

Practical Guide to Smoke and Combustion Products from Burning Polymers - Generation, Assessment and Control

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Preface

In the context of fire, smoke can have several meanings. According to definitions from both the American Society for Testing and Materials and the National Fire Protection Association, smoke comprises all the airborne solid and liquid particulates and the gases evolved when a material undergoes pyrolysis or combustion. By this definition, smoke includes also the volume of air entrained with, and contaminated by, the combustion products and generally somewhat depleted in oxygen. One common meaning is that smoke is a cloud of particles, generally individually invisible, which is opaque as a result of absorption or scattering of visible light. A dictionary definition is 'the volatilized products of combustion'. From a measurement standpoint, smoke is often loosely meant to signify visible smoke, i.e., the light-obscuring fraction of the more broadly defined smoke, as it might be measured by a photocell and standard light source. The dark, mostly solid, material emitted from fires and often loosely called smoke, particularly in the context of smoke damage or smoke deposition on surfaces, is more properly called soot. In fact, smoke encompasses four aspects: smoke obscuration (the most common usage), smoke toxicity, smoke corrosivity and the sum of combustion/pyrolysis products.

The importance of smoke, both visible and invisible, is self-evident. From the point of view of smoke obscuration, visible smoke, of course, interferes with the ease of fire victims to escape or be rescued. On the other hand, it has been pointed out that smoke can serve as a fire warning, both visual and olfactory, since smoke usually includes odorous materials (such as acrolein from cellulose, halogen acids and other malodorous or irritating decomposition products from various natural or synthetic polymers). From the point of view of smoke toxicity, autopsy data shows that about two-thirds of fire fatalities are caused by smoke inhalation and not by burns. However, those fire fatalities almost invariably occur in fires that have grown very large (have resulted in very high heat release rates). From the point of view of smoke corrosivity, smoke is usually corrosive and that can affect exposure of metals and of electronic circuitry. However, this is usually a property protection issue and not a life safety issue.

It is important to note that smoke generation is not an intrinsic property of any polymer, but depends on the size and shape of the associated flame and on a number of environmental variables, including oxygen availability. Smoke also depends on the nature of the polymer(s) undergoing combustion and on the presence of modifying additives in the polymer.

1 Smoke Obscuration/Opacity: Generation of Smoke from Polymeric Materials

1.1 Introduction

A recent review on smoke production from burning polymers and smoke suppression was published by LeBras and co-workers [1]. The reader also can find an introduction to the theory of smoke formation in older books by Cullis and Hirschler [2] and Aseeva and Zaikov [3]. As was already mentioned in the Preface, smoke generation is not an intrinsic property of a particular polymer, but depends on the size of the flame and oxygen availability (draft). Smoke generation also depends on the nature of the polymer and whether or not any modifying additives are present. This chapter will discuss the formation of visible smoke particles (soot). In this chapter, the terms ‘visible smoke’ and ‘soot’ are used interchangeably, but it should be noted that soot is often assessed gravimetrically (and thus refers to the mass of smoke), whereas visible smoke is usually assessed optically (and thus refers to the light obscuration by smoke).

1.2 Parameters of Smoke Obscuration

1.2.1 Maximum Specific Optical Density of Smoke

This parameter is typically measured by the National Bureau of Standards (NBS) smoke chamber and other static smoke tests. It is calculated as a maximum specific optical density achieved in the test chamber during the experiment. The specific optical density is calculated as the logarithm of light obscuration normalised to the volume of the chamber, the exposed area of the specimen and the length of the light path [4].

1.2.2 Smoke Developed Index

This parameter is specific to the Steiner Tunnel American Society for Testing and Materials, ASTM E84 test [5]. It is the ratio of the area under the curve of optical density of smoke (time integral of light absorption) for the tested specimen relative to

the area under the curve for the smoke density of a standard red oak flooring sample, multiplied by 100. Smoke densities are accumulated over a 10 minute test period.

Smoke parameters measured in the cone calorimeter and other dynamic tests have been reviewed by Hirschler [6].

1.2.3 Average Specific Extinction Area

Average specific extinction area is the instantaneous amount of smoke being produced by the sample, per unit mass of sample burned. The results are expressed in units of m^2/kg . This is the original method of expressing smoke obscuration results for the cone calorimeter, and it is unique to instruments that can continuously measure sample mass together with the fraction of light transmitted. The average specific extinction area results may be used as input data in some fire models to estimate the smoke obscuration performance of products in large-scale fire tests. Full-scale and small-scale results have been shown to correlate well only for products that burn up completely in the large-scale test.

1.2.4 Rate of Smoke Release

Rate of smoke release (RSR) is the instantaneous amount of smoke being released by the sample as it burns in the cone calorimeter, per nominal sample surface area. Results are expressed in units of $1/(\text{s m}^2)$. The specific extinction area is related to the RSR by the ratio of the mass loss rate relative to the sample area. Thus, the RSR is a more direct measurement property (volumetric flow rate times optical density divided by sample area times light-path length) than the specific extinction area. It is similar to specific smoke density measured in the NBS chamber.

1.2.5 Total Smoke Released

Total smoke released is the measure of accumulative smoke obscuration per unit of nominal sample surface area and corresponds to full sample destruction. The total amount of smoke released is, thus, unlikely to represent most real fire scenarios, in which samples are not normally totally destroyed. The total smoke release is calculated as the time integral of the RSR data and is expressed in units of $1/\text{m}^2$.

1.2.6 Smoke Factor

Smoke factor is a parameter of smoke/fire hazard used to estimate the potential amount of smoke that a product would generate under full-scale fire conditions. It is calculated by incorporating the burning rate at the peak rate of heat release. This takes into account the fact that those products made from materials with low peak rate of heat release are less likely to burn up completely in a fire, and will, furthermore, cause less smoke to be generated from the ignition of other products. This measure is calculated as the product of the total smoke released and the peak rate of heat release.

1.3 Visible Smoke (Soot) Formation

Although polymers have some specific features in terms of smoke formation, the general mechanism is similar for smoke formation from any organic material, including organic liquids and gases. Smoke formation has been extensively studied for mixtures of hydrocarbon gases and air in premixed flames. A premixed flame cannot be observed in the combustion of polymeric and other solid material, but serves as a model for understanding some aspects of smoke formation. Premixed flames help in establishing a critical air/fuel ratio below which soot formation doesn't occur. For example, for aliphatic hydrocarbons this ratio is about 10:1, and it doesn't depend very much on the molecular weight (M_w) and structure of the hydrocarbon. Oxygen-containing compounds (alcohols, ketones and so on) have much lower critical values.

Diffusion flames are typically found in the combustion of polymers. These flames are more sensitive to the nature of the fuel in terms of smoke formation. The beginning of smoke formation in diffusion flames can be measured simply by the size of the flame. Small diffusion flames are not smoky, but increasing the size of the flame, which can be done by increasing the fuel supply or the burning surface, eventually leads to a smoky flame. In terms of smoke (soot) formation, low M_w hydrocarbons can be ranked as follows: *n*-paraffins < branched paraffins < cycloparaffins < cyclic olefins < acyclic olefins < acetylenic hydrocarbons < alkylbenzenes < naphthalene derivatives < higher polycyclic aromatic hydrocarbons. Some oxygen- or nitrogen-containing compounds, such as methanol or urotropin (methenamine), do not produce smoke in diffusion flames of any size. Since methenamine burns without smoke, it has been a good choice of fuel for the 'pill test' for carpet flammability.

The formation of carbon particles can be detected inside the flames of burning polymers. A yellow luminous zone near the surface of a burning polymer is an indication that soot particles are being formed in the low-temperature zone of the flame. If particles of soot do not have time to burn when they pass through the high temperature flame zone, then smoke will be seen emanating from the tip of the flame. Transparent flames

produced by aliphatic nylons and some oxygen-containing aliphatic polymers are indicative of a very low tendency toward smoke formation.

The mechanism of soot formation is complex and is not completely understood. However, it is believed that acetylene or its derivatives, or the ethynyl radical C_2H -derived from acetylene, play an important role in soot formation independently of the hydrocarbon fuel burned. Acetylenic species are involved in polymerisation and formation of aromatic rings and in substitution reactions with already formed aromatic rings, which thus facilitate condensation and formation of polycyclic aromatic hydrocarbons (PAH).

The most interesting step in soot formation is the initiation of a new solid phase, which then serves as nuclei for particle growth. Only a few theories in the literature suggest the mechanism of initiation of the solid phase in the flame. One old theory suggests that gaseous fuel, if not oxidised and burned out, can achieve supersaturation such that small droplets of the liquid will be formed [3]. Dehydrogenation of the hydrocarbons in the droplets leads to polymerisation, aromatisation and condensation of aromatic rings. Formation of fog has actually been observed in acetylene flames, with the droplets changing colour from light yellow to black when travelling through the flames [7]. Interestingly, addition of hydrogen to a diffusion flame decreases smoke formation, which proves that dehydrogenation is an important reaction in the formation of soot particles. If the air supply to the flame is limited, soot particles can have liquids absorbed on their surface, which are hydrocarbons not able to undergo dehydrogenation and graphitisation because of the flame's low temperature.

Another theory suggests that positively charged hydrocarbon fragments serve as initiators of nuclei formation [8]. It is believed that fuel molecules will condense around electrically charged fragments, and the formed cluster will continue bearing a positive charge. Theoretical calculations confirm that, in the presence of ionic particles, hydrocarbons can form droplets at concentrations significantly below the saturation point. The clusters keep the positive charge until they grow to the size of 2-3 nm, after which individual molecules begin to condense and redistribution of the charge may occur. Further dehydrogenation increases the electrical conductivity of the particles, affecting both the electrostatic forces of their interaction and the particles' secondary aggregation processes. According to this theory, retention of the charge at the stage of soot crystallite growth implies the presence of ion-molecule or ion-radical reactions with the participation of both positively and negatively charged ions.

The free-radical theory was developed in great detail and accompanied by extensive computer modelling [9]. The main argument against this theory is the premise that neutral molecules (radicals) cannot possibly explain the fast growth of the particles [10], however, detailed kinetic modelling has proven that free-radical reactions can

be quick enough to support rapid particle growth. This theory proposes four steps in soot particle formation: (1) formation of the initial aromatic ring from aliphatic hydrocarbons; (2) formation of the planar PAH system; (3) particle nucleation consisting of coalescence of PAH into three-dimensional clusters; and (4) particle growth by coagulation and surface reactions. The formation of PAH (first and second step) was kinetically modelled by 729 reactions with the participation of 93 species [11]. Detailed modelling of the third and fourth steps has been published elsewhere [9].

Kinetically, soot particle surface growth can be described in terms of a first-order thermal decomposition of fuel on the surface. Hydrogen concentration in the soot is important in determining its reactivity with fuel at the surface of the soot. The surface growth rate increases steeply with decreasing hydrogen content.

The properties of the carbon particles formed in different flames are very similar. Usually, soot particles contain between 1% and 4% residual hydrogen. The particles present in the soot are spherical and consist of separate crystallites of graphite. Graphite crystallites are disoriented. This type of structure is characteristic for early stages of graphitisation and is called ‘turbostratic char’. The average diameter of soot particles ranges from 10-50 nm, but single particles can have diameters as small as 0.2 nm and as large as 20,000 nm. The particles tend to form necklace-type strings, but do not combine into bulk agglomerates. Grown soot particles are chemically inert because graphite sheets comprising them tend to close into a spherical shell, eliminating reactive edges on the surface.

1.4 Polycyclic Aromatic Hydrocarbons

Various types of aromatic compounds have been found in flames of fuels that don't contain aromatic structures themselves. These compounds include benzene, alkyl- and alkylene-substituted benzenes, partially hydrogenated cyclic polyacetylenes and PAH. All of these compounds easily react with free radicals and thereby increase their M_w . The tendency of aromatic compounds to contribute to soot formation can be ranked in the following order: benzene < cyclooctatetraene < styrene < naphthalene < toluene < 2-methylnaphthalene < phenanthrene < anthracene < 2-methylantracene. Evidence has shown that pyrene is less prone to form soot than anthracene. Interestingly, methyl-substituted aromatics (such as toluene) have a higher tendency toward soot formation than do higher-condensation products (such as naphthalene).

The occurrence of polycyclic aromatic hydrocarbons (PAH) in the environment has been intensively studied. PAH are produced when natural materials like wood, coal and so on, are burned, but burning plastics sometimes produce more abundant concentrations of PAH. More often, PAH containing three or four fused rings

(pyrene, anthracene, phenanthrene and so on) are found in the flames. This suggests that aromatic hydrocarbons with three or four rings are more stable than those with one or two rings, and that PAH are formed by similar mechanisms in the flames of polymers and simple fuels.

The most common PAH formed from burning plastics is phenanthrene. Stilbene and biphenyls are typically formed from burning polystyrene. Comparative studies of the combustion of polyvinyl chloride (PVC), polyethylene, and polystyrene have shown that polystyrene produces larger numbers of PAH in the sooty material. Some of the PAH resulting from polystyrene combustion differ from those from other polymers, e.g., oxygenated PAH and PAH with fused rings can be found in polystyrene smoke.

In smoke, PAH can be located both in the gas phase and in the aerosol fraction. PAH can also be found adsorbed on the surface of soot particles. PAH found on the surface are often relatively nonreactive hydrocarbons that were absorbed by condensed nuclei, but didn't react with the nuclei and didn't participate in the graphitisation. Careful sampling is required in order to determine the total PAH content in the smoke.

It is believed that PAH are stable by-products of the combustion reaction, rather than intermediates escaping the flame [8]. The same type of PAH with three or four rings are formed from different polymers with different tendencies to produce soot. It is believed that soot formation is due not to the presence or concentration of PAH, but rather to the aliphatic substituents on the PAH and their reactivity. For example, PVC gives a concentration of substituted PAH that is 16 times higher than that of polypropylene. Substituted PAH are more reactive and can result in a more efficient chemical build-up of multi-ring structures, which, in turn, lead to soot nuclei. Kinetic considerations indicate that this mechanism of formation is likely to involve ionic intermediates. Subsequent growth occurs by surface reactions and agglomeration processes.

1.5 Chemical Structure of Polymers in Relation to Smoke

Smoke formation during diffusion combustion of polymers depends on the polymer structure, the mechanism of thermal decomposition and the conditions of the pyrolysis and oxidation processes. As a general rule, aliphatic polymers (e.g., polyethylene, polypropylene, ethylene-vinyl acetate [EVA]) tend to produce little smoke. Polypropylene produces more smoke than polyethylene, which is consistent with the observations for low M_w hydrocarbons, in which branched molecules produce more smoke than their linear analogs.

Oxygen-containing polymers, such as polyacrylics and polyacetals, form mainly oxygen-containing nonaromatic products of thermal decomposition, which contribute little to the formation of smoke. Polymethyl methacrylate, which is very flammable because it tends to depolymerise, produces very little smoke. Polyoxymethylene depolymerises almost quantitatively to formaldehyde, which burns with a clean blue flame. Aliphatic nylons produce ammonia, carbon dioxide, amines, nitriles and oxygen-containing fragments. Very little smoke is observed from aliphatic nylons, with white smoke from nylon 6 probably comprised of caprolactam monomer crystals.

Thermoplastic polyesters (polyethylene terephthalate and polybutylene terephthalate) contain aromatic rings in the main chain, however, these rings are well separated by aliphatic chains. Such rings are probably deactivated by their carbonyl substituents such that they do not condense easily to produce polyaromatic species, therefore, they tend not to be as smoky as styrenic polymers. However, polyesters are smokier than nylons. Polyesters decompose by a statistical chain scission mechanism that liberates oligomeric fragments, terephthalic acid, aldehydes and alkenes. Thermoplastic polyurethanes behave similarly to polyesters. Polyurethanes undergo depolymerisation, regenerating isocyanates and polyols. Smoke is mostly produced from aromatic isocyanates, but can be further contributed to by aromatic polyols. Polycarbonates contain the bisphenol A fragment in their polymer chain, and that is the moiety responsible for smoke formation. Polycarbonates produce heavier smoke than thermoplastic polyesters. High-performance thermoplastic polymers, such as polyphenylene sulfide, polyether sulfones, polyether ether ketones, polyimides and aromatic polyamides, have inherently high fire performance because of their high tendency to char. These polymers produce very little smoke even though they have a high content of aromatic structures.

Among nonhalogenated thermoplastic polymers, polystyrene and its copolymers [high-impact polystyrene (HIPS), acrylonitrile-butadiene-styrene and styrene acrylonitrile] have the highest tendency to form copious black smoke. To a great extent, polystyrene decomposes via depolymerisation and also generates small chain fragments. As was discussed earlier, substituted aromatic hydrocarbons, especially those with unsaturated substituents, tend to produce more smoke than even PAH. Despite the presence of a highly charring component, polyphenylene ether/HIPS blends are also smoky because of the HIPS component.

Aliphatic elastomers do not form much smoke unless styrene is present in the copolymer chain. Rubbers give denser smoke if they are filled with carbon black. Polymethylsiloxane elastomers produce whitish smoke, due to volatilisation of silicone fragments that burn to form silica particles; however, siloxane elastomers with phenyl substituents can produce significant amounts of black smoke.

In general, thermoset polymers generate less smoke than similar thermoplastic polymers because crosslinks in thermoset polymers help retain more fuel in the condensed phase and produce more char. Crosslinks also stop propagation of dehydrogenation reactions and formation of conjugated dienes. However, some thermoset polymers, those which contain aromatic rings, still produce significant amounts of smoke. For example, unsaturated polyesters crosslinked with polystyrene bridges produce very dense smoke. Bisphenol A epoxy resins and novolac epoxy resins also give off significant smoke. On the other hand, phenol-formaldehyde resins, in spite of their structures' very high aromatic content, produce very little smoke because they yield abundant char, which keeps most of the aromatic species in the condensed phase. Very little smoke is produced from melamine- and urea-formaldehyde resins because they have high nitrogen content and yield significant char.

Figure 1.1 shows data on the evolution of total smoke from insulation building panels as measured in a half-scale room fire test [12]. As can be seen, phenolic foam produces very low smoke, almost as low as the background smoke that comes from the burning plywood (reference in Figure 1.1). On the other hand, polystyrene foam produces the highest smoke opacity.

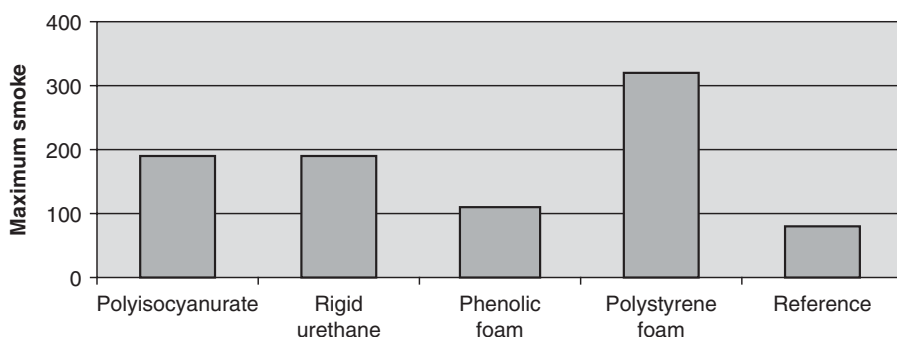


Figure 1.1 Total smoke evolved from insulation materials measured in the half-scale room-burning test. Based on data from T. Morikawa and E. Yanai, *Journal of Fire Sciences*, 1989, 7, 2, 131 [12]

Smoke production from rigid polyurethane foams and from isocyanate foams depends mostly on the chemical structure of the polyol component and on the isocyanate index. Polyester polyols tend to generate more smoke than Mannich-type nitrogen-containing polyols. The higher the isocyanate index in the foam, the less smoke it produces, because isocyanurate rings formed from the excess of isocyanate are thermally stable and tend to maintain foam integrity even when the foam is exposed to high temperatures and undergoes severe charring. Figure 1.2 shows the results of

Steiner Tunnel, ASTM E84 [5], testing of various construction insulation foams. There is no correlation between the flame spread index and the smoke developed index. In general, polyurethane foams, especially lower isocyanate index spray foams, produce more smoke than isocyanurate foam panels.

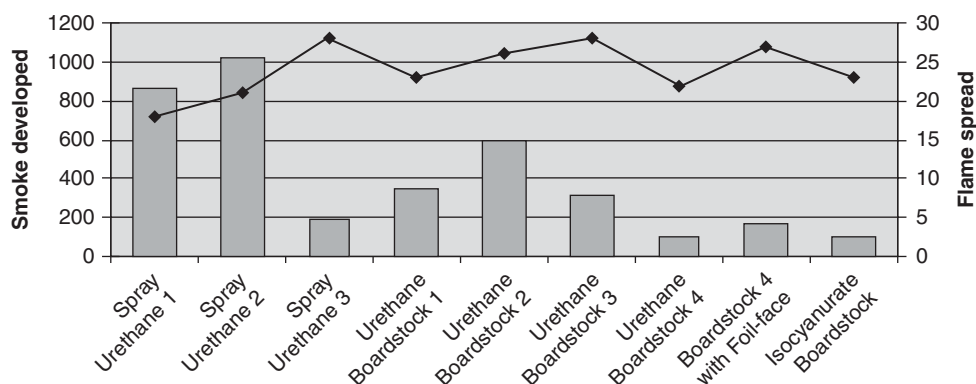


Figure 1.2 Smoke developed index and flame spread index of insulation building materials measured in the ASTM E84 test [5]. Based on data from J. Kracklauer in *Flame-Retardant Polymeric Materials*, Eds., M. Lewin, S.M. Atlas and E.M. Pearce, Plenum Press, New York, NY, 1978, 2, 285 [13]

PVC is a commercially very significant polymer. Given the fact that PVC is present in many construction materials and cables, smoke formation from PVC has been investigated very extensively. A large number of technical papers and reviews on the mechanisms of thermal decomposition of PVC are available [14–17]. Thermal decomposition of PVC starts with the evolution of hydrogen chloride (HCl) via a chain mechanism called ‘zipper elimination’ or ‘unzipping’. It is believed that slow elimination of HCl starts at polymerisation defects in the chain, which creates isolated double bonds. After this, dehydrochlorination proceeds very rapidly because of the activation of chlorine in allylic positions. Although the early stages of the thermal decomposition of PVC have been investigated very thoroughly because of the need for stabilisation of PVC, the secondary processes at higher degrees of HCl loss have received less attention [14].

The process of formation of conjugated polyenes usually stops at sequences shorter than approximately 25 double bonds. The polyene sequences undergo further reactions, one of which is an intermolecular Diels-Alder condensation (**Figure 1.3**) resulting in crosslink formation. Another reaction (**Figure 1.4**) is a cyclisation reaction leading to chain scission and generation of benzene and other aromatics.

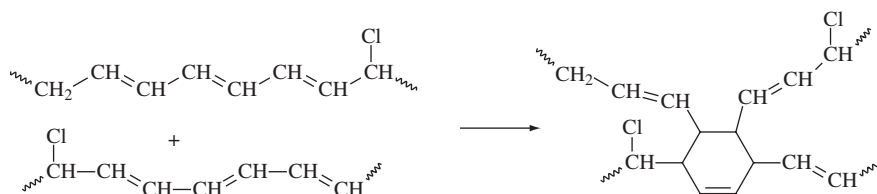


Figure 1.3 Intermolecular Diels-Alder reaction of decomposition of PVC

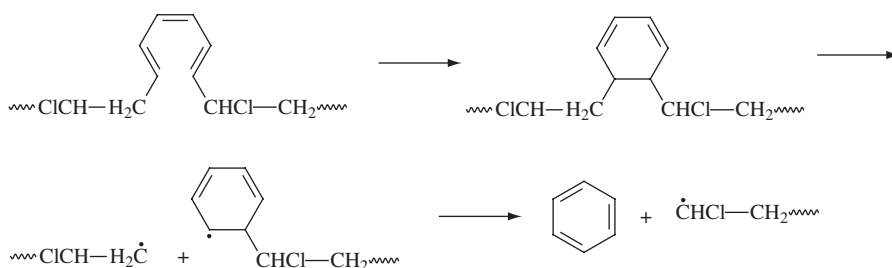


Figure 1.4 Cyclisation with chain scission in decomposition of PVC

At higher temperatures (550 °C), other conjugated aromatic volatiles such as styrene, naphthalene, biphenyl and anthracene are formed via intramolecular cyclisation. Mixed aromatic-aliphatic pyrolysates (toluene, indene, methylnaphthalene) are formed at least partially via intermolecular (crosslinking and hydrogen transfer) processes. The fact that benzene and other pyrolysates go into the flame zone is one of the factors most responsible for the copious smoke formation from PVC. An HCl aerosol is also believed to contribute to smoke obscuration when PVC burns, but the HCl is absorbed very quickly by soot particles and other objects and doesn't travel far (see **Chapter 4**). Nonplasticised PVC typically produces a remarkable 17 wt% char in spite of the aliphatic nature of the polymer. HCl evolution and high char yield make PVC a polymer with inherently high fire performance.

