxicity and particularly the contribution of HCN grows significantly with under-ventilation, and increasing severity of fire. FED values of 6 or 8 may be interpreted as a polymer loading of 167 g or 125 g, respectively, burning in a 50 m^3 room, under the specified conditions, will be lethal to 50% of the occupying population in 30 min exposure. The contribution of each toxic species to the FED has been calculated, and is presented in Fig. 2.

This shows that in well-ventilated conditions, ($\phi << 1.0$) the toxicity is low. For under-ventilated conditions ($\phi > 1.0$), the most significant contribution to the toxicity comes from HCN.

1.4. Fire hazards relating to electrical and electronic applications

Glass reinforced polyamides are particularly common in electrical connectors and fuse boxes. The hazards presented by fire in electrical and electronic applications are rather different to those of larger or bulkier items, such as upholstered furniture or flammable insulation materials [15]. In the latter cases, once ignition occurs, fire growth will be rapid until it is controlled by the availability of oxygen, when it will continue to burn with $\phi > 1$. In contrast, electrical and electronic components are at a higher risk of ignition due to the heating properties of electric currents, often under forced ventilation, but individual units tend to be smaller and better separated from other sources of fuel. Thus, while the under-ventilated fire is the most likely scenario for fire hazard assessment involving upholstered furniture, for a fuse box, or connector, it is more appropriate to focus on the fire toxicity in well-ventilated conditions.

1.5. Flammability and fire toxicity regulation

In Europe, the fire safety requirements for connectors and switches include IEC 60898 for circuit breakers, IEC 60947 for industrial control equipment and IEC 60335 for domestic appliances. The US Underwriters Laboratories (UL) standards have been widely

Table 1
Stages of a fire (adapted from ISO classification) [7].

Fire stage	Max temp/°C		Typical values	
	Fuel	Smoke	Equivalence ratio ϕ	CO/CO_2 ratio
Non-flaming				
1a. Self-sustained oxidative pyrolysis (e.g. smouldering)	450–800	25–85	–	0.1–1
Well ventilated flaming				
2. Well ventilated flaming	350–650	50–500	0.5–0.7	<0.05
Under ventilated flaming				
3a. Low ventilation room fire	300–600	50–500	1.5–2	0.2–0.4
3b. Post flashover	350–650	>600	1.5–2	0.1–0.4

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