Smoke formation from chlorinated aliphatic polymers is not proportional to the chlorine content. For example, chlorinated polyethylene containing only 20 wt% chlorine shows the same smoke density as PVC having 59 wt% chlorine. Further chlorination of PVC to 65 wt% (to yield chlorinated PVC or post-chlorinated PVC) results in a roughly 50% decrease in smoke production [18]. Polyvinylidene dichloride (PVDC) has two chlorine atoms per every vinyl group (75 wt% chlorine) and is very low in smoke formation. Elimination of HCl from PVDC leaves behind pure carbon, which doesn't volatilise easily into the gas phase.

Nonflaming combustion results in very similar amounts of smoke and PAH from different polymers, e.g., PVC and polypropylene [19]. The products of nonflaming combustion include liquid (and possibly some solid) organic compounds that are not carbonaceous soot, as well as the products of typical flaming combustion. The particle size is larger in nonflaming combustion. This suggests that pyrolysis products undergo further reactions in the flaming mode, whereas they undergo condensation in the nonflaming mode. The observed liquid drops are thus simply the result of physical condensation of high M_w pyrolysis products. The lower temperature in nonflaming combustion also does not favor dehydrogenation, therefore, carbonisation is not as pronounced.

1.6 Effects of Metals on Soot Formation

In early systematic studies of smoke-particle formation, it was noticed that additives containing metals can have profound effects on smoke formation [20]. For example, when metal oxides or salts were injected in to a propane-deficient oxygen diffusion flame, some metals showed significant smoke reduction, with barium being the most efficient [21].

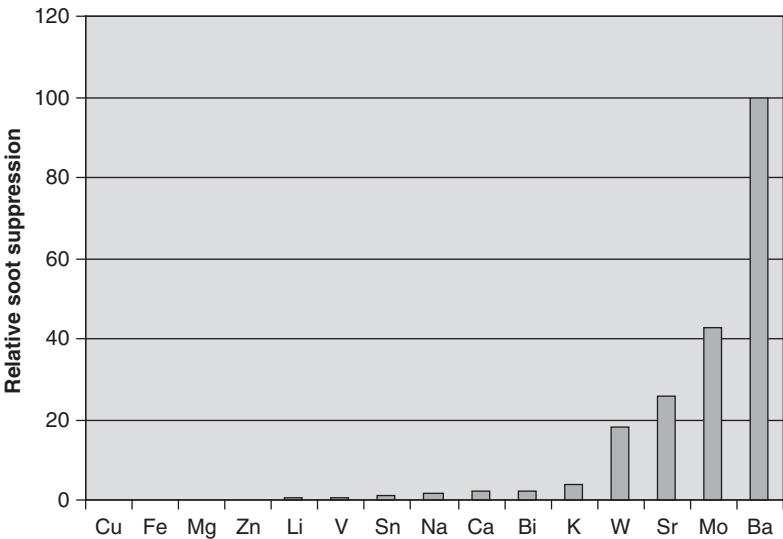


Figure 1.5 Relative efficiency of some metals in smoke reduction of propane-oxygen flame normalised to barium = 100. Based on data from D.H. Cotton, N.J. Friswell and D.R. Jenkins, *Combustion and Flame*, 1971, 17, 1, 87 [21]

Figure 1.5 shows the relative efficiency of some of the investigated metals in decreasing smoke production. The most efficient metals after barium included strontium, molybdenum and tungsten. It was also noticed that barium decreases total soot production, but doesn't affect median particle size, which led to the conclusion that barium most likely affects the nucleation process, probably by shifting equilibrium reactions toward a higher concentration of OH radicals that are able to oxidise carbon particle nuclei [20].

However, another study with barium oxide produced paradoxical results [22]. It was shown that the effect of barium, as well as of other alkaline earth metals, depends very much on what flame zone the metal species are introduced into. For example, barium species behave as effective smoke suppressants when they are introduced in the preheated zone, but they become smoke promoters if introduced in the luminous diffusion flame. It was also noted [20] that the overall effect of metals on smoke suppression/promotion correlates with their ionisation potential, e.g., the ability of the metals to easily release electrons and neutralise positive charges of the smoke nuclei. It was speculated that neutral smoke nuclei can easily agglomerate and create bigger particles, which do not oxidise in the luminous diffusion flame.

Overall, it is believed that metal ions may have two distinct mechanisms in their effect on smoke formation: They either decrease the rate of nucleation (destroying primary carbon particles) in the low temperature part of the flame, or they catalyse oxidation of the formed carbon particles in the hotter parts of the flame. Interestingly, it was found that manganese(II)sulfate can significantly decrease PAH formation in products of pyrolysis of polystyrene, even in inert atmospheres [23]. It is believed that Mn(II) interferes with the reaction of phenyl radicals and acetylene, which is a key reaction in the formation of polycyclic aromatic structures (PAH).

The effects of metal compounds, in particular Mo, Cu and Zn compounds, in controlling smoke from burning PVC is a commercially important topic dealt with in **Chapter 6**. The proposed condensed-phase mode of action is also discussed there.

1.7 Effects of Flame Retardants

The role of flame retardants in smoke formation is a controversial subject and should be considered not only with respect to increased visual smoke density, but also with regard to the total smoke produced and potential fire hazard. The role of flame retardants and smoke suppressants in the different aspects of smoke hazard will be discussed in detail in **Chapters 4, 5, 6 and 8**. In this chapter, we will discuss only the role of flame retardants in smoke obscuration (soot formation).

From observations of diffusion flames, it is known that the addition of hydrogen halides (e.g., HCl, hydrogen bromide) or halogen-containing aromatic compounds

increases the formation of visible soot. This relates to the inhibition of free-radical flame reactions, and the resulting decrease in the temperature of the flame causes incomplete combustion of the carbonaceous fuel. Therefore, chlorine- or bromine-containing flame retardants may potentially increase smoke production per mass unit of polymer burned. **Figure 1.6** shows the effect of the concentration of a brominated flame retardant on the smoke density from burning polystyrene. As can be seen from the graph, the specific optical density as calculated per gram of burned material increases, but the total smoke actually decreases. The burning rate of flame-retarded materials is usually lower than that of non-flame-retarded ones; therefore, the rate of smoke generation may also be lower even if the specific smoke density is high.

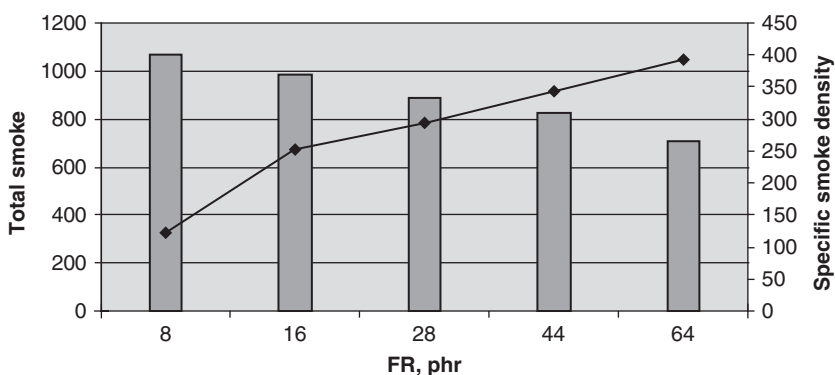


Figure 1.6 Influence of decabromodiphenyl oxide-antimony trioxide (ratio 3:1) loading on smoke generation of polystyrene. FR = flame retardant. Based on data from R. Chalabi and C.F. Cullis, *European Polymer Journal*, 1982, 18,12, 1067 [24]

In some cases, smoke obscuration is insignificant or not detectable when flame-retarded plastics do not ignite or extinguish immediately. This is illustrated in **Figure 1.7**, where light-absorption data for flame-retarded ABS plastics is measured in the smoke densitometer apparatus [25]. In these experiments, the flame retarded polymer was forced into continuous burning because the oxygen concentration was held above its self-extinguishment level (or limited oxygen index LOI). In this series, higher smoke production was observed as the fraction of the bromine flame retardant was increased in the plastic. However, when the same samples were burned in the air atmosphere, non-flame-retarded ABS showed the highest smoke obscuration in the series, followed by the 5 wt% bromine flame retarded sample, which burned slowly. ABS with 10 and 15 wt% flame retardant didn't produce any measurable smoke, because the materials extinguished immediately. Phosphorus-based flame retardants, which are normally active in the gas phase, exhibited similar performance.

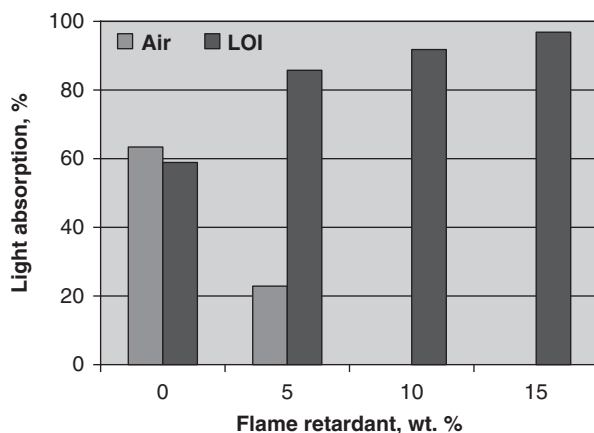


Figure 1.7 Smoke obscuration from ABS thermoplastics with bromine flame retardant. Based on data from J. DiPietro and H. Stepniczka, *SPE Journal*, 1971, 27, 2, 23 [25]

Flame retardants that operate at least partly, in the gas phase through a flame-cooling mechanism like melamine, melamine cyanurate or metal hydroxides [aluminum trihydrates (ATH) and magnesium hydroxides (MDH)] tend to decrease smoke density even if the polymer is forced to burn. This is attributed to the dilution of the flame with non carbonaceous gases and a decrease in the size of the flame. When ATH or MDH are introduced into the polymer, they act, like any inert filler, as a heat sink and also decrease the total amount of material burned. Significantly lower burning rates also contribute to a low rate of smoke production. Some soot is also absorbed on the aluminum and magnesium oxides formed, which have a very high surface area. **Figure 1.8** shows data from tests in the Steiner Tunnel, ASTM E84 [5], with polyester panels. The addition of ATH results in a significant decrease in both the smoke developed index and the flame spread index. The use of finely ground ATH is even more advantageous. Another example is shown in **Figure 1.9**, where significant smoke suppression from ABS is observed with an increase in the concentration of ATH. The LOI of ABS increases with an increase in ATH loading.

Condensed phase active retardants normally show a decrease in smoke obscuration because they promote charring of the polymer. Examples of such flame retardants are some phosphorus-based flame retardants, intumescent systems and borates. Small flame size and slow burning rate also help lower the smoke evolution rate. For example, cone calorimeter experiments of unsaturated polyesters flame-retarded with ammonium polyphosphate showed significant reduction of smoke evolved, which correlated with a decrease in the heat release rate [27]. Addition of zinc borate or nanoclay helps to further decrease smoke release.

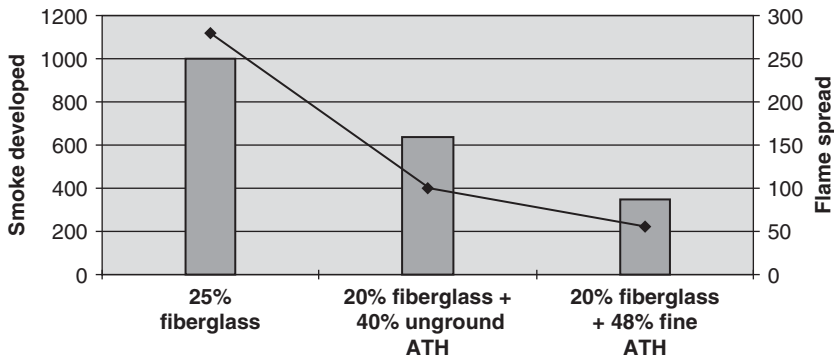


Figure 1.8 Smoke developed index and flame spread index measured in the ASTM E84 test for polyester fibreglass panels with added ATH. Based on data from J. Kracklauer in *Flame-Retardant Polymeric Materials*, Eds., M. Lewin, S.M. Atlas and E.M. Pearce, Plenum Press, New York, NY, 1978, 2, 285 [13]

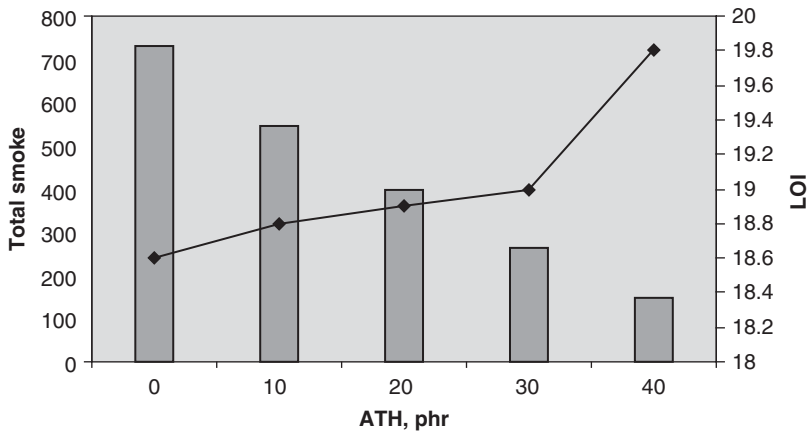


Figure 1.9 Smoke suppression by ATH in ABS plastic. Based on data from M.M. Hirschler, *Polymer*, 1984, 25, 3, 405 [26]

Although flame retardants may affect smoke production, they usually don't change the chemical composition of the soot particles and their precursors. Rossi and co-workers [28] studied the smoke composition from expanded polystyrene foams in the cone calorimeter by trapping condensable volatile products and soot particles. Apart from minor redistribution in oxidised volatile products, no other differences were noticed between flame-retarded and non-flame-retarded foams. However, other reports demonstrate that flame retardants can affect the particle size of soot. For example, in the case of phenolic laminates, halogens seem to decelerate the coagulation of soot particles, whereas phosphates act as strong accelerators for the coagulation.

Some synergistic coadditives (antimony oxide, tin(II)oxide, zinc stannate and so on), volatile products derived from them (tin(II)bromide, tin(IV)bromide, zinc bromide) or more highly volatile products (antimony chloride, antimony bromide and Sb-O-Br species) can all condense in the cooler zones of the flame and contribute to smoke opacity. The concentration of these species is relatively low, and they are often not observed as white smoke because they are commonly overshadowed by the black soot. Because soot is an effective absorbent, it can remove from the gas phase volatile flame retardants, such as chloroalkyl phosphates or some triaryl phosphates.

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2 Generation of Combustion Products from Polymeric Materials (Smoke Toxicity)

2.1 Introduction

Virtually all fires, independently of the material that is burning, produce very toxic effluents together with visible smoke. However, carbon monoxide (CO) is the dominant toxicant resulting from any burning material because it is formed when any organic material burns. If a burning material contains nitrogen atoms, there is a good chance that hydrogen cyanide (HCN) will be one of the combustion products formed. It is also common to find hydrogen chloride (HCl) and hydrogen bromide (HBr) resulting from the combustion of chlorinated plastics [typically polyvinyl chloride (PVC)] and flame-retarded materials (containing brominated or chlorinated flame retardants). One of the most toxic gases found in any smoke is acrolein. However, it is important to keep in mind that every polymer will give off about 10-20% of its weight in the form of CO when the fire becomes large [1]. This means that the concentration of CO is so high that it overshadows the toxic potency of other gases. This chapter will give a brief overview of smoke toxicity and will explain when small-scale toxicity tests are applicable.

The smoke toxicity of materials has been the focus of many investigations. Some of the most important work in this area was conducted at the US National Institute for Standards and Technology (NIST) in various stages: comparison of products made with fire retarded and non fire retarded materials [2], analysis of the CO yields in large full-scale fires [3], study of full-scale testing of materials (including a rigid PVC compound) and a comparison with small-scale test results [4] and the development of a small-scale radiant heat test for the measurement of smoke toxic potency [5]. It is essential to consider the work discussed above in conjunction with (a) the understanding that CO is the most hazardous toxicant affecting victims in real fire atmospheres, as shown in a comprehensive study of CO fatalities associated with fire and non fire [6, 7] and (b) an analysis of the effects of CO as a toxicant.

2.2 Common Smoke Toxicants

Toxic gases in smoke usually belong to one of three classes [8]:

- Asphyxiants or narcotics or narcosis-producing toxicants
- Irritants (sensory or pulmonary)
- Toxicants exhibiting other unusual effects

The term ‘narcosis’ in relation to smoke toxicity means the cumulative effect of asphyxiants, resulting in the depression of the central nervous system and leading to a loss of consciousness and, ultimately, death. The term ‘irritants’ refers to toxic gases causing sensory irritation of the eyes and the upper respiratory tract, or pulmonary irritation affecting the lungs. It is important to note a key difference between the lethal effects of asphyxiants and of irritants: asphyxiants cause their effects during exposure, whereas irritants cause their effects during and after exposure. Thus, during bioassay tests, the exposed subjects must be observed for a period (usually up to 14 days) after the exposure is complete to assess the full lethality of the smoke. Because they are rarely found, toxicants exhibiting other unusual effects have been studied very little. The principal combustion products found from the combustion of natural and manmade materials are listed in Table 2.1.

Table 2.1 Principal products of burning polymers and natural materials	
Gas	Source
CO, carbon dioxide (CO ₂)	All combustible materials
HCN – NO _x – NH ₃	Wool, silk, polyacrylonitrile, acrylonitrile-butadiene-styrene, polyurethanes (PU), Nylons
Alkanes, Alkenes	Polyolefins and other hydrocarbon polymers
Aldehydes	Wood, cotton, paper, phenolic resins
Acrolein	Wood, cotton, paper
Benzene	Polystyrene, PVC, polyesters
HCl – HBr	PVC, materials with halogenated flame retardants
SO ₂ , H ₂ S	Wool, vulcanised rubbers, S-containing polymers
Hydrogen fluoride (HF)	PTFE, fluorinated polymers
PTFE = polytetrafluoroethylene	
Based on data from M.M. Hirschler, <i>Journal of Fire Sciences</i> , 1987, 5, 289 [9]	

2.3 Calculation of Smoke Toxicity in Small Fires

Typical combustion gases are composed of many toxicants, especially if the burning object is a composite material or an assembled item. One way to calculate the toxic potency of smoke gas mixtures is to calculate the individual toxic potencies of each individual burning material or each individual toxic gas. The toxic potency of a burning material is usually described in terms of its LC_{50} . This is the concentration of toxic gases, in ppm or in g/m^3 , statistically calculated to result in lethality of 50% of the subjects (usually rodents, such as rats) exposed to the gas or smoke for 30 minutes. The most widely used apparatus and procedure for measuring smoke toxic potency via a bioassay of rodents is described in American Society for Testing and Materials, ASTM E1678 [10] or in National Fire Protection Association, NFPA 269 [11]. Toxic potencies for typical combustion gases are listed in Table 2.2.

Table 2.2 Typical lethal toxic potencies (LC_{50}) for 30 minute exposures of rats to the major individual smoke toxicants	
Gas	LC_{50} (ppm)
CO	4,000-5,100
HCN	150-200
HCl	3,700
HBr	3,000
HF	2,500-2,900
Acrolein	90-200
Oxygen	-54,000
Based on data taken from (a) V. Babrauskas, B.C. Levin, R.G. Gann, M. Paabo, R.H. Harris, R.D. Peacock and S. Yusa, <i>Toxic Potency Measurement for Fire Hazard Analysis</i> , National Institute of Standards Technology (NIST) Special Publication 827, NIST, Gaithersburg, MD, USA, 1991 [5]; (b) ISO 13344, <i>Estimation of the Lethal Toxic Potency of Fire Effluent</i> [12]; and (c) M.M. Hirschler in the <i>Proceedings of the BPF and IoM Conference - Flame Retardants '94</i> , London, UK, 1994, p.225 [13]	

Extensive smoke toxic potency studies performed in the 1970s and 1980s resulted in accumulation of lethal smoke toxic potency data for individual materials and products. It was concluded that although different toxic gases produce different physiological responses, the effect of the mixture of most potent asphyxiants and irritants provides a roughly additive contribution to incapacitation and death [14-16]. Based on this assumption, the N-gas model was developed at NIST [17, 18],

which calculates fractional effective dose (FED) values based on the exposures to individual gases:

$$\text{FED} = \frac{\sum_1 \sum_2 [C_i \cdot \Delta t]}{(\text{Ct})_i}$$

In this equation, $\sum_1$ (from 1 to n) corresponds to the summation of the effects of each one of n toxic gases, and $\sum_2$ (from t_1 to t_2) corresponds to the summation of the relative concentration time (Ct) effects of the toxicants at each individual time increment (usually 1 minute). C_i is the average concentration (in ppm) of the toxic gas i over the chosen time increment, and Δt and Ct_i are the specific lethal-exposure dose (Ct product, in ppm•min). With this analysis, overall smoke toxicity depends both on the concentrations of toxic gases and on the intrinsic smoke toxic potency of each component of smoke. The N-gas model also takes into account the fact that the effects of both asphyxiant gases and irritant gases are a function of their dose (i.e., concentration and duration of exposure). Abundant work, including that by the Federal Aviation Administration [19, 20], by NIST [21] and by the Southwest Research Institute (SwRI) [22-24], has shown that the N-gas model should not be limited to asphyxiants and that the effect of irritants is also dose-related and should be added to the FED equation. If the FED is calculated for the typical exposure duration of 30 minutes, the LC_{50} for individual gases (Table 2.2) can be used. In theory, an FED of 1.0 or more means that the exposed rats will die, whereas an FED of less than 1.0 means that the exposed rats will survive. In practice, the FED curve rises very rapidly, so that if the burned material generates enough combustible gases to achieve an FED = 1, then the smoke toxic potency is high enough to cause some exposed rats to die. If the FED is 1.3 or higher, it is likely that all of the rats will die; if the FED is below 0.8, it is likely that all of the rats will survive.

Although the N-gas model is a useful tool to calculate the toxic potency of smoke, one should keep in mind that this model is only applicable to small fires under conditions in which flashover is not achieved [21]. As will be discussed later, the toxicity of CO is dominant in big fires because its specific lethal exposure dose is much higher than other toxic gases.

2.4 Asphyxiants

2.4.1 Carbon Monoxide

CO is the most important combustion product, and it is produced by all organic materials [25]. The formation of CO depends on the fuel-to-air ratio (ϕ), which is usually expressed as the ratio of mass of fuel to the mass of air and normalised to the same ratio for a stoichiometric mixture. For $\phi < 1$, the fire is well ventilated, whereas for $\phi > 1$ the fire is fuel-rich and ventilation-controlled.

The toxic effects of CO relate to anemic hypoxia [26], which is the shortage of the supply of oxygen to bodily tissues due to lowered capacity of the blood to carry oxygen gas (O_2). This happens because CO has a 200 times higher affinity for binding with haemoglobin (to generate carboxyhaemoglobin (COHb)) than with O_2 (to generate oxyhaemoglobin). Even the partial conversion of haemoglobin to COHb can cause serious toxic symptoms, because oxyhaemoglobin tends to hold on to oxygen instead of releasing it to the body's tissues. There are well developed clinical methods of measuring COHb in the blood, which offer reliable methods of defining the cause of death of fire victims (see detailed discussion next).

Studies performed at NIST [5] showed that under well-ventilated conditions, the yield of CO is low and remains low until ϕ reaches about 0.5. After this point, the CO yield grows very quickly, reaching a plateau of 10-20% of the polymer's mass burned at $\phi > 1$. In the same study, it was found that for an average-size room in a residential building, flashover occurs at about the time ϕ reaches 0.5. After the flashover point, the concentration of oxygen available for combustion decreases very quickly and conditions change to the ventilation controlled fire. At this point, the CO yield becomes constant, reaching roughly 20 wt% and the rate of CO production depends on the rate of combustion (heat release rate) and the total amount of produced CO is proportional to the amount of material burned. This relationship is almost irrespective of fuel composition or ventilation [6, 7, 13]. The detailed mechanism of CO formation in post flashover fires is not completely understood, especially the factors determining the highest yield of CO. The main contributing factors are likely to be a fuel-rich atmosphere in the upper layers of the fire room that are close to the ceiling and relatively low oxygen concentration [27]. At a temperature close to 1,000°C, CO_2 can react with water and form CO. There are other suggested mechanisms for high CO production related to radical quenching or to the excessive presence of stable aromatic molecules [28]. It is also believed that some oxygen-containing fuels (such as wood) decompose in anaerobic atmospheres and yield CO too [27, 29, 30].

2.4.2 Hydrogen Cyanide

HCN can be found among the combustion gases of any nitrogen-containing combustible materials [31]. Because many synthetic polymers, like Nylons, PU, polyureas and melamine resins, contain nitrogen, it is common to expect HCN from combustion of polymers. Evolution of HCN is highly temperature dependent and the fuel to air ratio (ϕ) dependent. Significant concentrations of HCN can be seen in small (low temperature), poorly ventilated flames. However, fully developed (flashover) flames or well-ventilated flames produce little HCN because it decomposes or is oxidised.

HCN, just like CO, is an asphyxiant. The toxic effect of HCN relates to cytotoxic hypoxia [26], which is a mechanism of preventing cells from utilising oxygen because of complexation of cyanide ions with cytochrome oxidase and methaemoglobin. Because the brain and heart need the highest oxygen supply, they are most susceptible to this retardation of cellular respiration. Death usually occurs due to respiratory arrest. If the concentration of HCN is low enough not to cause serious toxic effects, detoxification proceeds relatively fast. In contrast to CO, which is present in the blood, the cyanide distributes evenly throughout the body, making its detection more difficult. There are very rare cases when HCN is considered the primary cause of fire intoxication fatalities.

There is no evidence of a synergistic asphyxiation toxic effect of HCN and CO. It is usually agreed that the effect is additive, as reflected in the N-gas model. It has also been found that incapacitation from asphyxiants occurs at levels very similar to those leading to lethality, and not at levels an order-of-magnitude lower [32].

2.5 Irritants

2.5.1 Organic Irritants, Acrolein

There are many organic gases in smoke that can cause some degree of irritation. The most important ones are formaldehyde, acrolein and isocyanates (found in burning PU). Acrolein, which can result from the combustion of many cellulosic products and some synthetic polymers (typically polyolefins), is considered to be the most important because it exhibits both high toxic potency (**Table 2.2**) and high irritating potential. Just like many inorganic irritants, acrolein is very irritating, but it rarely results in incapacitation. For example, a study with baboons [22] showed that relatively high concentrations of acrolein, up to 2,780 ppm, didn't incapacitate the animals after five minute exposures. However, even lower concentrations caused pulmonary complications and death a few hours after exposure. Thus, in many cases subjects do not become incapacitated as a result of the exposure to most irritants until the concentrations they are exposed to are high enough that the subjects will likely eventually die from the exposure.

2.5.2 Inorganic Irritants

Polymers containing halogens in their structure or in the additives (flame retardants) will release hydrogen halides during combustion. The most common sources of HCl are PVC and chloroprene rubber. **Chapter 4** discusses the key reason

that HCl concentrations are usually not very high some distances away from the fire source: decay. HF can be released from any fluorinated polymer, including polytetrafluoroethylene, polyvinylidene fluoride and fluorinated ethylene propylene. However, concentrations of HF in fires are very low, at least to some extent because the C-F bond is a chemically strong bond and partially because of decay. HBr can also be found in fires, usually as a result of the decomposition of bromine-containing flame retardants, often used in epoxies, styrenic polymers and polyolefins. There is a large body of information collected on the toxicology of PVC, in large part due to the commercial importance of this polymer.

Significant controversy is present in the literature about whether incapacitation occurs as a result of exposure to HCl, and there are disputes as to what concentration is hazardous to humans [8]. Some discredited work talked about an ‘instant clampdown’ effect from PVC smoke. This concept is contradicted by research chemists and others who have encountered emissions of HCl or other irritant gases in laboratories during their careers. There is no report available stating that such exposure results in incapacitation of humans or even of exposed rats or primates. On the other hand, there are many old reports, from the late 19th and early 20th century, when human exposure to HCl was conducted in Europe [1, 33, 34]. That work, together with an analysis of other properties of PVC, was summarised in a modern publication [35]. The toxicological work clearly showed that exposed researchers were able to continue being active and alert during exposure to HCl of 1,500 ppm for 15 minutes. A result of these studies, and others, is that the recommended eight hour workplace limits for HCl are now: (1) levels up to 10 ppm; work is unhindered; (2) at 10-50 ppm, work is possible but uncomfortable; and (3) levels of 50-100 ppm, work is impossible.

In more recent studies conducted at Southwest Research Institute in the late 1980s, it has been shown that HCl does not cause incapacitation of baboons (primates toxicologically similar to humans) or of rats at dose levels so high that the subjects eventually died of inhalation toxicity after the exposure [33]. It has also been shown that animals exposed to high doses of irritants were still capable of performing the necessary avoidance responses to escape the exposure. Moreover, the pungent odour of most irritant gases (and their low odour detection level, often in the order of 1 ppm [30]) means that the warning ensues at levels much lower than those at which any adverse effect occurs. This is very different from the highly toxic, but odourless, CO.

Because of the wide use of PVC and the controversies associated with its toxicity, combustion of PVC was studied very extensively. For example, work performed at NIST in the 1990s [21] showed that the FED of HCl in PVC smoke is much lower in full-scale studies than in small-scale toxicity test studies, at least partially due to the fast decay of HCl (see **Chapter 4**). This work also showed that the average

concentration of CO tended to be of the same order as that of HCl in one toxicity test, and 2.5-3 times higher in another toxicity test. In another study [36], four different PVC compounds were studied by three test methods, and it was found that the average HCl concentrations were in most cases lower than those of CO. This again indicates that CO represents at least half of the toxic load in PVC smoke. The smoke toxicity of PVC has been studied extensively and found to be quantitatively similar to those of most other polymers [1, 33, 34].

Interesting work compared the degree of irritancy, as assessed by respiratory depression, caused by four wire-coating materials - two containing halogens (based on PVC) and two that were halogen-free (based on polyolefins) - intended for similar applications [37]. The work, which used a bioassay on mice, showed that the smoke from the halogen-containing materials was much less irritating than the smoke from the halogen-free materials because the compounds that caused the highest degree of irritancy were organic products and not halogen acids.

Figure 2.1 shows the results of the LC₅₀ test using ASTM E1678 [10] on a number of polymeric construction materials. It is clear that materials that produce little, if any, acid gases can exhibit similar levels of toxic potency as those that are highly acid-producing, such as some of the PVC materials.

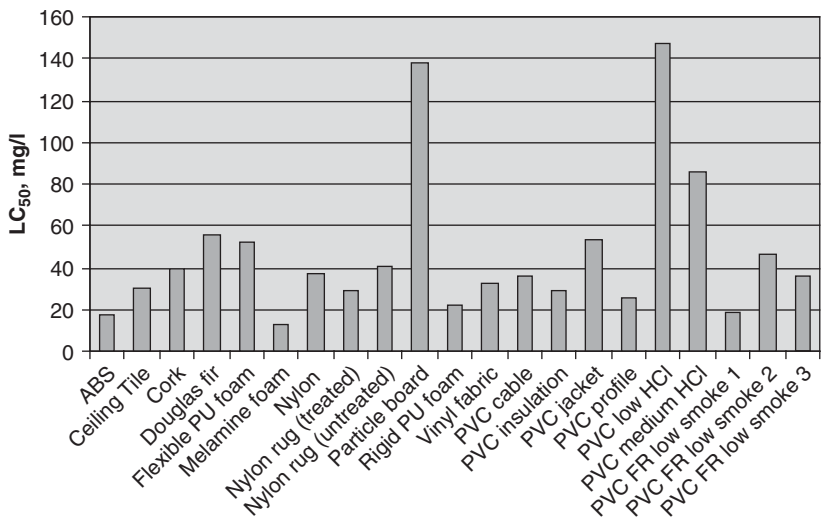


Figure 2.1 ASTM E1678 [10] radiant toxicity test of various polymeric materials, including PVC-based materials. Based on data from M.M. Hirschler in the *Proceedings of the BPF and IoM Conference - Flame Retardants '94*, London, UK, 1994, p.225 [13]

Figure 2.2 shows a plot of dependence of FED for CO, HCN and HCl on smoke acidity for a series of polymeric materials, including halogen-free polyolefins, wood, styrenics and PVC. The concentrations of the gases were measured in the smoke toxicity test chamber of ASTM E1678 [2, 10, 24, 38]. The concentrations were normalised to a common mass of material loaded into the chamber: 40 mg/l. The acid-gas data were taken from [39] and assessed by comparison for the materials not measured. This figure clearly indicates that there is no correlation between smoke toxicity and acidity. The data also shows that most polymeric materials have quite similar ranges of smoke toxicity, irrespective of chemical composition.

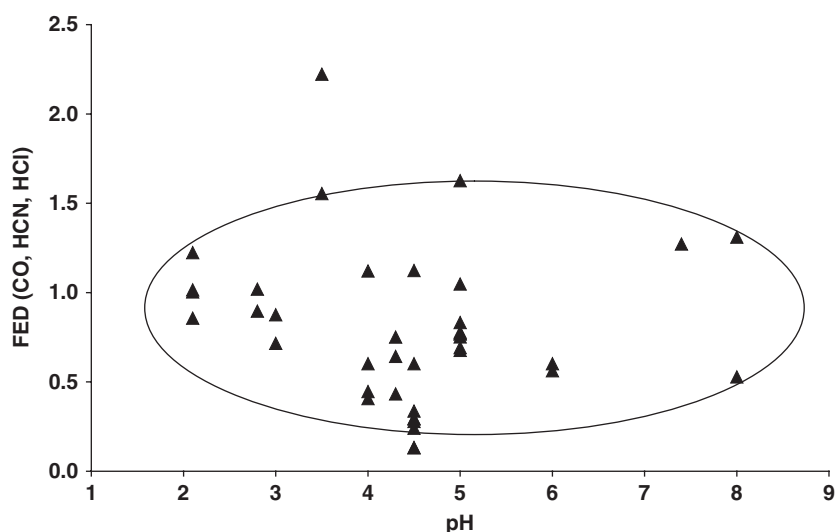


Figure 2.2 Comparison of smoke toxicity and acidity for various materials. Based on data from M.M. Hirschler in the *Proceedings of the BPF Conference - Flame Retardants 2006*, London, UK, 2006, p.47 [1]

When applying the *European Union Construction Products Directive*, significant discussion has ensued in Europe regarding whether to include acidity as a measure of toxicity for Euroclass cable classification. Acceptance of this criterion would strongly affect those cables with the best fire performance, based on PVC and other halogenated materials, but would not reflect the real fire hazard of the cables [40]. If acidity of gases were to become an important criterion in cable selection (other than in some specialised scenarios), this would result in a switch to halogen-free cables, which in many cases are technically inferior and less fire safe with respect to reaction-to-fire criteria. If smoke acidity were selected as a toxicity criterion, this would create the paradoxical situation where nitrogen-containing polymers, which are likely to produce alkaline smoke, would be considered as having a favourable effect on smoke toxicity, i.e., would be ‘antitoxic’ (something obviously impossible).

2.6 Overview of Smoke Toxicants - Is There Evidence for 'Supertoxic' Components?

The LC_{50} of CO is shown in Table 2.2 as being in the range of 4,000-5,100 ppm, which is about 4.5 g/m^3 for a 30 minute exposure. Therefore, the LC_{50} of post flashover smoke (20% by mass of which is CO) cannot be higher than a value of about 22.5 g/m^3 for a 30 minute exposure, regardless of the other substances present in the smoke. Many studies have shown that the LC_{50} of smokes of most synthetic materials are in the range from 5 to 60 g/m^3 [41] or, more often, from 15 to 30 g/m^3 . The LC_{50} of smoke from wood and other natural materials also falls within the same range. This indicates that there are no 'supertoxic' gases in the combustion products of the common synthetic plastics. A comparison of the toxic potency of smoke overall with the toxic potency of smoke of known toxic and supertoxic compounds indicates [42] that the toxic potencies of the smoke of virtually all known polymers falls within a very narrow range (in toxicological terms), so as to be statistically almost indistinguishable.

2.7 Oxygen Depletion

Since oxygen is consumed in combustion, its concentration can drop in the enclosed space where fire occurs. Oxygen depletion can be considered as one of the toxic effects of fire because it causes asphyxiation. If the concentration of oxygen in the air drops to about 17%, human motion become slow [43]. At a concentration of about 10-14%, a person is still conscious, but may show faulty judgement and fatigues quickly. At 6-10% oxygen concentration, a person loses consciousness within a few minutes and must be taken to fresh air immediately to survive. The toxic potency of oxygen depletion over an exposure period of 30 minutes, as an LC_{50} , is shown in Table 2.1 and is about 5.4%, which means that an oxygen concentration of 15.6% will tend to result in the death of half of the test animals.

2.8 Effect of Flame Retardants on Smoke Toxicity

2.8.1 Halogen Flame Retardants

Halogen-containing flame retardants operate primarily in the gas phase by inhibiting flame through free radical scavenging mechanisms. Since halogen-containing materials are more difficult to ignite and burn more slowly than non halogenated equivalents, they tend to produce gaseous combustion products at a slower rate, and, if delayed ignition or rapid self extinguishment occurs, the total amount of gaseous combustion

products may also be lower. On the other hand, they add inorganic irritant acids to the mix. These various contributions need to be considered when assessing smoke toxicity.

It is not unusual for small-scale tests to show higher smoke toxic potency levels for halogen-containing flame retarded materials [44]. However, the interpretation of such comparative data is not always straightforward. In some cases, flame retarded materials do not ignite and decompose in the nonflaming mode, whereas similar non flame retarded materials exhibit flaming combustion under the same conditions.

Results of larger-scale tests usually give a different result and a more balanced picture. For example, extensive testing was performed in the UK to evaluate the fire safety of upholstered furniture [45]. The tests were not set up for comparison of different flame retardants, but to assess the fire performance of flame retarded and non flame retarded furniture in typical domestic environments. Flame retarded chairs had covers treated with bromine-based flame retardants and flame-retardant treated PU foam. The non flame retarded chairs ignited quickly, and it took only 2.5 minutes before levels of CO and irritants achieved dangerous levels in the enclosed room. Because the time to ignition was longer and the flame propagation rate was much lower with the flame-retarded chairs, it took five minutes for the same levels of toxic gases to be reached, which doubled the time available for escape. Interesting results were obtained with fire tests in a room with the door open, where it was expected that due to well-ventilated conditions, a flame retarded chair would produce a higher CO concentration than a non flame retarded chair based on small-scale results. However, it was shown that even in well-ventilated conditions, the flame-retarded chair showed significantly lower CO yields because the size of the flame was smaller.

Earlier work was also conducted by National Bureau of Standards (NBS), using fire retarded and non fire retarded versions of five products: polystyrene TV cabinets, polyphenylene oxide business machine housings, upholstered furniture (made with PU foam), electrical cables (with polyethylene wire insulations and rubber jackets) and polyester/glass electric circuit boards [46]. That work found that, while the production of smoke (in terms of smoke obscuration) was not significantly different between the room fire tests using non flame retarded products and those using flame retarded products, the total quantities of toxic gases produced in the room fire tests were only one-third as large in the case of the flame retarded products. The analysis was made by calculating the toxic gases as 'CO equivalents'. For the room-scale tests, the time to untenability was 15-fold greater with the flame retarded products than with the non flame retarded products; in other words, the flame retarded products allowed fire victims much more time to escape unharmed.

2.8.2 Phosphorus Flame Retardants

Inorganic phosphorus flame retardants produce their flame-retardant action in the condensed phase and, mostly, stay with the combustion char in the form of polyphosphoric acid. Although the main mechanism of action of organic phosphate esters is also in the condensed phase, some part of the fire retardants can also volatilise. Because of this, there is concern that some highly toxic phosphorus compounds can be contained in fire effluents. However, this is not the case, because most phosphate esters are not thermally stable enough to survive the temperature of the flame and are stripped of their organic component. Thus, only phosphorus oxides (neutral or in the form of radicals) have been detected in flames [47, 48]. Eventually, phosphorus oxides are hydrolysed and can be found in the smoke in the form of phosphoric acid.

The literature contains only one example of an extremely toxic effect of the smoke of rigid PU foam flame retarded with a phosphorus-containing flame retardant in laboratory conditions [49]. It was found that trimethylolpropane phosphate, formed during the thermal decomposition of trimethylolpropane-based polyol present in the foam, was responsible for seizures in and death of exposed rats. Later experiments in which trimethylolpropane phosphate aerosols were sprayed onto rats showed similar results [50]. Further, a more detailed study of the same type of formulations showed that the very toxic trimethylolpropane phosphate is formed only under nonflaming pyrolysis conditions, whereas under actual flaming combustion, the smoke toxicity was in line with the toxicity of cellulosic materials [51]. Large numbers of other fire retardants have been tested in rigid PU foams, but no additional unusual toxic effects have been observed [52]. The overall toxic potency of the combustion and decomposition products from PU foams and coatings under fire conditions appears to be similar to those of products from wood or wool under comparable fire conditions [53].

Similar to halogen-containing flame retardants, phosphorus flame retardants may perform poorly with regard to smoke toxic potency in small-scale tests, in which flame-retarded specimens may not even ignite but pyrolyse in a nonflaming mode that produces abundant organic products of thermal decomposition of specific polymers. These results are experimental test artifacts and should be interpreted carefully with a complete understanding of the difference between flaming and nonflaming modes of combustion. However, in large-scale tests, phosphorus flame retardants routinely perform well. For example, armchairs containing PU foam with a flame-retardant chloroalkyl phosphate were tested in an enclosed room-corridor-room apartment rig [54]. In addition, the upholstered fabric on the chairs was treated with a phosphorus flame-retardant to resist cigarette ignition. In a smoldering ignition scenario, the flame retarded chairs didn't catch fire, whereas the non flame retarded chairs went from

smoldering to flaming spontaneously. Since the flame retarded chair was designed to withstand only a small flame, both types of chairs ignited in the large flaming ignition, but the flame retarded chair burned more slowly. The results for the CO concentration and calculated FED are shown in Figure 2.3a and b. The concentration of CO in the non flame retarded chair test reached 3,000 ppm in about eight minutes and at about the same time the FED reached the critical value of one. In contrast, the flame retarded chair reached a CO concentration of 3,000 ppm and an FED > 1 after 11 minutes. The flame retarded materials essentially provided an additional three minutes for escape.

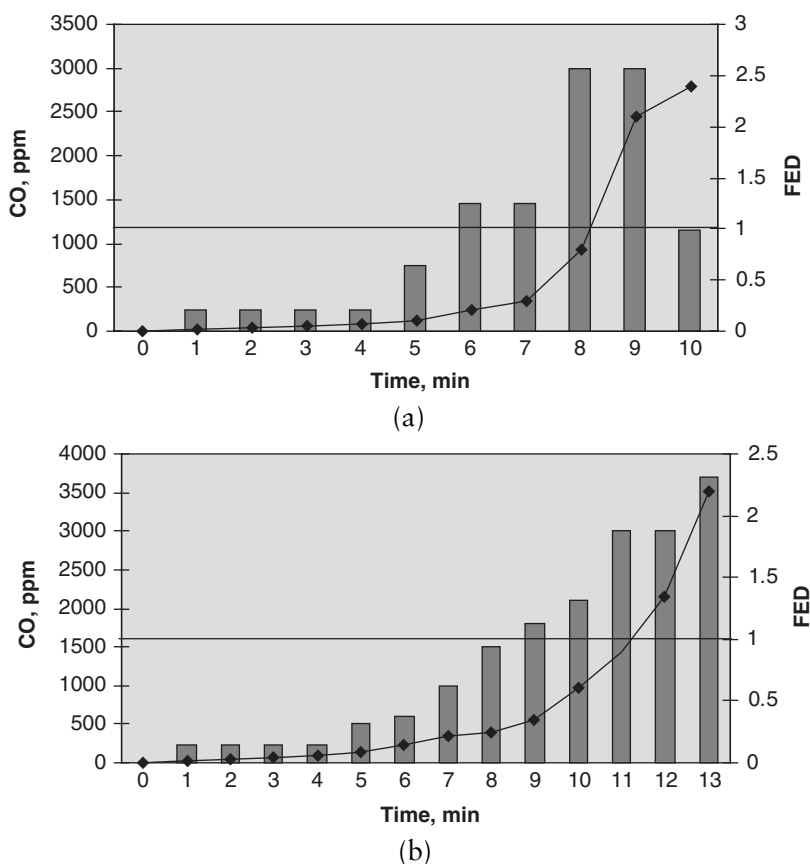


Figure 2.3 CO concentration (bars) and FED values (dots) for (a) non-flame-retarded chair and (b) phosphorus flame-retarded chair tested in a room-corridor-room rig by NIST. Based on data from E. Braun, B.C. Levin, M. Paabo, J. Gurman, L. Holt and J.S. Steel, *Fire Toxicity Scaling*, US Department of Commerce, National Institute of Standards and Technology, Report No. NBSIR 87-3510, 1987 [54]

2.8.3 Miscellaneous Flame Retardants

Metal hydroxides for example, aluminum trihydrate (ATH) and magnesium dihydroxide (MDH) - are commonly used in PVC and polyolefin formulations. Besides the advantage of passing fire tests, these additives provide significant decreases in visible smoke density (see **Chapter 6**). ATH is typically used in PVC at levels of 25-30 wt%, whereas in polypropylene, polyethylene, ethylene vinyl acetate (EVA) and in some elastomers it is used at levels of up to 65 wt%. MDH is typically not used in PVC, but is used in polyolefins and Nylons at the level of 60-65 wt%. As a result of such high loadings, less polymer remains available for combustion. Thus, metal hydroxides are effective in decreasing smoke in both small- and large-scale tests. Only water is observed as a product of thermal decomposition of hydroxides themselves. For PVC, ATH also decreases the evolution of HCl [55].

In a comprehensive study performed by NBS (now NIST) [2], a series of flame retarded and non flame retarded office and consumer products were assessed in large-scale tests. The following flame retarded materials were tested in different configurations: television housing made of high-impact polystyrene (HIPS) and flame retarded with a brominated flame retardant and antimony trioxide, business machine housings made of polyphenylene oxide/HIPS flame retarded with a phosphorus flame retardant, upholstered chairs containing flame retarded PU foam with a brominated flame retardant, a chloroalkyl phosphate and ATH (probably in a textile back-coating), an array of EVA cables with a chlorine-containing flame retardant and antimony trioxide, and printed wiring boards with brominated flame retardant and ATH. Similar non flame retarded materials were tested as well. The main findings of these tests were: the amount of consumed polymer mass in the room equipped with flame retarded materials was half that of the room with non flame retarded materials, with three-quarters less total heat released and one-third less toxic gases produced. Total visible smoke was similar in both experiments. Further calculations showed that the flame retarded products increased 15-fold the escape time from the room.

2.9 Autopsies of Fire Victims and Real-fire Monitoring

The toxicity of smoke in a fire is a function of four factors: the amount of material/product burnt, the distribution of combustion products within the smoke, the individual toxic potencies of each combustion product found in the vapor phase, and the duration of exposure. Clearly, the greater the amount of toxic gases and the longer the materials burn, the greater the toxicity of the smoke. In fact, although roughly two-thirds of fire victims die from the effects of smoke inhalation, it is extremely rare for the cause of their deaths to be the smoke that comes from a specific, very toxic material. Fire fatalities are usually the result of inhaling too much smoke of

average toxicity. More than 83% of fire deaths in building fires in the United States occur in fires that have become so large that they extend beyond the room of origin, and thus generate too much toxic smoke for victims to survive [56]. This means that very few people actually die in fires that are small, and that fire deaths are rarely due to burning or heat effects.

Two highly representative studies were conducted in the United States involving, in total, more than 5,000 fire victims. One study covered a period between 1938 and 1979 in a localised area (Cleveland, Ohio), and another study was nationwide and spanned a few years in the early 1990s [6, 7]. The studies investigated autopsies on fire victims and on non fire victims in which CO was involved. The autopsies looked for the presence of CO and also for HCN. The autopsies did not search for HCl since human stomach acid contains HCl, and any HCl resulting from the fire cannot be distinguished from that naturally present in stomach acid. The concentrations of HCN found in the fire victims were relatively low and were virtually always accompanied by high concentrations of COHb. The studies also showed that fatalities associated exclusively with CO toxicity can be linked to COHb levels as low as 20% and that it is likely that any COHb level above 30-40% is lethal. A strong correlation was also observed between levels of CO absorbed by fire victims (from big fires) and non fire victims (e.g., victims of CO poisoning due to malfunctioning of space heaters or suicides) within the same age groups and gender. This extensive study clearly concluded that CO is the main cause of fire deaths, irrespective of whether the fire occurred in the 1930s, when plastic materials were rare or nonexistent, or in the 1990s, when the plastic load of houses was significantly higher. Similar conclusions were obtained earlier by other authors, with smaller data bases [57, 58].

Two investigations were conducted in the United States in the late 1970s, where fire fighters equipped with gas monitors were sent into buildings [42, 59, 60]. In the fires investigated, high concentrations of CO were often detected, with the maximum concentration found being 7,450 ppm (approximately 150% of the 30 minute LC_{50}). The three other most common gases found in fires in those studies were acrolein (with a maximum concentration of 100 ppm, approximately 50-80% LC_{50}), HCl (with a maximum concentration of 280 ppm, approximately 8% LC_{50}) and HCN (with a maximum concentration of 10 ppm, approximately 6% LC_{50}).

2.10 Post Flashover Fires, Mass-loss Model

The size of a fire is usually defined in terms of the peak energy, or heat, released, in kilowatts. Small fires, which typically result from the burning of a single object, are in the range of 20 to 200 kW. This can represent the combustion of paper trash in

a wastebasket or the combustion of a small chair (generally non upholstered). Fully developed fires, or flashover fires, typically exceed 1,000 kW of heat release. In relatively large fires, the heat release and burning rate usually approach an asymptotic value and can then stay relatively constant until the available fuel starts decreasing [61]. The burning rate, as represented by the mass loss rate or the smoke production rate, depends on the heat release rate. With typical materials, the effective heat of combustion of polymeric materials is around 25 MJ/kg - this means that about 2.4 kg of combustible material is consumed every minute [8]. Because CO represents about 20% of post flashover smoke [5], a post flashover fire generates about 0.5 kg of CO per minute. For the average-size room of 36 m³, such a fire will produce a CO concentration of 14 g/m³ in a matter of one minute, which is almost triple the toxic potency of CO (Table 2.1), LC₅₀ = 4,000-5,100 ppm (about 4-5 g/m³).

Because it is very difficult to obtain the same type of temperatures and heat fluxes in small-scale laboratory tests with underventilated conditions, as in flashover fires, small-scale toxic potency values generally overestimate actual toxicity by about a factor of two [62]. It was also found that laboratory test results can predict real-scale toxic potency only to within about a factor of three [5], resulting in the conclusion that laboratory LC₅₀ values higher (less toxic) than 8 g/m³ must be considered indistinguishable from each other. Since most common construction and furnishing materials have laboratory LC₅₀ values substantially higher than 8 g/m³, the toxicity of smoke would most often be determined by the fire's ventilation, rather than by the specific products being burned.

In a simplified approach, overall smoke toxicity can be calculated under the general assumption that all smoke is similar in toxicity. This means that the overall smoke toxicity of the smoke from most common materials or products is very similar, rather than that every component in smoke has the same toxic potency. With this approach, it is sufficient to assess an overall mass loss, and the criterion for the concentration time product (Ct) for lethality can then be considered to be 900 g min/m³ [63]. This is consistent with various calculations that have been made by summing up abundant data from multiple sources [36, 64, 65]. In general, the values of toxic potency of smoke have been found to range between 15 and 30 g/m³, leading to Ct products of 450 to 900 g min/m³ (for a 30 minute exposure, which is what is typically used in smoke toxicity tests). Using the lower toxicity (i.e., the higher value) criterion in an average-size room with a volume of about 36 m³, lethality occurs following an exposure to the smoke resulting from burning no more than approximately 10 kg in just over three minutes (actually, a mass loss of exactly 10.8 kg over the three minutes).

2.11 Meaning of Smoke Toxicity Tests

The main justification of the development and extensive use of smoke toxicity methods in the 1970s and 1980s was the premise that ‘supertoxic’ gases [62] existed among the combustion products of man-made materials, mostly plastics. This represented a belief that every polymer and every formulation needs to be tested, because it may have unique combustion products. This concept was never proven, but instead it was found that the smoke toxicity of polymeric materials, just like that of natural products, can be qualitatively and quantitatively explained on the basis of the combination of a few toxic gases common to all of them [41]. It was also realised that the output of toxic gases often is more test dependent than material dependent. Most test methods reproduce only a single combustion condition, for which the relationship with a full-scale fire is not established [66]. A special problem exists with CO output, which is strongly dependent on the oxygen supply and temperature. The conditions of a full-scale post flashover fire simply cannot be simulated in the small-scale test. In the best-case scenario, small-scale tests can correlate the CO₂/CO ratio of large-scale tests only for early low-temperature developing flames [67].

There are some rare cases in which smoke toxicity as measured by small-scale tests can play an important role in fires. That is the case when people die in small localised fires that destroy minimal amounts of material. In most of these cases, the victims perish from smoldering fires while sleeping. Statistics indicate that such scenarios are few and that they very rarely generate enough smoke (toxic material) to cause lethality. Other examples of such cases involve materials in specific environments, such as those on ships, aircraft, military combat vehicles and so on, where people may be in confined spaces with immediate exit not available and without the ability to get the fire under control.

As discussed previously, it is not important to measure individual toxic gases for hazard assessment purposes. However, the measurement of toxic gases is sometimes helpful in developing materials and in understanding the fire performance of any material or product, especially before bringing it to the market. Interestingly, in one extensive study at NIST using the NBS smoke chamber, it was found that fluoropolymers produce smoke with 2-3 times higher toxic potency than most common plastics or wood. However, a large-scale toxicity test performed with 30 kg of communications cables made out of that same fluoropolymer did not reveal unusual effects, since exposed animals accumulated near-lethal doses of COHb which probably arose from the additional fuels supporting combustion. The lethal smoke contribution of the cables themselves was estimated at 1.6 mg/l, a level about 80 times less toxic than the fluoropolymers found in the NBS chamber [68].

There is another reason to study gases emitted during burning, and it is not related to fire hazard or to fire safety, but to the marketing of materials. There are some specifications and requirements demanding that materials be certified as lacking in a certain component, typically halogen flame retardants or PVC. In such situations, the measurement of combustion products is often associated with ‘passing’ certain specifications for material composition.

2.12 Long-term Effects of Smoke Toxicity

The long-term effects of smoke toxicity is a controversial issue that has even been politicised to a certain extent. Although only fire victims or people in direct contact with fire are exposed to the toxic gases discussed previously, a much larger portion of the human population is potentially exposed to persistent airborne pollutants, which can be distributed throughout a significant portion of the atmosphere. There are three types of products of specific concern, namely: (1) polycyclic aromatic hydrocarbons (PAH); (2) polyhalogenated dibenzofurans and dibenzodioxins; and (3) smoke particulates.

PAH can be found among the effluents of any fire. PAH are especially abundant in pyrolysis and smoldering fires. Many of the PAH that have been investigated exhibit mutagenicity or even carcinogenicity. A short overview of the mechanism of mutagenic activity of PAH can be found in [69]. Benzo[*a*]pyrene (BaP) is considered to be a very toxic member of the PAH family and has been assigned a toxic equivalency factor (TEF) of 1 (**Figure 2.4**). Another PAH with a similar TEF is dibenzo[*ab*]anthracene (DahA). It has also been officially assigned a TEF of 1, however, in cases of low-dose exposures, which may occur in the environment, it is believed that DahA may have a TEF as high as 5 [70]. All other PAH have lower carcinogenic potency, varying from 1 to 3 orders of magnitude lower than that of BaP and DahA. PAH are found in large concentrations attached to soot particles. For example, the percentage of benzo[*a*]pyrene in soot can reach 5% [71]. The mutagenic activity of smoke condensates was confirmed by Ames tests and was attributed to PAH [72].

If combustible material contains halogen (particularly Br or Cl) groups, polyhalogenated dibenzodioxins or dibenzofurans can be formed. There is no need for the halogen and the carbon atoms to come from the same molecule. Polyhalogenated dibenzodioxins and polyhalogenated dibenzofurans can be formed even if the halogen source is an inorganic material (e.g., table salt, which is common in municipal solid waste going through incinerators). The family of polyaromatic dioxins and furans is very broad, but only 17 compounds, all of which exhibit substitution in aromatic rings at the

2,3,7,8 positions, are toxic. Since polyhalogenated dioxins and furans were recognised as an environmental problem, a significant amount of toxicological data has been accumulated [73]. Similar to the case of PAH, the toxic potency of polyaromatic dioxins and furans has been ranked based on TEF. The TEF of 17 toxic polychlorinated dibenzodioxins (PCDD) and polychlorinated dibenzofurans (PCDF) are shown in **Figure 2.5**. The most toxic is 2,3,7,8-tetrachlorodibenzodioxin (TCDD), which has been assigned a TEF of 1. Since the early 1990s, the World Health Organization has held periodic meetings to update the TEF of polyhalogenated dioxins and furans.

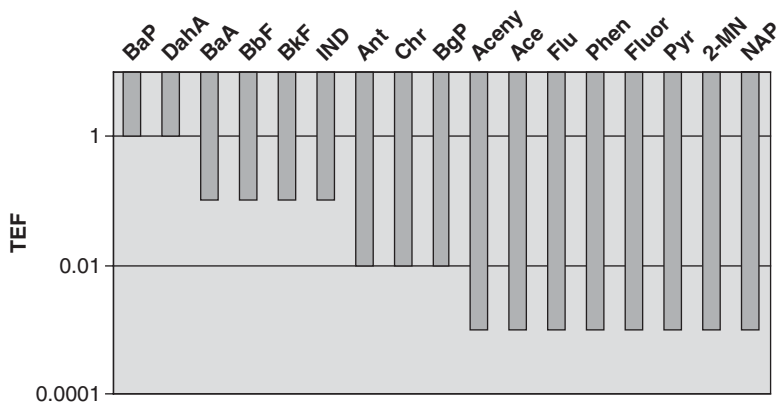


Figure 2.4 TEF of PAH (benzo[*a*]anthracene (BaA), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), indeno[123-*c,d*]pyrene (IND), anthracene (Ant), chrysene (Chr), benzo[*g,h,i*]perylene (BgP), acenaphthylene (Aceny), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phen), fluoranthrene (Fluor), pyrene (Pyr), 2-methylnaphthalene (2-MN) and naphthalene (NAP)). Based on data from J.L. Neviaser and R.G. Gann, *Fire Technology*, 2004, **40**, 177 [70]

There is no official TEF assignment for polybrominated dibenzodioxins (PBDD) or polybrominated dibenzofurans (PBDF), or for dioxins and furans with mixed bromine and chlorine substituents. However, in Germany five PBDD and three PBDF are regulated in the German Dangerous Goods Exception Ordinance, and they are all assigned the same TEF as the related PCDD and PCDF [71]. One also needs to keep in mind that TEF are good only for ranking toxicity in the same series of compounds. For example, the toxic potency of chlorinated dioxins and furans cannot be compared with that of PAH.

Although direct comparison of the TEF of different series cannot be made, there is another tool that allows for comparison of different carcinogenic air pollutants. It is based on Unit Risk Factors, which are calculated in epidemiological statistical studies and give an estimate of how many people will contract cancer over their lifetime

with continuous inhalation of 1 mg/m^3 of the pollutant. Based on the risk factors, 2,3,7,8-TCDD is 20 times more toxic than BaP. However, based on the average concentration of 2,3,7,8 TCDD and BaP encountered in air by a human, the risk of BaP is five orders of magnitude higher [71].

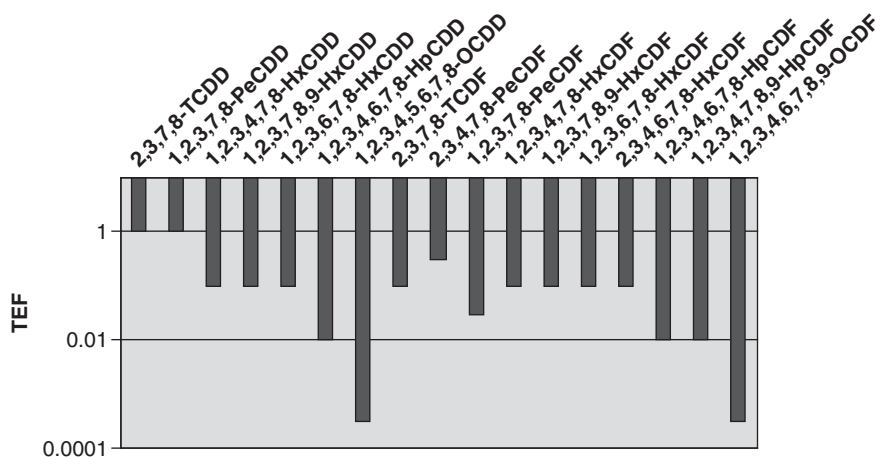


Figure 2.5 TEF of PCDD and PCDF. (Pentachlorodibenzodioxin (PeCDD); hexachlorodibenzodioxin (HxCDD); heptachlorodibenzodioxin (HpCDD); octachlorodibenzodioxin (OCDD); tetrachlorodibenzofuran (TCDF); pentabromodibenzofuran (PeCDF); hexabromodibenzofuran (HxCDF); heptabromodibenzofuran (HpCDF); and octabromodibenzofuran (OCDF))

The issue of the contribution of halogenated polymers (primarily PVC and brominated flame retardants) to smoke pollutants involves two contradictory trends. There are two main issues: (1) the occasional exposure of people to the smoke of fires, which involves the exposure of fire victims, the exposure of firefighters during incidents and the exposure of fire investigators and postfire cleaning sanitation personnel and (2) the potential exposure of the general public due to long-term contamination of the atmosphere. A thorough investigation of two large fires in Germany (the Lengerich fire in 1992 and the Düsseldorf Airport fire in 1996), both of which involved the combustion of large amounts of PVC and flame-retarded plastics, showed that the cancer risk factors associated with PAH always exceeded the cancer risk factors associated with polychlorinated dioxins and polychlorinated furans (PCDD and PCDF) by factors of 25-500, depending on whether the presence of these chemicals was measured in the smoke, the soot or when absorbed on surfaces [71]. Concentrations of polybrominated dioxins and furans (PBDD and PBDF) were two orders of magnitude lower than those of similar chlorinated congeners.

Modern incinerators can reduce the formation of PCDD, PCDF and PAH to very low levels by using proper air-fuel ratio, good mixing and adequate high temperatures, plus scrubbers and dust collectors. It has also been shown that there is a lack of direct correlation between PCDD production and chlorine input in the waste stream being fed to the solid waste incinerators [74]. Advances in the modern technology of safe incineration of solid waste, including environmental aspects of incineration, are discussed in a book by Niessen [75].

It is difficult to assess the impact of accidental fires on the health of the general public because of the absence of emission data. However, relative cancer risk factors can be estimated based on the life cycle assessment model [76]. The model includes two potential sources of air pollutants: from incidental fires and from incineration and disposal of consumer products at the end of their life. Two cases studied involved television sets and upholstered furniture; they showed from three to six orders of magnitude higher cancer risk factors from PAH than from polyhalogenated dioxins or furans. Furthermore, non flame retarded furniture and television sets have significantly higher impacts on the environment than corresponding flame retarded products due to the higher risk of accidental fires and evolution of large amounts of PAH in such fires.

Diesel-exhaust gases are recognised as human and animal carcinogens, and their toxic effects are primarily attributed to the soot particles [77, 78]. It is believed that particles from other burning materials can also produce similar effects. In general, particulate yield depends both on the material burned and on the combustion conditions [79]. Bioassay toxicity studies conducted on rats with carbon black smoke indicate that, at relatively low doses, exposed lungs tend to clear up over time without long-term effects [80]. Higher doses can produce pulmonary inflammations that eventually lead to chronic diseases and cancer, however, such exposures are likely to be found only among the population professionally dealing with fires (i.e., firefighters). It should be noted that firefighters are usually supplied with self-contained breathing equipment and are normally required to wear it when fighting fires.

In view of the fact that some polymer composites contain glass or carbon fibres, there is also a concern that airborne fibres can be inhaled and may produce respiratory damage similar to that of asbestos. Extensive studies have been performed indicating that fibre fragments produced in fires are too large to penetrate deeply into alveoli and that lungs can usually self-clean from such fibres before any chronic conditions develop [81]. Data from fire tests and aircraft postcrash investigations indicate that most airborne fibres are 2-10 times larger than the critical fibre size associated with asbestos toxicity [82].

2.13 Conclusions

The question of the importance of smoke toxicity in relation to fire hazard is commonly misdirected. Although roughly two-thirds of fire victims die as a direct effect of smoke toxicity, it is extremely rare that their deaths are caused by the inhalation of smoke from a specific, very toxic material. Good correlations have been found between blood CO concentrations in fire victims and the resulting fire fatalities, indicating that the toxic effects of other combustion products are relatively much less important. At flashover, every polymer will give off approximately 20% of its weight as CO - that CO is toxic enough for the atmosphere to be lethal without needing any other toxicant. If a fire remains small, or develops slowly, it will usually not cause fatalities unless people are unable to escape. Therefore, fire hazard is directly related to the fire's heat-release rate (i.e., the fire intensity), with other issues (such as smoke toxicity) being of minor relevance. The toxic potency of the smoke of almost all individual polymers lies within a very small band, so that they are almost indistinguishable.

Although flame retarded materials may show higher smoke toxic potencies in small-scale tests, in most large-scale tests they show definite benefits in terms of lower toxicity and overall lower fire hazard.

The long-term toxic and environmental effects of fires are not well understood. An issue that is especially poorly defined is the importance of toxic effects on the general population that is potentially exposed occasionally to the long-term effects of smoke toxicants or that is exposed, through air pollution, to very low concentrations of air pollutants for very long periods. However, some detailed investigations of large fires indicate that the impact of PAH in terms of toxic equivalency significantly exceeds the toxic equivalency of polyhalogenated aromatic dibenzodioxins and dibenzobenzofurans.

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3 Smoke Corrosivity

3.1 Introduction

The combined effects of fire, corrosive smoke and particulates have been defined as ‘fire corrosivity’. Corrosivity of smoke is a well recognised problem that has been studied extensively. Corrosivity of smoke is not an imminent fire hazard, but is mostly a property protection issue, dealing with postfire cleaning and rebuilding of noncritically damaged constructions. Reliable functioning of the machinery and electronic equipment exposed to smoke directly relates to smoke corrosivity and soot deposits. The damaging effect of smoke is a complex phenomenon and depends on both acidic and basic products, as well as on ionic species and products of hydrolysis of smoke components. A review of nonthermal fire damage was published by Tewarson [1].

3.2 Corrosivity of Construction Materials

Metal corrosion can occur in two different scenarios [2]. The first scenario involves metals exposed to smoke under humid conditions, absorbing enough water on their surface to dissolve corrosive gases. Another variant of this scenario considers deposited hygroscopic particles, which contain or absorb water. The first scenario produces local moist conditions and corrosion. The second scenario entails direct precipitation of particles and absorption of gases that produce a uniform cover, which can later absorb atmospheric moisture. This scenario generally results in uniform corrosion of the metal surface.

Water solubility of specific corrosive gases is an important factor determining corrosivity. Table 3.1 shows the equilibrium distribution of potentially corrosive gases between the gas phase and water-surface film. Oxygen and nitrous dioxide have low solubility in water and therefore have limited contribution to corrosivity. On the other hand, acetic acid, ammonia, hydrogen chloride (HCl) and nitric acid are highly soluble gases, and they will contribute most to the first-scenario corrosion.

Table 3.1 Equilibrium distribution concentration (wt.%) of different gases between gas phase and surface water film		
Gas	Water film (%)	Gas phase (%)
O ₂	3.0 x 10 ⁻²	21
O ₂	6.2 x 10 ⁻⁸	4.0 x 10 ⁻⁶
NO ₂	6.3 x 10 ⁻⁹	1.0 x 10 ⁻⁶
HCHO	3.7 x 10 ⁻⁴	5.0 x 10 ⁻⁸
H ₂ O ₂	3.4 x 10 ⁻³	2.0 x 10 ⁻⁷
CO ₂	1.5 x 10 ⁻³	3.3 x 10 ⁻²
SO ₂	1.8 x 10 ⁻³	5.0 x 10 ⁻⁷
HCOOH	8.6 x 10 ⁻³	5.0 x 10 ⁻⁸
NH ₃	1.9 x 10 ⁻³	1.0 x 10 ⁻⁷
HCl	1.9 x 10 ⁻³	1.0 x 10 ⁻⁷
HNO ₃	3.8 x 10 ⁻³	2.0 x 10 ⁻⁷
Based on data from P. Warneck in <i>Chemistry of Multiphase Atmospheric Systems</i> , Ed., W. Jaeschle, NATO ASI Series, Springer-Verlag, Berlin, Germany, 1986, 6G, p.473 [3]		

Different metals show different susceptibilities to the corrosive effects of smoke. For example, Patton [2] tested four metals typically used in construction, stainless steel, carbon steel, copper/nickel alloy (70:30; CuNi) and Monel alloy. Coupons of these metals were exposed to the gases from polyvinyl chloride (PVC) smoke collected from cone-calorimeter combustion and transferred to the humidity chamber. As **Figure 3.1** shows, the CuNi alloy suffers a significant depth of corrosion even after one hour of exposure, but corrosion of this alloy slows down with time, especially after two days. Surprisingly, stainless steel was more susceptible to corrosion than carbon steel, especially at low exposure time. Monel, as expected, was found to be the metal most resistant to corrosion.

A similar study of the corrosion of carbon steel, stainless steel, Monel 400 and brass was performed in a full-scale test simulating the instrument room of a warship [4]. In this study, carbon steel performed especially poorly in a humid atmosphere, with a 45-fold increase in its corrosion rate at 100% humidity. Increasing the humidity from 70% to 100% in the postfire exposure resulted in a 12-fold increase in corrosion rate. As expected, cables made with crosslinked polyethylene (PE) jackets performed

better than PVC cables, with no noticeable corrosion of brass, stainless steel and Monel, even in a high humidity atmosphere.

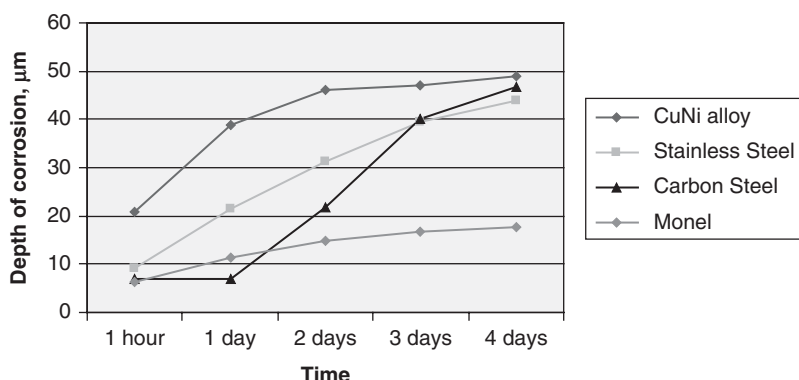


Figure 3.1 Susceptibility to corrosion of different metals exposed to PVC smoke.
Based on data from J.S. Patton, *Journal of Fire Science*, 1992, 10, 294 [2]

Acidity of smoke is only one of the contributors to smoke corrosivity. Typically, HCl, hydrogen bromide, hydrogen fluoride and sulfur oxides, as well as organic acids such as acetic acid or formic acid, are responsible for smoke acidity. Acidic gas emissions are measured as the pH of a water extract of the smoke or as the conductivity of aqueous solutions. However, there is no general correlation between acidity of smoke and its corrosivity. For example, **Figure 3.2** shows dependences of smoke corrosivity toward copper (Cu) and the pH of water extracts of smoke. It can be seen that there is no correlation between the acidity and corrosivity of gases. In fact, highly acidic smokes from Neoprene and PVC are less corrosive to copper than are basic smokes from wool and Nylon.

Investigations of fires, as well as large-scale fire tests, have shown that the most serious corrosion damages are observed in the room of the fire's origin, even though the density of visible smoke in adjacent rooms can be as high as that in the room of origin. Because the most corrosive gases tend to be the most polar and the most water-soluble ones, they tend to absorb on surfaces relatively fast and their concentration drops very quickly with increasing distance from the source. This phenomenon is known as the decay of combustion products and is discussed in detail in **Chapter 4**. For example, large-scale tests of burning and smoldering PVC floor coverings showed that about 50% of evolved HCl was deposited on the walls of the room [6]. The concentration of deposited HCl depends on the wall covering (**Figure 3.3**). As expected, porous wall coverings tend to absorb more HCl.

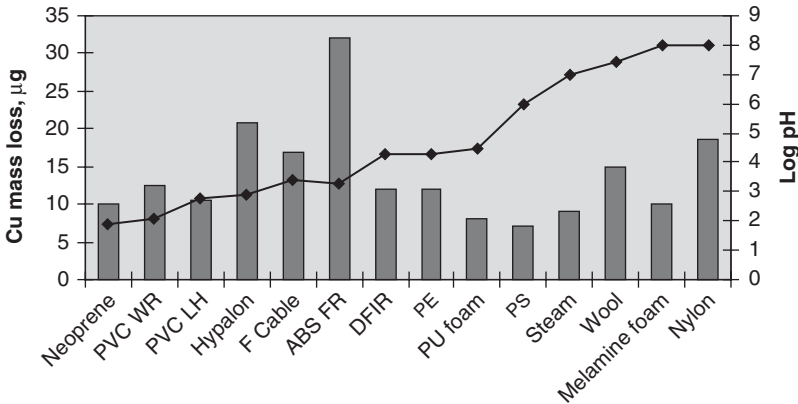


Figure 3.2 Corrosivity (mass loss of Cu) and acidity of water extracts of smoke from different plastic materials. Cu, PVC wire and cable (PVC WR), PVC low halogen (PVC LH), fluorinated cable (F cable), fire retarded acrylonitrile-butadiene-styrene (FR ABS), Douglas fir wood (DFIR), polyethylene (PE), polyurethane foam (PU Foam), polystyrene (PS). Based on data from M.M. Hirschler in the *Proceedings of 39th International Wire and Cable Symposium*, US Army Communications-Electronics Command, Fort Monmouth NJ, Ed., E.F. Godwin, Reno, NV, USA, 1990, p.661 [5]

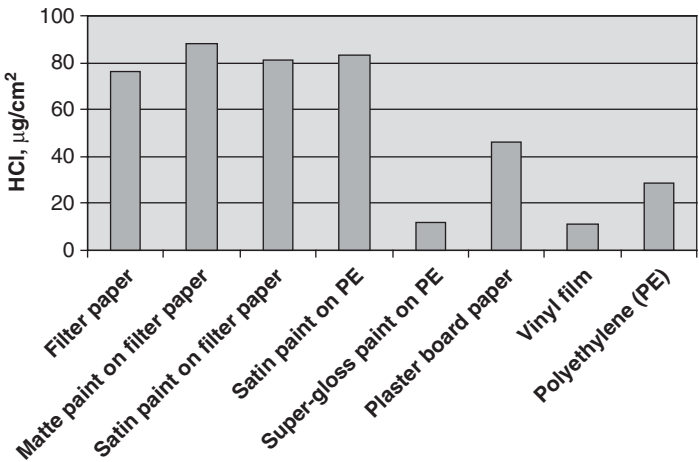


Figure 3.3 Concentration of deposited HCl on wall coverings. Based on data from K.G. Martin and D.A. Powell, *Fire and Materials*, 1992, 3, 132 [6]

3.3 Smoke Corrosivity of Electrical and Electronic Equipment

Fires in telecommunication facilities, computer centres and other research, production or office facilities where large numbers of computers and electronic equipment are present can be very costly, even if the equipment is not directly exposed to the heat, but only to smoke. Exposure of the equipment to smoke gases and soot particulates can result in malfunctions, leading to extensive cleaning or replacement in order for a business to continue operating. The problem was more serious when relay switches were common in electronic equipment, and especially in telecommunications centres. With the conversion to electronic switches, electronic equipment has become more resistant to corrosive gases and soot, however, the problem has not totally disappeared.

If electronic equipment is exposed to combustion gases, one should keep in mind that cleaning should be performed as soon as possible. One reason for this is that corrosion does not stop after the flame exposure ceases, due to deposits of corrosive gases being present on the surface. Deposited soot also undergoes structural changes, becoming more compact with the passage of time and more difficult to remove by regular cleaning procedures. Soot in the particulate fraction of smoke efficiently adsorbs corrosive compounds and corrodes the surfaces by deposition. The presence of high molecular weight, sticky, organic compounds in the non particulate fraction of smoke increases the efficiency of deposition of soot with corrosive compounds on surfaces to enhance corrosion and leakage of current.

Reagor [7] studied the most common cause of corrosion from fires involving combustion of PVC cables and other halogenated plastics (potentially brominated flame retardants and polytetrafluoroethylene). Interestingly, she noticed an important role of zinc-galvanised or zinc-chromated finishes, which are very common as structural elements of the equipment, as well as of heating, ventilation and air conditioning ductwork. Zinc is very reactive toward HCl and forms highly hygroscopic zinc chloride. This electrically conductive solution can move, drip or run onto equipment, resulting in electrical shorting problems. It was found that, in major fires, zinc chloride was the most important compound to remove during cleaning in order to be able to salvage equipment.

It is expected that, over its normal service life, an electronic switch will accumulate 5-10 $\mu\text{g}/\text{cm}^2$ of zinc chloride on its surface. After exposure to fires involving PVC and other halogenated materials, levels of up to 1,000 $\mu\text{g}/\text{cm}^2$ have been observed. It is believed that equipment with contamination levels below 30 $\mu\text{g}/\text{cm}^2$ can be restored to service with little impact on long-term reliability. Equipment with exposures from 30 to 100 $\mu\text{g}/\text{cm}^2$ can also be restored as long as no unusual corrosion problems arise and the environment was controlled soon after the fire. However, if the contamination

levels are above 100 $\mu\text{g}/\text{cm}^2$, the cost of cleaning approaches the replacement cost of the equipment.

In another study, the immediate effect of smoke on the functionality of digital, printed wiring boards was studied [8]. This is particularly important for protecting control rooms of military command centres or nuclear power stations. The tests included study of three possible failure modes of a functional board: (1) circuit bridging; (2) corrosion (metal loss); and (3) induction of stray capacitance. It was found that smoke can increase leakage currents between biased contacts and cause shorts. The shorted electrical signals cause digital systems to receive faulty data and to upset systems, causing failure. High smoke density, high humidity and flaming fires cause more failures than low smoke density, low humidity and smoldering fires. The smoke permanently increased resistance of the circuits tested for corrosion, implying that the contacts were corroded. Failure was also dependent on the type of the boards. For example, high-voltage boards failed permanently, whereas operation was restored for high-speed, low-voltage boards when smoke exposure ceased. It was also found that boards with a protective coating and the use of chip packages with large lead-spacing significantly improved smoke tolerance.

Clean-up procedures for electrical and electronic equipment exposed to smoke from fires were recently reviewed in [9]. It is believed that dry-cleaning methods are not sufficiently reliable and can be used only as an immediate response and precleaning procedure. Sonic cleaning is not suitable because of potential damage to sensitive electronic components. Degreasing cleaners and corrosion inhibitors are also not recommended because of their unpredictable long-term effects. Completely satisfying results can be achieved only with water-based cleaning using slightly alkaline solutions of pH 9-12. Total removal of the flux agent is recommended because it may migrate after water exposure.

3.4 Measurements of Smoke Corrosivity

Measurement of smoke corrosivity can be done according to different chemical or physical principles [10]. The easiest way of assessing corrosivity, which is used in a number of national and international standards, is the indirect measurement of acidity or alkalinity (pH) of the water extraction of effluents. Measurement of electrical conductivity of solutions, together with pH, gives a better idea regarding the presence of ionic species. However, such indirect methods are based on the assumption that higher acidity means higher corrosivity, and that is not always true, as discussed previously. Another method of measuring smoke corrosivity is the direct measurement of the weight loss of metal coupons exposed to smoke. An alternative

to this method is to measure the change of metal resistivity due to the loss of metal thickness. Commercial corrosivity probes based on this principle are being produced. The third method consists of measurements of the leakage of electrical current between closely situated copper strips simulating a printed wiring board.

The International Electrotechnical Commission, IEC 60754 Part 1 method [11] is based on the first principle of indirect measurements by capturing hydrogen halides and titrating them. This method's primary target is electrical cables and, more specifically, PVC cables or cables flame retarded with halogenated fire retardants. In this test, a small amount of a plastic material is heated in the stream of dry air, and gases pass through a 0.1 M solution of sodium hydroxide [9]. The control solution is then acidified with nitric acid, and a known volume of 0.1 M solution of silver nitrate is added. The excess of silver nitrate is then back-titrated with ammonium thiocyanate. This method is not recommended for low concentrations of halogen halides in the smoke.

The IEC 60754 Part 2 method [12] is based on DIN/VDE 0472 Part 813 [13]. It also is based on the absorption of effluent gases, but the decomposition of a polymer specimen (1 g) is performed in a quartz tube furnace preheated to 935 °C. The effluent gases pass through washing bottles filled with distilled water. The pH and the conductivity of the solution are measured afterward. Although this Part 2 method is designed only for halogen-containing gases, it is still an indirect method of assessing corrosivity.

The Centre National d'Etudes des Télécommunications (CNET) test uses only 600 mg of a pelletised or pulverised material, which is pyrolysed at 800 °C. The smoke is contained within the chamber, at controlled humidity and temperature (**Figure 3.4**), and the corrosivity is evaluated based on the change in resistance of a circuit that has been cooled to accelerate the deposition of smoke. This method represents the first example of direct measurement of smoke corrosivity because resistance is changed due to current leakage. The method is designed to test materials and is not suitable for testing real manufactured parts [14]. The International Organization for Standardization, ISO 11907 Part 2 test [15] is based on the CNET test.

Another corrosion test was developed in Germany and is based on a quartz furnace described in the DIN 53436 standard [16]. This furnace is also used for smoke toxicity testing in Germany. It consists of a moving-tube furnace configured in such a way that a constant level of smoke is created for the duration of the combustion period (generally 30 minutes). Air is passed through the furnace at a specific rate. The corrosion sensor, like the one in the CNET test, is a printed wiring board that is cooled down to promote deposition of corrosive gases. Change of resistivity is recorded as the measure of corrosion. This test also allows use of metal coupons that

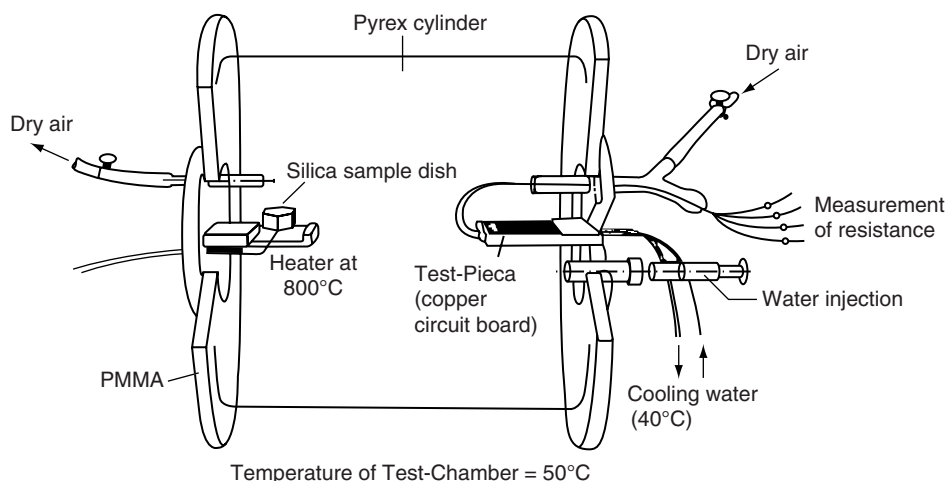


Figure 3.4 Schematic of the CNET corrosivity test chamber

will be exposed to the smoke, and corrosivity will be assessed as a weight gain [17]. The furnace can operate in flaming or non flaming (smoldering) mode. This test was developed into the ISO 11907, Part 3 test [15].

In the US, the American Society for Testing and Materials, ASTM D5485 test [18] is used to directly assess corrosivity of smoke. The test can use the cone calorimeter fire-test instrument or can be a stripped-down version of the cone calorimeter test designed only for smoke corrosivity. The cone calorimeter test, ASTM E1354 [19], is widely accepted as a bench-scale test for measurement of heat release, smoke, carbon monoxide and CO₂. In ASTM D5485, the instrument is equipped with a gas sampling collection device mounted above the cone heater. This device is used for taking a sample stream of smoke and passing it through an 11.2 litre exposure chamber (Figure 3.5). In the exposure chamber, two circuit board corrosion targets are mounted (one of the targets is protected and is used as a reference to compensate for temperature variation). Sampling lasts for 60 minutes or until 70% weight loss of the tested specimen has occurred. The advantage of this test is that relatively large samples (10 × 10 cm) can be tested, which allows for assessment not only of materials but of parts of assemblies and composites. This test is known as the cone corrosimeter and was also adopted by the ISO committee on plastics as ISO 11907, Part 4 [20].

In Canada, a test for the creation of acid gases from the combustion of polymeric materials in a tube furnace has been used to estimate the corrosiveness of smoke [14]. The gases emitted are trapped, and the acidity of the water extract is measured. An analysis of test conditions showed how the results can be significantly altered by small differences in the way the test is conducted [21]. The basis for this test is the assumption

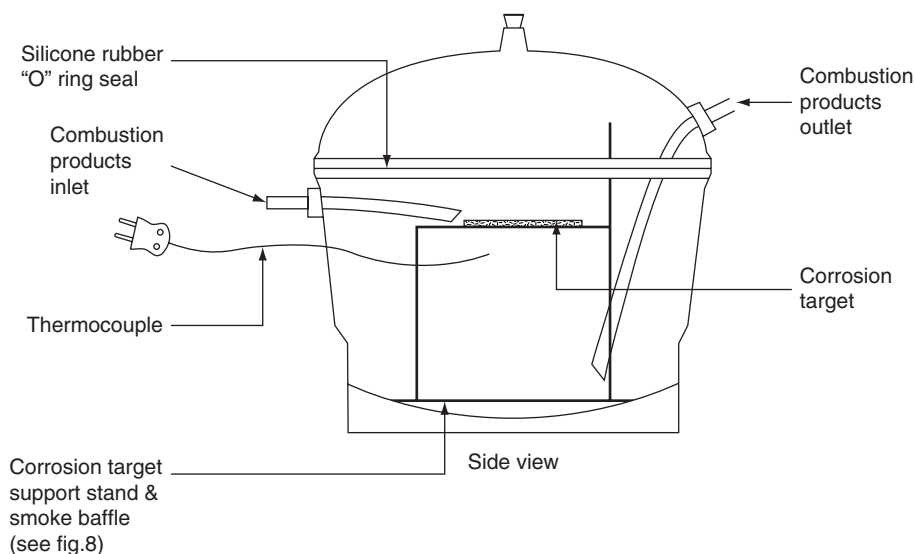


Figure 3.5 Smoke exposure chamber of ASTM D5485 [18] corrosivity test

that acid gases are the only corrosive products of any importance in polymer smoke. As was discussed earlier, this hypothesis has been proven to be wrong.

The fire propagation apparatus (FPA) described in ASTM E2058 [22] was originally developed at Factory Mutual (now FM Global) and is used there for assessing smoke corrosivity [1]. The FPA uses a resistivity corrosion probe similar to that used in the cone corrosimeter, and the probe is inserted directly into the sampling duct of the FPA. The corrosion is tested in the dynamic mode for the time of about 10 minutes of sample combustion, and for an additional 10 minutes while deposited corrosive gases attack the probe.

Factory Mutual also operates 5000 kW and 20,000 kW flame propagation calorimeters, which are capable of running combustion tests of cable arrays in their real configuration and measuring smoke corrosivity, amongst other parameters. Another possibility is running such tests in enclosed spaces simulating real rooms. Recently, a report [10] was issued of a study of smoke corrosivity of power cables and communications switch assemblies in a 272 m³ room in a realistic configuration. It was shown that the use of water (sprinklers) increases the non particulate fraction of smoke and thus makes soot with corrosive compounds stick tightly onto surfaces, resulting in the enhancement of corrosion. It was also noted that switch assemblies produced a more sooty type of smoke, which came from the printed wiring boards flame retarded with brominated flame retardants and caused more corrosion than a PVC cable array.

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4 Transport and Decay of Combustion Products

4.1 Introduction

A Fire hazard has three components:

1. Generation of heat and combustion products in a fire
2. Transport of heat, fire gases and particulates to the vicinity of the fire victim
3. Response of the subject to thermal, toxic or visual insult

The generation of fire effluents depends on a variety of factors, including ignitability and properties of the burning material or product such as the associated flame spread, rate of heat release, total amount of heat released and the type and amount of combustion products released. The present chapter will address mainly the transport considerations.

Transport has traditionally been mathematically treated as a buoyancy-driven, multi-room problem of gas and heat dynamics, often by means of zone-type fire models (such as the (FAST) model [1], contained within the National Institute of Standards Technology (NIST) Hazard I model [2, 3]). Common combustion products are sufficiently unreactive so that they do not react to any significant extent during transport. The most important material that is an exception to this rule is hydrogen chloride (HCl), a very reactive common combustion product that decays (i.e., decreases in concentration) by deposition [4–22]. Other halogen acids (hydrogen bromide (HBr) or hydrogen fluoride (HF)) should act in a similar fashion. The entrainment of air, containing reactive fire gases, also affects the density of smoke, as well as various characteristics of the soot particles contained in the smoke.

In order to understand what happens in fires, it is essential to study the effects of high temperatures, of thermal radiation, of lack of visibility and of the toxic potency of individual components of the smoke and their potential interactions. This chapter will discuss only the issue of transport and decay. The hygroscopic nature of halogen-acid gases is well known, and this is a key reason why its presence in a fire atmosphere is usually transient. Experimental studies have shown that it is very difficult to recover

all of the HCl evolved into an atmosphere, even when the reactions occur in small pieces of equipment [4]. Evidence for HCl decay ranges from early work in a smoke chamber similar to the National Bureau of Standards smoke chamber American Society for Testing and Materials, ASTM E662 [6] to animal toxicity experiments carried out in a standard-size room [15] to a series of experiments involving room/plenum [16, 17] and room/corridor configurations [23, 24]. Plenums are enclosed portions of the building structure that are not occupiable and that have been designed to allow air movement and serve as part of an air distribution system. In all cases, the peak HCl concentration measured was much lower than the theoretical value, based on the stoichiometry of the chlorine content of the material decomposed. Furthermore, HCl concentration soon decreased to a very low value. This decay was enhanced by the presence of water [11–14, 17–20, 22] and that of typical construction surfaces, which are sorptive [19, 20].

The work described was analysed by parameterisation of the results [18–20, 22, 23], an approach that yields rapid information on the effects of the variables involved. However, parameterisation has the disadvantage that the model involved is not general enough to be applied to situations other than the specific ones for which it has been designed. In 1987, a zone model for HCl generation, transport and decay was presented in a fashion consistent with generic-zone fire models, in particular, FAST [25]. In this model, there are ‘lumped’ parameters rather than ‘distributed’ parameters. In other words, concentrations are integrated over space to maintain the variation over time while becoming spatially independent. The basic model assumes well-mixed layers for all compartments (within the smoke layer); mass-transfer coefficients (estimated using the same approach as is used for convective heat transfer in fire models) for transport of HCl from its source, i.e., the hot smoke layer, to the surface where it will decay; partition coefficients for representing gas-solid equilibria at the surface; and a combination of diffusion into a surface and reaction with the surface for the decay on any surface. This model [25] was applied to data obtained in small-scale experiments [17, 18, 20] to calculate surface-specific parameters describing the decay process, and the results were then used to predict large-scale experimental behaviour [16, 22, 23].

4.2 Early Small-Scale Experiments

In the first series of experiments conducted to develop this decay model, the fire resulted from thermal decomposition of polyvinyl chloride (PVC) electrical insulation materials by electrical overload [16]. The tests were conducted in the same 180 litre polymethyl methacrylate (PMMA) chamber as used in the ASTM E1678/National Fire Protection Association, NFPA 269 smoke toxicity test [26, 27]. The amount of wire insulation

used represented loadings of 22.4, 44.7 and 89.4 mg/l in the chamber. The wire was placed on a porous surface (Kaowool) to prevent material loss by melting. The results showed that the concentration of HCl emitted from PVC decomposition passed through a maximum and then decreased. Moreover, the maximum concentration of HCl measured was less than 40% of the amount that should have been measured based on the Cl content of the PVC. This was the first clear indication of HCl decay. The rate of HCl decay was fast at the beginning of the fire, but gradually decreased as the HCl concentration reached an asymptotic value. It was not until HCl had already started to decay that any of the other combustion products (carbon monoxide (CO), carbon dioxide (CO₂), total hydrocarbons) reached their peak values. The peak concentrations of all products other than HCl were able to be clearly associated with the stoichiometry of the chemical composition of the fuel.

The second set of small-scale experiments involved studying the effects of surfaces on HCl decay in a small 3 litre box, lined with various construction materials (gypsum board, painted gypsum board, ceiling tile, cement block, Marinite, PMMA and painted PMMA) [19]. Painted surfaces had two layers of white latex paint. The box was evacuated and purged with either dry air or air at certain preset humidity values. After HCl was injected with a syringe, the atmospheric concentrations of the box were measured over time. Most experiments were conducted in a quiescent box, but forced convection was used in some experiments to enhance mixing. The decay of HCl occurs in two stages: (1) a very fast (almost instantaneous) decay; and (2) an exponential, first-order, decay, as shown next:

$$\ln [(C_0 - A_0) / C] = k t$$

The preexponential parameter, A_0 , and the rate-decay constant were calculated by nonlinear curve fitting. Results (see **Tables 4.1** and **4.2**) indicated:

1. The rate of decay decreases as the surface gets reused.
2. The type of surface has a strong effect: PMMA is very inefficient in causing HCl decay, while cement block, Marinite, unpainted gypsum board and ceiling tiles are extremely efficient.
3. Painted PMMA is much more effective than plain (unpainted) PMMA, but less effective than painted gypsum board, in causing HCl decay.
4. Painted gypsum board is much less effective than unpainted gypsum board in causing HCl decay.
5. Humidity strongly enhances decay.

Table 4.1 Kinetic HCl decay parameters of surface exposures (no humidity)				
Surface materials	Conditions		Reaction Constant, k (min^{-1})	A_0/C_0 *
	HCl (cm^3)	Temperature ($^{\circ}\text{C}$)		
PMMA	3	25	0.008	0.21
Painted PMMA	7	24	0.110	0.45
Painted gypsum board	5	82	0.69	~ 0.59
Ceiling tile (back)	7	100	2 approximately	0.5
Cement block	7	197	3.3	~ 0.92
Ceiling tile (front)	7	100	>5	0.75
Unpainted gypsum board	7	100	5.9	~ 0.24
Cement block	3	84	>8	~ 0.75
Marinite	7	100	>12	0.75
Painted PMMA ^a	7	24	0.110	0.45
Painted PMMA	7	24	0.036	0.44
Painted PMMA	7	25	0.025	0.40
Painted PMMA	7	24	0.020	0.30
Painted PMMA	7	24	0.020	0.44
Painted PMMA	7	24	0.14	0.36
Painted PMMA	7	24	0.013	0.44
Painted PMMA	7	23	0.014	0.34
Painted PMMA	7	25	0.013	0.31
Painted gypsum board ^a	3	77	1.14	0.59
Painted gypsum board	3	79	0.69	0.42
Painted gypsum board	3	79	0.5	0.37
Painted gypsum board	3	80	0.29	0.58

Painted gypsum board	3	82	0.26	0.44
Painted gypsum board	7	84	0.30	0.49
Painted gypsum board	3	78	0.34	0.54
Painted gypsum board	3	79	0.31	0.48
Painted gypsum board	3	80	0.27	0.47
Painted gypsum board	3	81	0.31	0.46
Unpainted gypsum board ^a	7	100	5.94	0.24
Unpainted gypsum board	7	100	5.37	0.11
Unpainted gypsum board	7	103	4.02	0.37
Unpainted gypsum board	7	102	4.81	0.30
Unpainted gypsum board	7	100	4.58	0.31
Unpainted gypsum board ^b	7	102	4.25	0.25
Unpainted gypsum board ^b	7	100	3.45	0.31
Unpainted gypsum board ^b	7	100	1.09	0.67
Unpainted gypsum board ^c	10	100	2.07	0.49
Unpainted gypsum board	10	100	3.83	0.56
*: A0/C0: ratio of pre-exponential parameter and initial HCl concentration a: Test on surface used for first time and subsequent tests reuse same surface b: 200 cm³ of HCl injected before test and box was purged c: 99 g of HCl injected before test and box was not purged				

Table 4.2 Effect of humidity on kinetic HCl decay parameters (3 cm ³ of HCl injected)				
Surface material effect of humidity				
Material	Conditions		Reaction Constant, k (min ⁻¹)	A ₀ /C ₀ [*]
	Temperature (°C)	Water (%)		
Painted gypsum board ^a	48	0.0	0.42	0.85
Painted gypsum board	51	0.0	0.44	0.53
Painted gypsum board	51	3.0	0.49	0.40
Painted gypsum board	51	5.0	1.64	0.81
Painted gypsum board	82	1.5	0.52	0.87
Painted gypsum board	82	3.0	0.94	0.75
Painted gypsum board	81	5.0	1.23	0.59
* A ₀ /C ₀ : ratio of pre-exponential parameter and initial HCl concentration				
a: Test on surface used for first time and subsequent tests reuse same surface				

Figure 4.1 shows how ineffective PMMA is in causing HCl decay and that unpainted gypsum board is about seven times more effective than painted gypsum board. **Figure 4.2** indicates how much effect humidity has on painted gypsum board.

Surface effectiveness order, to enhance HCl decay:

PMMA << Painted PMMA < Painted Gypsum Board < Gypsum Board

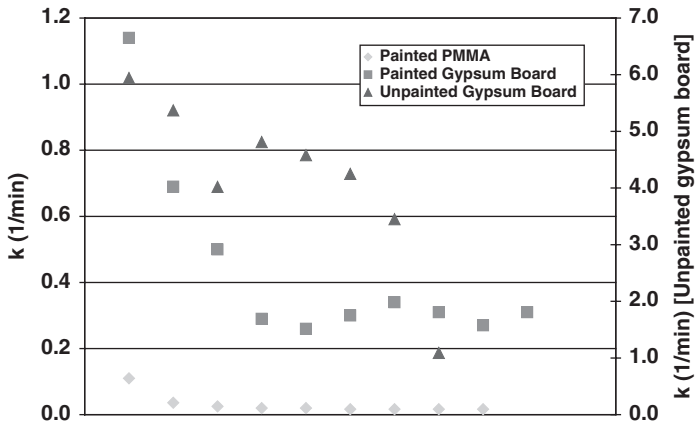


Figure 4.1 Effect of re-exposure on HCl decay. Based on data from M.M. Hirschler and F.M. Galloway in *Hazards of Combustion Products: Toxicity, Opacity, Corrosivity and Heat Release*, Interscience Communications, London, UK, 2008, p.73 [21]

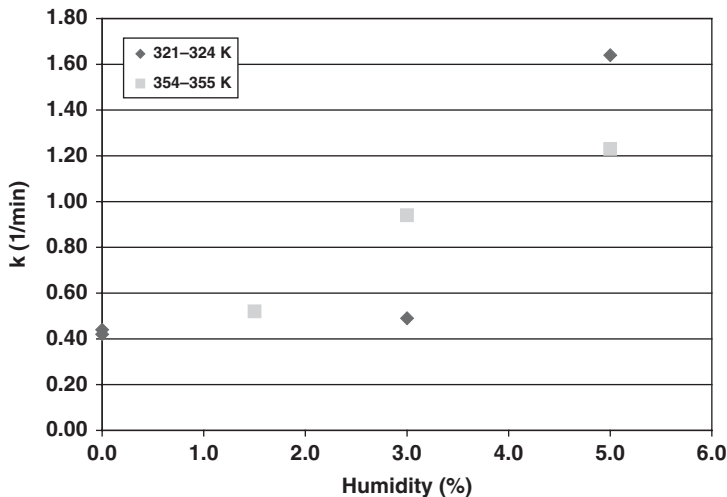


Figure 4.2 Effect of water on HCl decay effectiveness of painted gypsum board. Based on data from M.M. Hirschler and F.M. Galloway in *Hazards of Combustion Products: Toxicity, Opacity, Corrosivity and Heat Release*, Interscience Communications, London, UK, 2008, p.73 [21]

4.3 Large-Scale Experiments

4.3.1 Room-plenum Scenario

The small-scale experiments on wire discussed earlier were preliminary to the first set of large-scale experiments involving 9.14 m of PVC-coated building wire [16–18].

The wire was laid on the floor of a simulated plenum above a room. The dimensions of the plenum were 2.4×3.7 m, with a 1.2 m height, and it had painted gypsum board walls and ceiling and ceiling tile floor. The floor of the simulated plenum was simply covered by ceiling tiles laid on metal tracks, above a standard room ($3.7 \times 2.4 \times 2.4$ m). The decomposition of the wire was carried out at currents of 180-250 A.

These tests demonstrated that the efficacy of the analytical instrumentation used for the experimental measurements was sufficient to have expected that the vast majority of the HCl present in the atmosphere would have been measured. In fact, however, the peak concentrations of HCl measured represented less than 35% (actually 21-33%) of the stoichiometric chlorine content in the 'fuel'. In other words, two-thirds or more of the HCl was lost to decay. Moreover, measurements made on the ceiling tiles (which represented the floor of the plenum and, thus, the ceiling of the room below) were found to have a very high chlorine content after the test. Using the chlorine deposited on the surfaces, a mass balance resulted in virtually complete accounting of the original chlorine.

Measurements of gas concentrations were made in the room below the plenum for the key gases: HCl, carbon oxides and hydrocarbons. Virtually no HCl was found, indicating that there was no transport of HCl into the room below the plenum, but that there was significant transport downward of both CO and CH_x, as well as of CO₂. In the case of the carbon-containing gases, some 10-20% of their maximum concentration was found in the room below the plenum, while the peak HCl concentration found in the room was less than 3%, after 30 minutes. Of all the HCl that remained in the plenum, most of it ended up in the ceiling tile and gypsum board surfaces. Moreover, considerable amounts of HCl initially decayed very rapidly, just as in the small-scale experiments, while the other gases measured did not. The slight decrease in CO and CH_x concentrations results from diffusion to the outside, occurring through small leaks in the room and plenum outer surfaces, and not from decay. The effects discussed here are illustrated by **Figures 4.3–4.6**.

A rough analysis of these data indicates that HCl disappears from the atmosphere by reactive gas decay at a rate of up to 270 ppm/min (based on peak concentrations), which corresponds to a first-order half-life of some seven minutes. This means that a very large proportion of the HCl generated disappeared before the other key combustion-product gases achieved peak concentrations. In particular, within the time frame of typical fires, say 30 minutes, the HCl concentration will have both peaked and decayed to less than 25% of its maximum value.

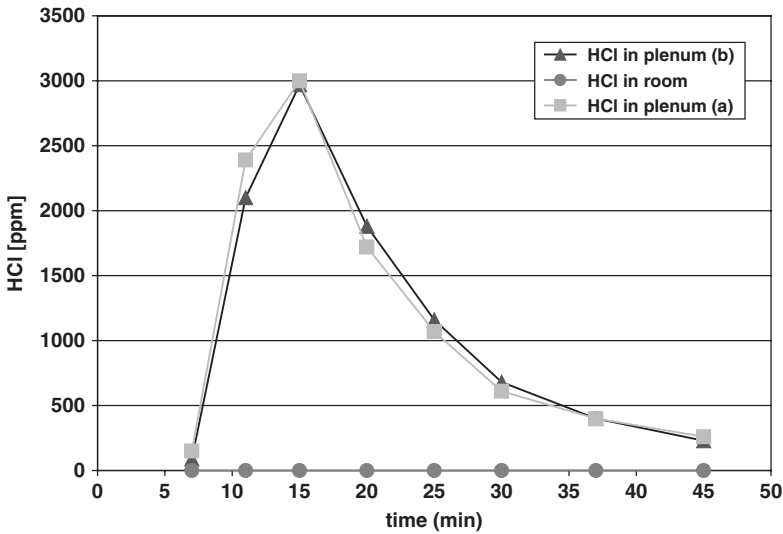


Figure 4.3 Concentration of HCl in plenum and room. Based on data from M.M. Hirschler and F.M. Galloway in *Hazards of Combustion Products: Toxicity, Opacity, Corrosivity and Heat Release*, Interscience Communications, London, UK, 2008, p.73 [21]

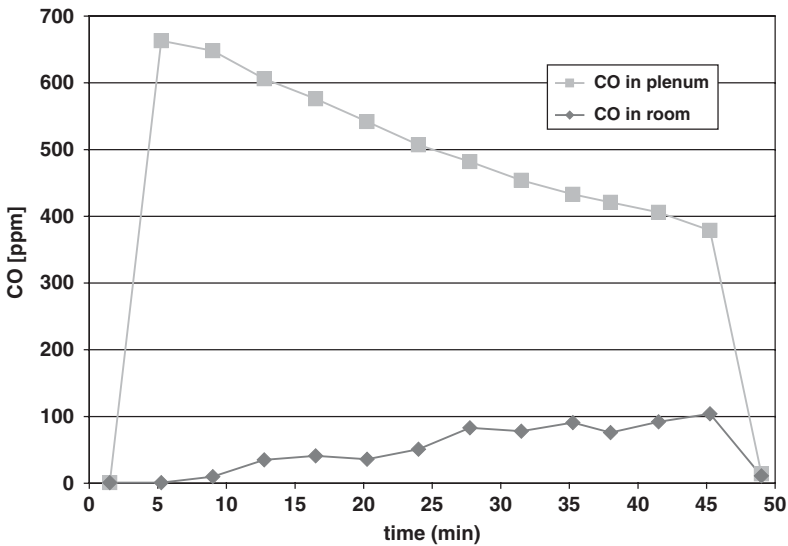


Figure 4.4 Concentration of CO in plenum and room. Based on data from M.M. Hirschler and F.M. Galloway in *Hazards of Combustion Products: Toxicity, Opacity, Corrosivity and Heat Release*, Interscience Communications, London, UK, 2008, p.73 [21]

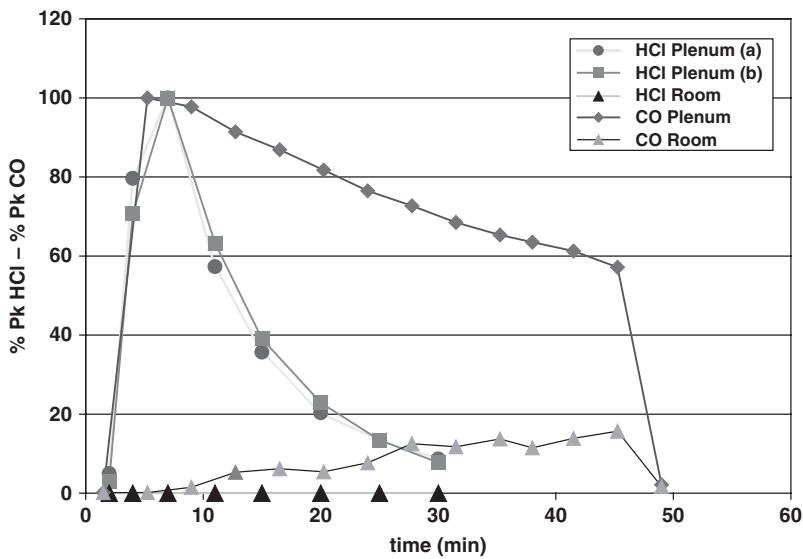


Figure 4.5 Percentage of HCl and CO in plenum and room. Based on data from M.M. Hirschler and F.M. Galloway in *Hazards of Combustion Products: Toxicity, Opacity, Corrosivity and Heat Release*, Interscience Communications, London, UK, 2008, p73 [21]

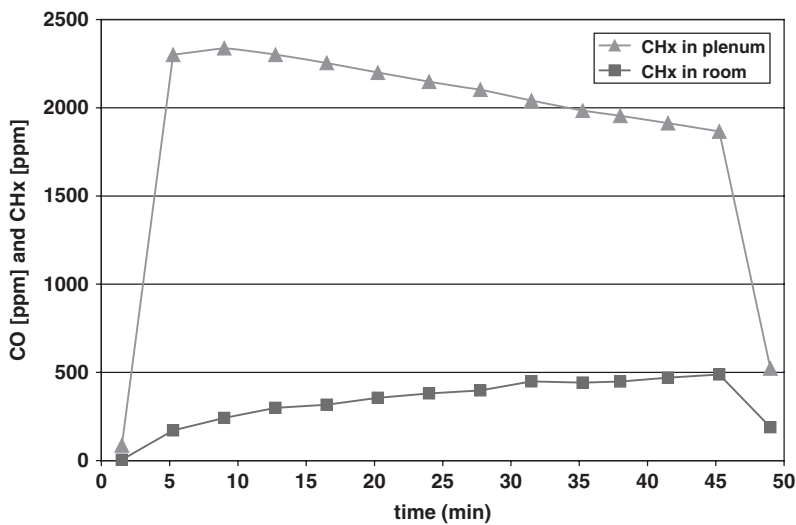


Figure 4.6 Concentrations of CH_x in plenum and in room. Based on data from M.M. Hirschler and F.M. Galloway in *Hazards of Combustion Products: Toxicity, Opacity, Corrosivity and Heat Release*, Interscience Communications, London, UK, 2008, p73 [21]

Data analysis conducted in the room-plenum experiments [17] showed that the kinetics of the reactions can be represented by the following mechanism:



For the above mechanism, three first-order reaction rate constants would apply: k_{12} (for the dehydrochlorination), k_{23} for the deposition of HCl (going from atmospheric HCl to deposited HCl) and k_{32} for the desorption (reverse of HCl deposition). The rate constants calculated showed excellent data fits. The fastest reaction was the dehydrochlorination, followed closely by the deposition reaction (both of them with rate constants in the range of 0.12-0.36 l/min), while the desorption reaction was extremely slow (rate constants in the order of 0.005 l/min). The rate of desorption was twice as high in the presence of a very non sorptive surface such as PMMA (which is not a construction surface): 0.01 l/min. The construction surfaces assessed (Marinite, gypsum board, ceiling tile, mineral fibre, cement block and painted gypsum board) all gave similar, and lower, desorption rate constants. It is of interest that higher humidity enhances considerably the rate of HCl decay and also enhances, but just slightly, the rate of HCl desorption from construction surfaces.

Quantitative analysis of the fate of chlorine in the room-plenum experiments showed that virtually all the chlorine in the ‘fuel’ could be accounted for in the experiments, according to the following percentages:

Chlorine fate: 53% walls, 25% char, 19% ceiling tiles and 3% filters

4.3.2 Room-corridor Scenario

A test scenario was built [23, 24] with a standard ASTM burn room (3.7 m × 2.4 m × 2.4 m high), connected by a doorway to a 19 m long corridor. The corridor was closed off at the end closest to the burn room and was open on the other end. The room and corridor were all built with painted gypsum board walls. The fire source was a set of three burners forming a 30 cm × 30 cm radiant panel, generating a molecular weight (M_w) of 2.7 g/mol with a small gas-fed pilot flame (174 W) and a sandbox radiant methane burner, identical to the one in the NFPA 286 room- corner test [28] and set at a M_w of 5.8 g/mol. In these experiments, plaques were manufactured from a standard rigid PVC (with only some 2 wt% of processing aids). The plaques were made into 30 cm square test specimens, 0.22 cm thick, so that a mass of approximately 500 g (actually 400-600 g) of PVC was exposed. The burner’s gas flame was used to ensure that flaming combustion occurred. All experiments lasted 30 minutes and there was no artificial forced convection, other than that generated by the fire itself. HCl concentrations were measured in the burn room’s doorway and along the corridor. Fresh surfaces were used in each experiment. In the experiments where the thermal input was very small (8

kW), HCl decay was relatively small due to several factors: (1) low smoke flow rates; (2) very low entrainment levels; (3) lower temperatures; and (4) the fact that there was an unrealistically low probability of the smoke flow reaching a surface on the corridor end (which had no doorway). The experiments where the methane burner operated at 40 kW and 200 kW showed much higher levels of decay. It is worth pointing out, as will be discussed later, that there was good correlation between the data and the predictions of the 1987 parametric HCl decay model [25].

4.3.3 Room-corridor-room Scenario

In these tests [22, 29], the room was also an ‘ASTM’ room and was identical to the burn room in the room-corridor scenario, but the corridor was slightly longer (26 m) and, critically, had two features that differed from the room-corridor scenario. They were the following: (1) a target room, identical in dimensions to the burn room, was at the other end of the corridor, with a doorway between it and the corridor; and (2) the corridor ended in a wall with a standard doorway. In these experiments, the rigid PVC used was the same type of PVC as in the room-corridor scenario experiments. The amount of PVC used per test was approximately 1,900 g. In three of the experiments, the HCl was generated by burning PVC and using the same burners as in the room-corridor scenario. In other experiments, HCl was introduced directly into the ‘burn room’. HCl concentrations were measured in the burn room, burn room doorway, along the corridor and in the target room. Fresh surfaces were used in each experiment. It was, once more, found that a very large fraction of the HCl was deposited on the walls, which were built of painted gypsum board. The decay of HCl found in these experiments was consistent with what had been found in earlier work, and showed that there was almost no decay in the burn room, but that decay along the corridor ranged from 10% (at the doorway) to 30% (at the end of the corridor). Much more significant was the decay in the target room, where the differences between the expected concentration (i.e., the HCl concentration that would have resulted if there had been no HCl decay) and the actual concentration ranged between 60 and 90%. It is important to note that the expected concentration in the target room (and even along the corridor) was lower than that associated with 100% stoichiometry since much of the HCl was lost through the twin effects of entrainment and dilution of smoke. Thus, for example, in one experiment the burn room concentration reached an expected peak of approximately 1,500 ppm after a few minutes (from burning almost 2 kg of PVC), but was down to approximately 900 ppm after 30 minutes. The actual concentration measured in the target room reached a peak of less than 450 ppm (after 15 minutes) and rapidly decreased from there. This value is approximately 60% lower than the predicted peak HCl concentration based purely on entrainment and smoke dilution. **Figure 4.7** shows how, for two experiments (one with burning PVC and one directly injecting HCl), the decay is considerable and can be modeled satisfactorily using the 1987 model [25] formulation.

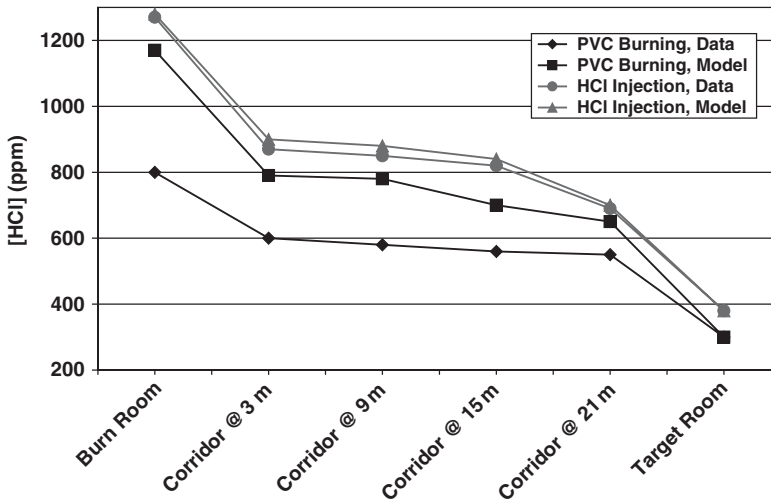


Figure 4.7 HCl decay in room-corridor-room experiments. Based on data from M.M. Hirschler and F.M. Galloway in *Hazards of Combustion Products: Toxicity, Opacity, Corrosivity and Heat Release*, Interscience Communications, London, UK, 2008, p73 [21]

4.3.4 Heating, Ventilation and Air Conditioning Scenario

The transport and decay of HCl was studied in a simulated heating, ventilating and air- conditioning (HVAC) system [30] in the final large-scale set of experiments. The scenario involved a system with eight sections of an HVAC system, each section being 15.24 m long and 0.305 m wide. Thus, the total width of the HVAC system was 2.44 m. In this way, the air stream (i.e., the smoke stream, including HCl) was injected with an air blower in one end and exited the other end, into exhaust, after going through all eight sections and reaching walls at each turn. Four experiments were conducted. In the first two, the first five sections had surfaces composed of painted gypsum board, whereas the last three sections were built of unpainted gypsum board. In the other two tests, the walls and ceiling of the first five sections were made of PMMA, with the floor made of painted gypsum board, and the last three sections were again made of unpainted gypsum board. All of the painted sections were replaced after each test. The HCl was injected from a cylinder, at a rate controlled via a load cell. The first three experiments were conducted for 30 minutes and the last one for 22 minutes. HCl concentrations were measured at several distances from the entrance of the simulated duct system. In every one of the cases, there was virtually no HCl remaining and exiting at the HVAC exhaust, despite the fact that HCl concentrations were as high as more than 4,000 ppm at a distance of 3 m into the HVAC system. It is very noticeable how the rate of HCl decay was much lower in runs 3 and 4, where

PMMA surfaces were used, than in the two earlier runs. For example, at 50 m, there was very little HCl left after the initial two tests (see **Figure 4.8**), but a distance of almost 100 m was required before the HCl concentration decreased down to those levels in the last two tests (see **Figure 4.9**).

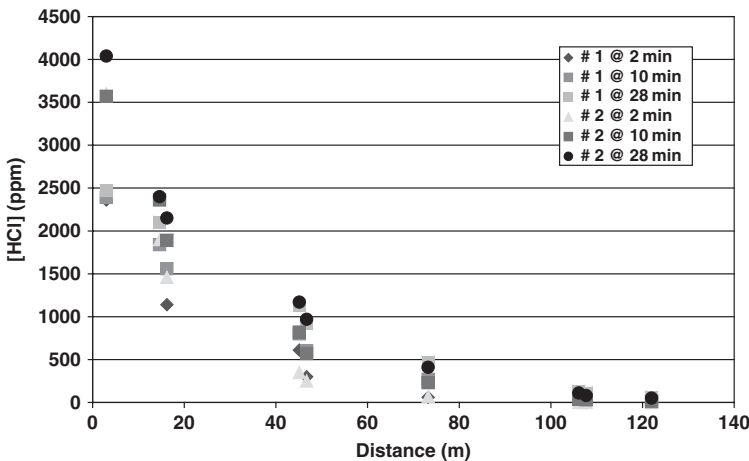


Figure 4.8 HCl decay in HVAC tests using gypsum board. Based on data from M.M. Hirschler and F.M. Galloway in *Hazards of Combustion Products: Toxicity, Opacity, Corrosivity and Heat Release*, Interscience Communications, London, UK, 2008, p73 [21]

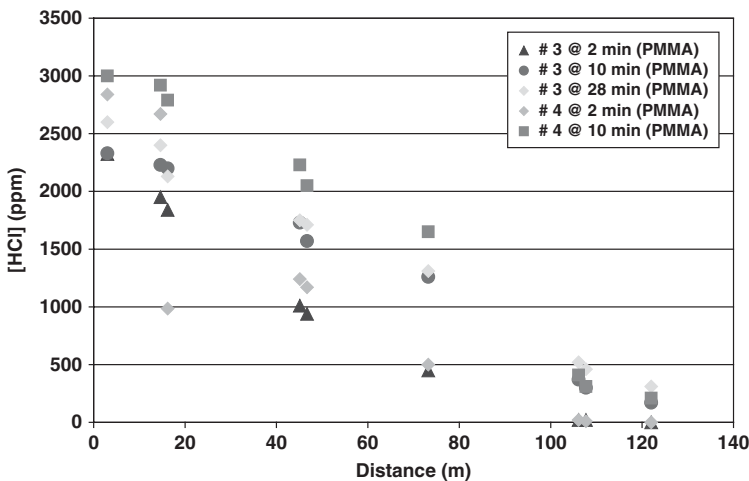


Figure 4.9 HCl decay in HVAC tests using PMMA. Based on data from M.M. Hirschler and F.M. Galloway in *Hazards of Combustion Products: Toxicity, Opacity, Corrosivity and Heat Release*, Interscience Communications, London, UK, 2008, p73 [21]

4.4 Later Small-scale Experiments

Analysis of the previous data and development of a mathematical model required that an additional number of experiments be conducted using small-scale equipment. An additional series of experiments were designed and conducted [31–34], and the results were analysed together with those of the small-scale experiments discussed previously [16, 19]. The key issue was to try to investigate separately the generation and the decay aspects.

First set: In a set of 36 experiments, HCl was generated under conditions of forcefully minimised decay; the experiments were labeled as ‘HCl generation without decay’ (GWD) [31]. In these experiments, HCl was generated in three glass reactors (two spheres: 12.7 litres and 13.1 litres in volume, and a 7 litres tubular reactor), with walls heated by means of heating tape. The HCl was generated through electrical decomposition of PVC wire coating (with copper or carbon steel wire) under well-stirred conditions. Efforts were thus made to minimise the amount of HCl decay so that the decay rate remained much smaller than the generation rate. These experiments were used to create a model for generation of HCl from PVC, based on physico-chemical principles and on the temperature-time pattern measured. This model was, thus, only partly empirical and replaced the previous model, which was purely empirical. The results obtained from using the model were then used to obtain a very adequate fit for the entire set of experiments. The results were also used to determine the effects of two different types of metal wire (copper and carbon steel) on the HCl decay rate. The results of the GWD experiments were also fitted in conjunction with those of the earlier experiments, in a larger reaction chamber [16]. This was done in order to verify that the new overall model is, indeed, a good representation of the entire process. The successful outcome showed that the new model provided an independent confirmation of the validity of the total model for HCl generation, transport and decay reported previously.

In these GWD experiments, close to 100% of the theoretical amount of HCl was found in the tests, indicating that HCl decay is, indeed, as expected, minimal on hot glass walls. Another finding was that ambient temperature significantly affects both the generation and the decay rates of HCl. The results also showed that the mode of generation (i.e., whether using steel wire or copper wire) affected the generation and decay: copper is much more reactive than carbon steel. In fact, the presence of even a small amount of wire (either copper or steel) will noticeably increase the rate of HCl decay when other surfaces are non sorptive (PMMA or glass). However, the effect of a small copper wire is dwarfed in practical applications by most construction surfaces, including painted gypsum board, due to the differences in surface area. **Table 4.3** shows the HCl decay rates on various surfaces.

Table 4.3 HCl decay rates on various surfaces in GWD experiments	
Surface	Decay rate (mol/cm ²) x 10 ⁶
Copper	21
Carbon steel	2.6
PMMA	0.036
Painted gypsum board	0.78
Ceiling tile	5.3
Cement block	4.4
HCl: 4,000 ppm at 27% relative humidity and 40 °C	
Metal surfaces at 800 °C	
Nonmetal surfaces at 27 °C	

Second set: In another set of tests, a total of 63 experiments were carried out in a 200 litre PMMA chamber. In these tests, a large amount of HCl was injected in the absence and presence of various fluids and surfaces [32]. These experiments were labelled as ‘HCl decay without generation’. The fluids used were: water, ethylene glycol, ethylene glycol/water in a 50/50 mixture, a fluid considered to be a model for airborne smoke particulates (and several fluids considered to be partial models for such synthetic smoke) and mineral oil. The interior surfaces used for the chamber were PMMA (i.e., no added surface), painted gypsum board, ceiling tile and soot. These results showed the efficiency of many fluids as sinks for HCl, with water and synthetic smoke being the most effective. The previously developed parametric model for HCl transport and decay [25], based on parameters obtained from experiments with HCl formation from PVC combustion or pyrolysis, was used to predict the results in order to confirm whether a model based on HCl generation from PVC could be applied to cases where no PVC was present. The correlation between experimental and predicted atmospheric HCl concentrations, without fitting any new parameters, was excellent, indicating that the model is robust enough that it can be applied to a number of scenarios where HCl is present, irrespective of its origin.

Additional experimental study: The study of various surfaces [33] showed that, for unexposed nonmetallic surfaces, HCl decay is faster on unpainted gypsum board (with a half-life of less than 1 minute) than on painted gypsum board (with a half-life in the range of 1-2 minutes). HCl has an almost 10-fold longer half-life on painted PMMA than on painted gypsum board, with the half-life on unpainted PMMA 2-3 times longer still. There is a nonlinear effect of repeated exposures to HCl for both painted gypsum board and painted PMMA, but repeated exposure to HCl has no effect on HCl decay on unpainted gypsum board, at least up to 10⁻⁶ g mol HCl/cm²

(which is equivalent to 10,000 ppm of HCl initially in the gas phase). In fact, normal (unpainted) gypsum board essentially shows no effect up to well over 1% HCl concentration (unrealistically high).

4.5 Modelling

Several modelling studies [35–38] developed ways to incorporate the 1987 parametric model [25], developed for HCl generation and decay, into version 1.1 of the NIST Hazard I zone room fire model [3]. The basic building block of Hazard I is the model FAST [1, 2].

From the beginning of the modelling work described here, the intent had always been to formulate the model in a manner consistent with the treatment of convective heat transfer in multicompartment zone fire models, particularly FAST [1, 2]. This would, ultimately, allow a generalised HCl transport and decay model to be incorporated into such models. These studies [35–38] developed the technical basis of the HCl generation and decay model further, and showed its validity by comparing computational results with data generated in two full-scale fire tests, and then demonstrated the usage of the model in a hypothetical private-residence fire scenario. Finally, these studies provided guidelines for use of the model in the context of the zone fire model Hazard I. The key concern was that the study of decaying gases, especially HCl, had not been included in the tenability calculations of Hazard I. Thus, the use of Hazard I for fires in which HCl is a major combustion product needed to be restricted to the use of FAST, a subsection of Hazard I. The next overall concern was that the initial ambient humidity, as calculated by the FAST software, is much higher than is realistic. This causes predictions of excessive HCl decay, and could be solved very easily by the developers of the Hazard I software.

In these four studies, the HCl generation and decay model were applied to several full-scale tests in room-corridor-room and room-plenum scenarios. The results were compared to the experimental data, to earlier predictions obtained by using the HCl deposition model and FAST separately, and to the results to be obtained in the absence of HCl decay. The studies culminated in a demonstration run, which showed the predictive power of the HCl capability in a realistic fire scenario (a two-storey, single-family residence). The HCl decay application in Hazard I showed how HCl levels are much lower, particularly remote from the fire, than would have been the case if HCl had not undergone decay. The overall results of this analysis indicate that the released version of Hazard I is an excellent first step in the use of the HCl decay and generation model. However, a few difficulties still exist. Some of them are easily solvable (e.g., the overall wall surfaces present), while others are more inherent in the method (e.g., no deposition on floors).

4.5.1 Model Description

The model for HCl decay during the transport of fire gases has four basic assumptions:

1. The HCl concentration is uniform in the bulk gas phase.
2. Transport across the gas boundary layer is described by a mass-transfer coefficient.
3. Partitioning of HCl at the gas/wall interface is described by a surface-specific equilibrium coefficient.
4. The rate of disappearance of HCl into the wall is described by a first-order rate constant that is specific to the surface material.

In most applications of the model, the experimental layout permits the approximation that large surface areas (e.g., the entire ceiling in a room) can be treated uniformly. Thus, the model can be formulated in terms of ordinary differential equations with time as the independent variable. This treatment is consistent with ‘zone modeling’ of convective heat transfer in multicompartment fire models.

The mathematical formulation is shown in an appendix to this chapter. The values for the seven key constants in the appendix equations for the five principal surfaces studied in this work are shown in **Table 4.4**, so that easy visual comparisons can be made.

4.5.2 Assessment of the Hydrogen Chloride Decay Model in Hazard I

The HCl decay model contained within the Hazard I, version 1.1, software was applied to three cases [38]: (1) room-plenum (discussed previously); (2) room-corridor-room (also discussed previously); and (3) scenario 5, Christmas tree fire, one of the example cases for the Hazard I method [3].

The Christmas tree fire example involves a townhouse, which has two floors. For Hazard I use, on the lower floor there are two ‘compartments’ [the burn room ($8.2 \times 4.9 \times 2.4$ m) and the hall ($2.1 \times 5.2 \times 2.4$ m)], a set of stairs [in two more ‘compartments’: a low ($1.2 \times 2.1 \times 2.4$ m) and a high ($1.2 \times 3.0 \times 4.9$ m) level] and on the higher floor there are two more ‘compartments’ [bedrooms 1 ($5.3 \times 3.3 \times 2.4$ m) and 2 ($2.9 \times 6.1 \times 2.4$ m)]. In reality, the house has, of course, several compartments and furniture, but is divided in this way for calculation purposes. The walls and ceilings are painted gypsum board and the floors are concrete (lower floor) and wood (Douglas fir, upper floor). The first item ignited is a natural Christmas tree,

Table 4.4 Surface coefficients for HCl decay at five surfaces

Surface	b1 (m)	b2 (m ³ /kg)	b3 (1/s)	b4 (J/g mol)	b5 (m ³ /kg)	b6	b7
PMMA	0.6×10^{-5}	0.0137	0.0205	7476	29	1.0	0.431
Ceiling tile	4.0×10^{-3}	0.0548	0.123	7476	30	1.0	0.431
Painted gypsum	6.3×10^{-3}	191.8	0.0587	7476	193	1.021	0.431
Cement block	1.8×10^{-2}	5.48	0.497	7476	30	1.0	0.431
Marinite	1.9×10^{-2}	0.137	0.030	7476	30	1.0	0.431

b1: Fitted surface parameter, representing temperature dependency, in m

b2: Fitted surface parameter, representing temperature dependency, in m³/kg

b3: Fitted surface parameter, representing the first-order reaction preexponential factor, in 1/s

b4: Fitted surface parameter, representing the activation energy, in J/g mol

b5: Fitted surface parameter, representing dependency on humidity, in units of (m³/kg) ^(b7-b6)

b6: Fitted surface parameter, representing dependency on humidity; it is dimensionless

b7: Fitted surface parameter, representing dependency on humidity; it is dimensionless

which eventually ignites a ‘bean bag chair’ (vinyl covered, with polystyrene foam beads). For this application, 454 g of polystyrene beads were replaced by an equal mass of rigid PVC. The generation of HCl was calculated on the basis of a 56% HCl content of the PVC. The HCl generation was based on the assumption that this PVC

formulation contained no fillers or other HCl retention catalysts; this is a simplistic approximation. It was assumed, for simplicity, that the replacement of polystyrene by PVC had no effect on heat release or other fire performance.

The key final outcomes of a Hazard I run are the expected mortality in the fire and the time available for escape. This is accomplished based on one of several tenability criteria, addressing heat, smoke toxicity or a combination of both. The smoke toxicity tenability criterion is based on the *N*-gas model, which uses a combination of the toxic potencies of various primary toxic gases: CO, CO₂, hydrogen cyanide (HCN) and low oxygen, but does not include HCl, although NIST has already developed a modified formula for the *N*-gas model that does include HCl [39]. Thus, it is not possible to adequately assess the effect of chlorinated materials on the toxicity of the smoke atmosphere using this criterion. This is an easily solvable problem. There is, unfortunately, an added problem. A further criterion for assessing tenability via smoke toxicity is the use of a generic smoke toxic potency, and the calculation of tenability based on overall mass loss concentration time. This is a very adequate calculation and is, in fact, a better calculation method than the one that is based on individual toxic potencies. However, when HCl is generated, this overestimates the smoke toxicity hazard because the tenability is calculated based on mass lost by the fuel burnt and not on the amount of smoke present. The difference between the two is, of course, the amount of HCl that has decayed. This is a problem that is less easily solved, but is a small issue.

Case a: Hazard I predicts much less HCl decay than is shown by the experimental data. One of the most important reasons for this discrepancy is the fact that the ‘hot layer’ never reached the floor level in Hazard I, whereas it clearly did so in the actual experiment. Thus, HCl decay on a very substantial fraction of the surface (the ceiling tile floor) was ignored. This is even more important since the rate of HCl decay on ceiling tile is considerably faster than on painted gypsum board. Another concern has to do with the mass flows. This fire involved over 9 m of cable, stretched across the floor, but Hazard I used a ‘point source’, thereby requiring the smoke (and HCl) to travel much further to any wall surface.

Case b: Hazard I satisfactorily predicts this scenario, with the *caveat* that it is essential to subdivide the long corridor (in the room-corridor-room) into several ‘virtual compartments’ for the zone model and that a few excessively high values are found early on.

Case c: An analysis was made of the ‘compartments’ in this ‘packaged’ example found in the Hazard I reference guide. During this analysis, it was noted that the ‘compartments’ are simply one way in which the same floor and ceiling area, and the same compartment height, could be distributed along walls. It was, moreover,

observed that other walls present in the house (bathrooms, closets, kitchen furniture) were not used, although they would clearly have served as added sinks for HCl. A simple arithmetical calculation shows that the dimensions of these compartments can easily be changed within the same house scenario to achieve higher wall surfaces. Thus, Hazard I had to be run in an ‘enhanced decay’ mode, in which every ‘compartment’ had 50% more walls but the same floor and ceiling surfaces and the same overall volume. With this change, the Hazard I model did an excellent job of representing realistic HCl decay data.

4.5.3 Update on Modelling

FAST and Hazard I are both zone fire models, as was discussed earlier. A zone fire model is one in which a compartment is subdivided into two zones: a hot zone where the fire is (top of the compartment) and a cool zone where relatively normal conditions apply (and life is still tenable). This model requires relatively low computing times and was the most frequent way of conducting fire modelling at the time that the HCl decay model was developed. If added detail was needed, ‘virtual compartments’ were created (as in the room-corridor-room scenario discussed previously), and the problem was solved in that way. A field-fire model subdivides the space (or compartment) of interest into thousands of ‘cells’ and solves the problem of the parameters in each cell individually. This is a multi-dimensional approach that requires a much more powerful computer than a zone fire model. With the advances in computer hardware, the use of field-fire models has become much more extensive than in the past and, in fact, they have overshadowed the use of zone fire models, which are now rarely used. This created a problem for the modelling of the decay of reactive fire gases such as HCl: the model described above and discussed in this chapter will now need to be revised to use with field-fire models to avoid the effects of reactive fire gases being overpredicted by field-fire models that ignore transport and decay. Unfortunately, the expertise needed to conduct such modelling is probably lacking among those interested in the issue.

4.6 Other Gases

HCl is not a unique gas when it comes to decay in fires. Other gases with similar characteristics are likely to exhibit similar phenomena in fire atmospheres. Thus, for example, HBr and HF, which are the other two common halogen acids found in fire atmospheres, can be expected to behave the same way as HCl.

HCl has been studied extensively and is the subject of more than 20 published papers, to a large extent because HCl is a major product resulting from the combustion of

a widely used synthetic material, PVC [7, 8, 40, 41], which is often present in fires because of its wide range of applications. In fact, the results of two studies, in which firefighters equipped with gas-sampling probes, entered buildings on fire, found HCl in one-third of the 312 sets of measurements obtained in separate incidents [42, 43]. Interestingly, the highest HCl concentration measured in either of these studies was only 280 ppm [44], in spite of typical emissions of HCl from PVC (and other materials) that can fall in the range of thousands of ppm. For example, a total of 38 of the CO measurements exceeded the typical toxic potency of CO, which is in the range of thousands of ppm. Therefore, studies of fire hazard need to take into account HCl decay in order to avoid overestimating the fire hazard of materials containing PVC. HCl can also be generated from the combustion of materials containing chlorinated fire retardants or from the combustion of other chlorinated polymers or even from reactions involving common chlorinated salts. It is not uncommon for any of these phenomena to occur.

HF is generated from the combustion of fluorinated polymers, which are also very common in the built environment. HBr is generated from the combustion of polymers that have been fire-retarded with brominated materials, or that contain some brominated sections in their backbone. It is rare to have high volumes of inherently brominated polymers or of polymers containing high levels of fluorinated additives (as fire retardants or in other roles). Both HF and HBr are strong acids, similar in that respect to HCl. It can be assumed that the rate of decay of HF and of HBr in fires will be similar to that of HCl. Unfortunately, no studies have been published that have looked into this issue, and that is why the present work has focused primarily on HCl.

Another common gas found in fire atmospheres that has key toxicological importance is HCN. It is, at best, a very weak acid with limited reactivity to the type of construction surfaces that are common in the built environment. A few years ago, a study looked into the yields of several combustion products in large-scale fires, including HCl, HCN and CO [45], but some experimental difficulties in the study have made it difficult to rely quantitatively on the data obtained [46]. In 1991, another NIST study measured some HCN concentrations in full-scale fires and found some differences with small-scale yields [47]. Unfortunately, while the 1991 study clearly showed that HCl decayed, it was less clear about HCN decay. In summary, it is not possible at present to assess the importance of decay to the toxic hazard from HCN in fires.

4.7 Conclusions

HCl decay has been studied in a variety of large-scale and small-scale fire scenarios. It has also been studied in scenarios where HCl was not generated in a fire, but introduced directly. Additionally, the effects of a variety of atmospheric conditions

and surfaces (especially construction surfaces) have been investigated. Large-scale scenarios involved are: (1) a room and a plenum, (2) a room and a corridor, (3) a room leading to a corridor leading to another room and (4) a simulated HVAC system. The small-scale scenarios involved box-like containers, with 3 litre and 200 litre volumes, as well as heated glass flasks with spherical and cylindrical shapes.

The surfaces studied included: PMMA, glass, gypsum board, cement, Marinite, ceiling tile, painted gypsum board, painted PMMA and soot. Other conditions investigated included temperature, humidity and presence or absence of a variety of fluids. In view of the very rapid HCl decay on most of the surfaces studied, the effects were often analysed with small ‘chips’ of materials in a PMMA chamber, with fresh walls for each experiment. Experiments were also done to investigate the effect of surface ageing on painted gypsum board, painted PMMA and unpainted gypsum board walls.

As a result of this experimental work, a parametric model was developed, gradually improved and then transformed into a zone model. These models were able to predict HCl generation and decay under the anticipated conditions. The eventual model generated by all of this work contained scale-independent parameters for all fitted surfaces so as to allow generalisation of the results to scenarios of a number of scales (ranging from very small-scale to full-scale).

The HCl generation and deposition model was incorporated by NIST into their Hazard I zone fire model. Both the experimental work and the HCl decay model showed that HCl levels are much lower, particularly those levels remote from the fire, than would have been the case if HCl had not undergone decay.

This work shows that transport and decay of reactive gases (such as the halogen acids) is an important phenomenon that is essential for fire hazard assessment and that a robust model exists that can be applied to a number of scenarios where HCl is present, whether PVC is or is not present. Thus, both the acid-gas decay and the associated model must be considered in fire hazard assessment.

It is worth noting that a significant amount of information [48–51] indicates that the smoke toxicity from most materials falls within a very narrow range (see **Figure 4.10**) and that CO is the overwhelmingly important toxicant in fires, especially those that go to flashover.

With regard to acid gases (and particularly HCl), the debate has ended: the concentrations of HCl that can be found in fires in real buildings are much smaller than would have been predicted from an analysis of the chlorine content of the ‘fuel’. This is an essential consideration for toxic hazard since the concentrations of other combustion gases, such as CO, decrease only by physical entrainment and dilution

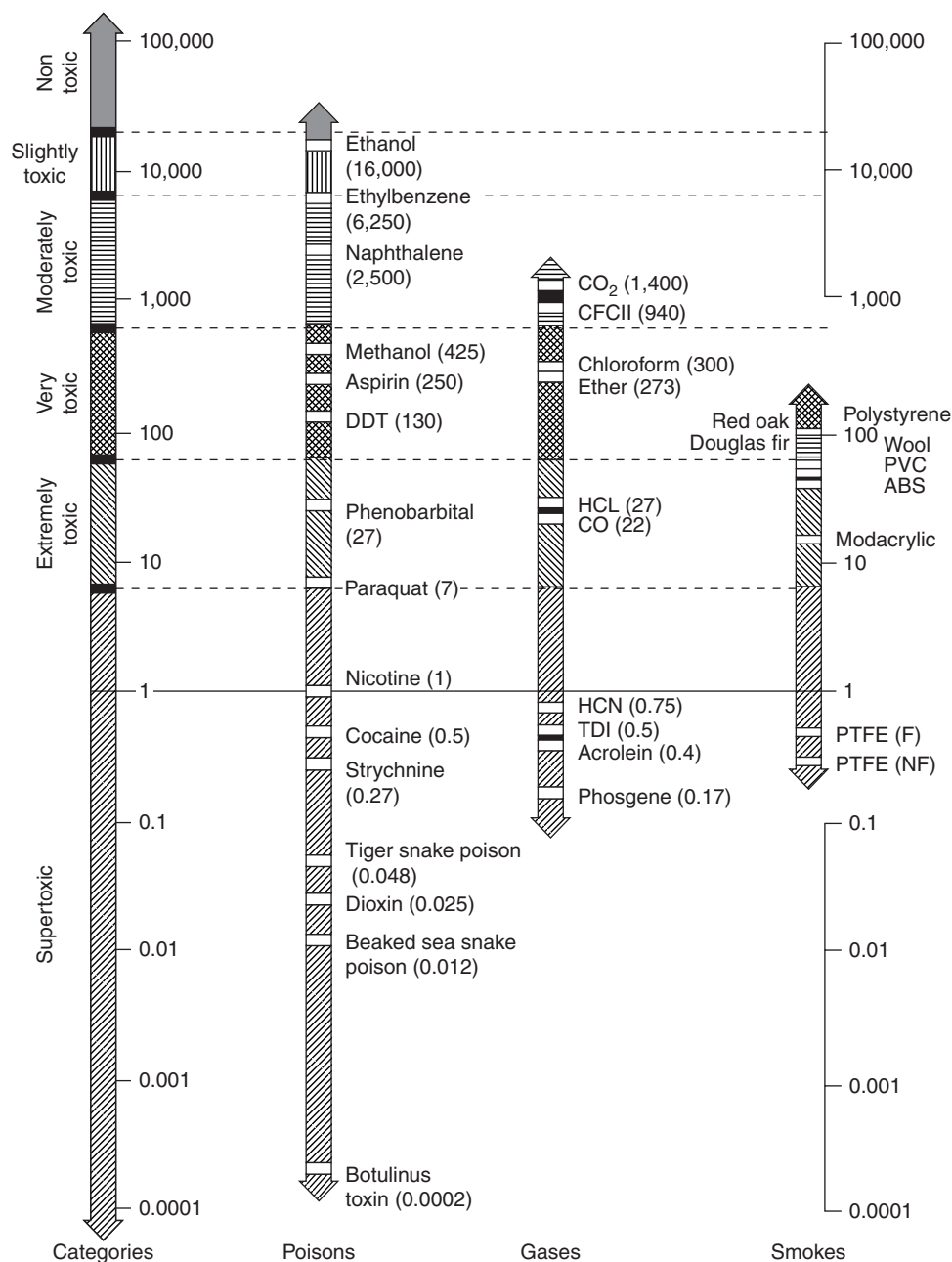


Figure 4.10 Ranges of smoke toxic potency of polymeric materials and other gases

processes. Thus, the relative toxic importance of HCl, as compared to CO, decreases as the smoke layer moves away from the fire zone.

4.8 Appendix

4.8.1 Mathematical Formulation

The gas transport equation for HCl is shown in **Equation 4.1**:

$$\{d[\text{HCl}]\}/\{dt\} = -k_c * A * ([\text{HCl}] - \{[\text{HCl}]_w\} / \{k_e\}) \quad (4.1)$$

where:

$d[\text{HCl}]/dt$: Rate of change of HCl atmospheric concentration, in $\text{kg}/(\text{m}^3 \text{ s})$

$[\text{HCl}]$: Concentration of HCl in the gas phase, in kg/m^3

k_c : Convective mass-transfer coefficient, in m/s

$[\text{HCl}]_w$: Concentration of HCl on the wall, in kg/m^2

k_e : HCl partition (or gas/wall equilibrium) coefficient, in m

A : Surface area where decay takes place, in m^2

In this equation, the left side represents the rate of HCl gas-phase concentration change, and the right side represents the rate of HCl transfer from the gas to the wall. The variable A represents the area of the surface where the decay is taking place. The constants k_c and k_e are the mass-transfer coefficient through the gas phase and the HCl-partition coefficient (equilibrium constant) between the wall and the gas phase, respectively. The calculation of flows in and out of all compartments is not explicitly shown in **Equation 4.1**, but is calculated by FAST. The mass-transfer coefficient, k_c , has units of distance/time. In general, it is a function of the local velocity field and the diffusivity of the transferring species. The similarity of convective mass and heat transfer has been known in the field of transport phenomena for a long time. In its simplest form, this similarity can be expressed as the relationship between the convective-heat and mass-transfer coefficients, known as the Reynolds analogy [37]. Fire-driven flows generally meet the conditions assumed in the Reynolds analogy. Thus, in the FAST implementation of the HCl transport and decay model, the Reynolds analogy is used to obtain k_c from the convective heat-transfer coefficient. It has been shown that, in most practical situations, the decay rate of HCl from fire gases is not

very sensitive to the convective mass-transfer rate [38]. The predicted values of k_c should, therefore, be sufficiently accurate in the great majority of cases.

The wall-conservation equation for HCl is shown in **Equation 4.2**:

$$\{d[HCl]_w\}/\{dt\} = k_c * ([HCl] - [HCl]_w/K_e) - k_r * [HCl]_w \quad (4.2)$$

where:

$\{d[HCl]_w\}/\{dt\}$: rate of loss of concentration of HCl in the wall phase, in $kg/(m^2/s)$

$[HCl]$: Concentration of HCl in the gas phase, in kg/m^3

k_c : Convective mass-transfer coefficient, in m/s

$[HCl]_w$: Concentration of HCl on the wall, in kg/m^2

K_e : HCl partition (or gas/wall equilibrium) coefficient, in m

k_r : HCl decay-rate coefficient inside the surface, in $1/s$

In **Equation 4.2**, the left side corresponds to the HCl surface-concentration rate of change, the first term on the right side is the rate of transfer of HCl from the gas to the wall, and the second term is the rate of HCl disappearance of HCl into the wall (first-order kinetics). The equilibrium gas concentration at the gas-surface interface (which is not explicitly calculated) is given by **Equation 4.3**:

$$[HCl]_i = [HCl]_w/\{k_e\} \quad (4.3)$$

where:

$[HCl]_i$: Concentration of HCl at the interface, in kg/m^3

$[HCl]_w$: Concentration of HCl on the wall, in kg/m^2

k_e : HCl partition (or gas/wall equilibrium) coefficient, in m

In general, k_e and k_r are functions of temperature, humidity and HCl concentration, as well as the specific type of surface material. The effect of water (humidity) is to increase the number of surface sites available for HCl adsorption, leading to the functional form for the effect of water on HCl adsorption shown in **Equation 4.4**:

$$k_e = F1 ([HCl], T) * F2 ([H_2O]) \quad (4.4)$$

where:

[HCl]: Concentration of HCl in the gas phase, in kg/m³

k_c: HCl partition (or gas/wall equilibrium) coefficient, in m

F1: Partition coefficient dependency on [HCl] and temperature - it represents adsorptivity of the surface for HCl in absence of water, in 1/m

F2: Partition coefficient dependency on water concentration - it represents added capacity for HCl adsorption as a function of the water present in the gas. It is a dimensionless function

[H₂O]: concentration of water, in kg/m³

T: Temperature, in K

In Equation 4.4, F1 represents the partition coefficient at zero humidity, as shown in Equation 4.5:

$$F1 = \{b1 * e^{(12500/R*T)} * [HCl]\} / \{1 + b2 * e^{(12500/R*T)} * [HCl]\} \quad (4.5)$$

where:

F1: Partition coefficient dependency on [HCl] and temperature; it represents adsorptivity of the surface for HCl in absence of water, in 1/m

b1 and b2 are constants which are a function of the surface

R: Ideal gas constant, 8.314 J/K/mol

T: Temperature, in K

[HCl]: Concentration of HCl in the gas phase, in kg/m³

In the case of painted gypsum board, the constants are:

b1 = 0.063 m and b2 = 192 m³/kg.

At the other extreme, when the HCl-H₂O binary reaches saturation conditions in the gas phase, any surface will have an infinite capacity to adsorb HCl. There are, thus, two limiting conditions for F2 (as defined previously), as shown in Equation 4.6:

$$F2(0) = 1; F2 ([H_2O]_s) \rightarrow \infty \quad (4.6)$$

With these limiting conditions, the final form for F2 is shown in **Equation 4.7**:

$$F2 = 1 \{b5 * [H_2O]^{b6}\} / \{([H_2O]_s - [H_2O])^{b7}\} \quad (4.7)$$

The values for the constants for the key construction surfaces used in the HCl decay and generation experiments are shown in **Table 4.4**.

The expression for the saturation concentration of water, $[H_2O]_s$, was developed by linear regression of 'data' points generated from a rigorous vapour/liquid phase dissociation equilibrium model for the HCl-water system. **Equation 4.8** shows how to calculate the saturated water concentration from polynomial expressions. These expressions are fifth-order in $[HCl]$, third-order in temperature and also contain combined temperature/concentration terms, all of which are a function of ambient temperature.

$$[H_2O]_s = \{0.556 * 10^{-4} * (\text{polynomial expression})\} / \{R * T\} \quad (4.8)$$

where:

$[H_2O]_s$: saturation concentration of water, in kg/m^3

R: Ideal gas constant, 8.314 J/K/mol

T: Temperature, in K

The term kr in **Equation 4.2** is the coefficient for the decay rate of HCl on the surface, which is assumed to be a first-order process in the surface concentration $[HCl]_w$. Previously kr was assumed to be a constant independent of temperature, with a different value for each type of surface. However, when investigating larger temperature ranges, it became obvious that some temperature dependency needed to be allowed for, and an Arrhenius form was assumed for this dependency. The expression obtained for kr from this analysis is in **Equation 4.9**:

$$kr = b3 * e^{(-b4)/(R*T)} \quad (4.9)$$

Equation 4.1 can be expanded to include a generation term, which is only nonzero in the burn room when HCl is being generated from burning materials. In the GWD study [30], a specific HCl generation function was developed for the electrical decomposition of flexible PVC coated onto wire. In other studies involving burning of rigid PVC, generation functions were developed on the basis of the mass-loss rate of PVC (measured) and the chlorine content of the PVC. In some cases, HCl was injected directly, in which case the generation function is simply the rate of introduction

of HCl into the compartment. Other equations can be developed depending on the scenario and the source of the HCl.

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5 Fire Tests to Assess Smoke and Combustion-Product Generation

5.1 Introduction

There are three main ways in which fire, whatever the products involved, can cause harm to people, property or operations. These are, in decreasing order of their importance to fire hazard:

- (1) Effects of heat or flames spreading from the item first ignited to other products, potentially resulting in thermal injury to people, destruction of property or loss of operation;
- (2) Production of smoke which obscures vision and can inhibit both the escape of trapped victims and the action of firefighters; and
- (3) Generation of toxic products (gases and particulates in smoke) which can be inhaled by victims and injure them.

In this chapter, smoke includes all of the airborne solid and liquid particulates and gases evolved when a material burns. However, the focus of the chapter is specifically on smoke obscuration.

The test methods used to measure smoke obscuration accompanying a fire can be classified into six categories:

- Static small-scale smoke obscuration tests on materials
- Dynamic small-scale smoke obscuration tests on materials
- Traditional full-scale smoke obscuration tests on products
- Full-scale tests measuring heat and smoke release
- Specialised full-scale tests measuring heat and smoke release on specific products
- Small-scale tests measuring heat and smoke release

Table 5.1 shows the key tests from the major organisations developing fire standards: American Society for Testing and Materials (ASTM), National Fire Protection Association (NFPA), Underwriters Laboratories (UL), International Organization for Standardization (ISO) and International Electrotechnical Commission (IEC).

This chapter will briefly discuss these different types of methods, while giving a few examples of tests in each category. The descriptions will involve mostly general features that are common to most methods in a particular category. The chapter will also briefly discuss the key tests for smoke toxicity and smoke corrosivity.

Table 5.1 Equivalent or similar smoke tests standards from different organisations			
ASTM	NFPA	UL	ISO or IEC[§]
Steiner tunnel surface flame spread			
E84 [1]	255 (withdrawn)	723 [2]	
	262 [3]	910 (withdrawn)	
Lateral flame spread			
E162 [4]			
E1317 [5], E1321 [6]			5658 [7]
Smoke obscuration (static)			
E662 [8]	258 (withdrawn)		
E1995 [9]	270 [10]		5659-2 [11]
			IEC 61034 [12]
Floor coverings			
E648 [13]	253 [14]		9239-1 (smoke) [15]
Room corner heat release tests			
	265 [16]	1715* [17]	
	286 [18]		
E2257 [19]			9705 [20]
Large-scale product heat release tests			
E1537 [21]	266 (withdrawn)	1056 (withdrawn)	

	267 (withdrawn)	1895 (withdrawn)	
	289 [22]		
E1822 [23]		1975 [24]	
D5424 [25], D5537 [26]		1685 [27]	IEC 60332-3* [28]
Heat and smoke release (bench scale and intermediate scale)			
E1354 [29]	271 [30]	2360 [31]	5660 [32, 33]
E906 [34]	263 (withdrawn)		
E1474 [35]	272 (withdrawn)		
E1740 [36]			
D6113 [37]			
F1550 [38]			
E2102 [39]			13927 [40], 17554 [41]
E2058 [42]	287 [43]		
E1623 [44]			14696 [45]
Smoke toxicity			
E1678 [46]	269 [47]		
Smoke corrosivity			
D5485 [48]			11907-4 [49]
			11907-2 [50]
			11907-3 [51]
Note: This table contains NFPA and ASTM fire test standards and those fire test standards from UL and ISO that are similar, even if not technically equivalent. § ISO standards unless stated otherwise * Tests are not technically equivalent to the NFPA or ASTM tests in columns 1 or 2.			

5.2 Static Small-scale Obscuration Tests on Materials

Static small-scale obscuration tests on materials include the single most widely used smoke test, i.e., the National Bureau of Standards [NBS, now the National Institute of Standards and Technology (NIST)] smoke chamber test (ASTM E662 [8]), its successor with a conical radiant heater (ISO 5659-2 [11], also standardised as

ASTM E1995 [9] and NFPA 270 [10]) and one of its predecessors: the Rohm and Haas chamber (ASTM D2843 [52]). These tests tend to be similar in design, with the main differences being the light-beam direction and the burner/radiant heater. It has been shown that results from these tests do not usually represent the smoke emission to be expected in full-scale fires. A large amount of information has been published regarding the deficiencies of the NBS smoke chamber approach [53-57], some of which are shown in **Table 5.2**. These tests have some limited usefulness as laboratory tools to observe effects of changing a base formulation. Effects must still be confirmed by a reliable fire test.

Table 5.2 Key deficiencies of the NBS smoke chamber	
1	Results do not correlate with full-scale fires
2	Vertical orientation leads to melt and drip
3	Time dependency of results cannot be established
4	No means exists of weighing sample during test
5	Maximum incident radiant flux is 25 kW/m ²
6	Fire self-extinguishes if oxygen level becomes <14%
7	Therefore, composites often give misleading results.
8	Wall losses are significant
9	Soot gets deposited on optics
10	Light source is polychromatic
11	Rational units of m ² /kg are not available

In the ASTM E662 test (smoke chamber originally developed by NBS, a vertical test specimen, 7.5 mm × 7.5 mm by up to 50 mm thick, is exposed to a 25 kW/m² radiant heat source, with or without a pilot igniter, inside a closed chamber which has an approximate volume of 0.5 m³ (**Figure 5.1**). Using a vertical light beam, the reduction in visibility within the chamber is assessed by measuring the light transmitted. It is very widely used throughout the world for material development and results from this test are included as parts of many specifications and requirements, typically for transportation vehicles and for carpets or other floor coverings. Some of the deficiencies, especially the problem of test-specimen dripping, have been addressed by the development of ASTM E1995 [9]/NFPA 270 [10]/ISO 5659-2 [11], which uses an horizontal test specimen, a conical radiant heater and a load cell (for continuous assessment of mass loss) in the same chamber. The radiant heater can be used for testing at heat fluxes of 25 or 50 kW/m², with or without pilot ignition. This test is used extensively in the marine environment. Neither of these tests have intrinsic pass/fail criteria.

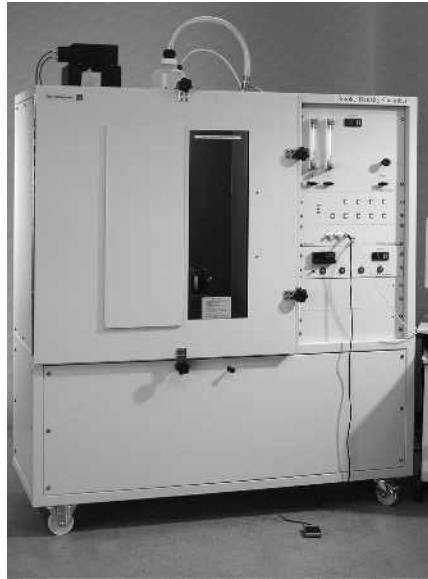


Figure 5.1 ASTM E662 [8] or ISO smoke chamber. Reproduced with permission from Fire Testing Technology Limited, East Grinstead, West Sussex, UK

An earlier type of smoke chamber, ASTM D2843 [52], was developed for testing light-transmitting plastics and is still included in codes as one of the qualifying tests for such materials. Codes do have pass/fail criteria for this test.

One serious problem with all of these small-scale smoke tests is that they normally cause complete destruction of the test specimen. Thus, a material that would not burn up completely in a fire (and thus yield less total overall smoke obscuration) can appear to have poor smoke performance in these tests due to the characteristics of the test itself.

For electric cables, European requirements call for the three metre cube test (IEC 61034 [12]), which is a large static smoke chamber (Figure 5.2). It is a closed cubical chamber, 27 m³ in volume, with a horizontal light beam assessing smoke at a height of more than two metres. Its fire model is a very intense liquid hydrocarbon pool that is often sufficient to consume completely the combustible portion of the cables, due to the geometrical arrangement. Thus, the test suffers from most of the same defects that plague small-scale static smoke chamber tests. The test assesses the decrease in light transmission, and the normal pass/fail criterion is 60% light transmission.

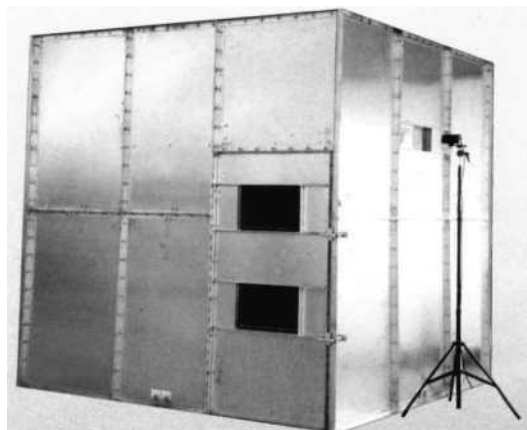


Figure 5.2 IEC 61034 [12] smoke chamber. Reproduced with permission from Fire Testing Technology Limited, East Grinstead, West Sussex, UK

5.3 Dynamic Small-scale Smoke Obscuration Tests on Materials

Most of the tests in this category measure smoke obscuration together with another property, although this was rarely an original objective of the test designers. Probably the three key tests of this kind still in use are the radiant-panel flame-spread test (ASTM E162 [4] or ASTM D3675 [58]), the lateral ignition and flame transport (LIFT) test (ASTM E1321 [6] or ASTM E1317 [5]) and the flooring radiant-panel test (ASTM E648 [13] ISO 9239-1 [15] or NFPA 253 [14]). The use of these tests recognises, implicitly, the fact that the issue of smoke obscuration is not an isolated phenomenon, but is always a result of the fire itself.

The radiant-panel flame-spread test apparatus (ASTM E162, **Figure 5.3**) can be used to measure smoke obscuration in the exhaust stream. The radiant panel flame spread apparatus assesses flame spread rate/surface flammability of building products and cellular plastics. The results are expressed in terms of an index, but it is different from the one assessed by the Steiner tunnel (see next), which is why it is now known as the radiant-panel index. The radiant-panel index is calculated as the product of a ‘flame spread factor’ and a ‘heat-evolution factor’, using techniques described in the standard. The test equipment consists of a gas fed radiant panel, which exposes test specimens to a radiant flux equivalent to a black-body temperature of 670 °C (approximately 45 kW/m²), in the presence of a small gas pilot flame. The test specimen (150 × 460 mm, with a normal maximum thickness of 25 mm) is inclined at a 30° angle. Alternate specimen holders can accommodate thicker specimens. The ignition is forced near the upper edge of the specimen, and the flame front progresses downward. The flame spread factor results from the measurements of flame-front position and time. The heat evolution factor is proportional to the

maximum temperature measured in the exhaust stack. This test has also been shown not to be an adequate predictor of real-scale fire performance and not to be suitable for fire safety engineering calculations. Again, if the specimen melts or causes flaming drips, such behaviour is likely to affect the flame spread in a way that is uneven. The standard simply requires that such events be reported. Moreover, if flame spread is very rapid, flame spread information is potentially lost unless recording is continuous, which is not a requirement. This apparatus is often referred to as the radiant panel test, and a variant has been developed for testing foamed materials, ASTM D3675 [58]. The smoke obscuration is optionally measured via a photometric detector added into the system's vertical duct.



Figure 5.3 ASTM E162 [4] radiant panel test method. Reproduced with permission from Fire Testing Technology Limited, East Grinstead, West Sussex, UK

An updated version of the radiant panel was also developed and standardised as ASTM E1321 [57] (with a marine version as ASTM E1317 [5]). Another test apparatus suitable for assessing flame spread of materials is the LIFT test (ASTM E1321). The LIFT apparatus was developed as an improvement on the radiant panel apparatus in ASTM E162 [4], as it can produce data in engineering units and its results can be used successfully for predictions of full-scale flame spread performance [59]. The specimen size for flame spread studies is 155 × 800 mm by a maximum thickness of 50 mm (and a smaller specimen is used for ignition studies). The test method determines the critical flux for flame spread, the surface temperature needed for flame spread, and the thermal inertia or thermal heating property (product of

the thermal conductivity, density and specific heat) of the material under test. These properties are mainly used for assessment of fire hazard and for input into fire models. A flame spread parameter, Φ , is also determined, and this can be used to directly compare the responses of the specimens. This test method is well-suited for nonmelting materials (or composites), which can be ignited without raising the incident flux to potentially dangerous limits. A slight variation on the LIFT test is one used by the marine industry to assess flammability of surface finishes: ASTM E1317 [5], also known by its International Maritime Organization (IMO) designation as ‘Part 5 of the IMO Fire Test Procedures Code’. This test is required extensively for marine deck finishes and overlays.

The flooring radiant-panel test was designed in the early 1970s to solve the problem of carpets spreading fire outside the room of fire origin. Consequently, virtually none of the commercial carpets currently sold in the United States are likely to cause such a problem. The maximum incident flux to this test is, however, much too small (10 kW/m^2) for it to adequately address the flooring product contribution to fire hazard, if the fire reaches significant intensity. The test method (**Figure 5.4**) is conceptually similar to the corresponding test for building products, ASTM E162 [4], radiant panel test, using a gas fired radiant panel. There are some key differences: the test specimen is horizontal and the radiant panel is at a 30 degree angle to the specimen, so the incident radiant- heat flux to the test specimen varies with the distance from the pilot igniter. The test assesses the critical radiant flux, which is the minimum heat flux needed for materials to propagate flame and is assessed as the distance from the pilot igniter at which flame spread ceases. The standard ASTM or NFPA tests do not include smoke measurements, but ISO 9239-1 [15] does. Just as in the ASTM E162 test, smoke is measured in the exhaust duct.

5.4 Traditional Full-scale Smoke Obscuration Tests on Products

Many full-scale tests have been proposed for products, and the most important ones are all associated with the Steiner tunnel test. The original tests were usually designed in response to a specific need and were not designed to measure heat release, but, often, flame spread. Smoke obscuration was, in some cases, added later, almost as an afterthought. These tests are important because the product is allowed to ‘do its own thing’ and, thus, a material (or product with good fire performance) is not necessarily burnt to completion. Moreover, smoke obscuration is always measured continuously, together with some other fire property. The results of these tests have, however, as a rule, not been shown to correlate with the results of tests in more realistic scenarios.



Figure 5.4 Flooring radiant panel test method. Reproduced with permission from Fire Testing Technology Limited, East Grinstead, West Sussex, UK

The Steiner tunnel test was first standardised by ASTM in 1950 as ASTM E84 [1]. The ASTM E84 test specimen is a building material (normally up to 0.15 m thick), either in one unbroken length or in separate sections joined end to end, which is mounted facedown so as to form the roof of a horizontal tunnel 305 mm high (**Figure 5.5** shows a schematic of the test method). The fire source, two gas burners, ignites the sample from below with an 88 kW fire source (**Figure 5.6** shows the test flame, seen from the tunnel air input side). The test is normally conducted for 10 minutes and the results are expressed as a flame spread index (FSI) and a smoke developed index (SDI), which are relative values, based on area calculations, related to the values for a noncombustible board (values of 0) and red oak flooring (values of 100). There are no pass/fail criteria in the standard, but codes require the tested materials to fall into one of four classes, depending on the application. Classes A, B and C are the ones applicable to most occupancies, except for products in plenums, which must meet a more severe smoke obscuration limit (see **Table 5.3**). Another variation used in codes is the ‘extended 30 minute ASTM E84 test’, which has not yet been developed into a formal standard, but which requires materials to exhibit an FSI of ≤ 25 , with no evidence of significant progressive combustion at the end

of the test and a flame front that does not progress more than 3.2 m beyond the centre line of the burners at any time during the test. This is typically used for fire-retardant treated wood, but can be used for other materials as well. Normal wood tends to exhibit Class C performance.

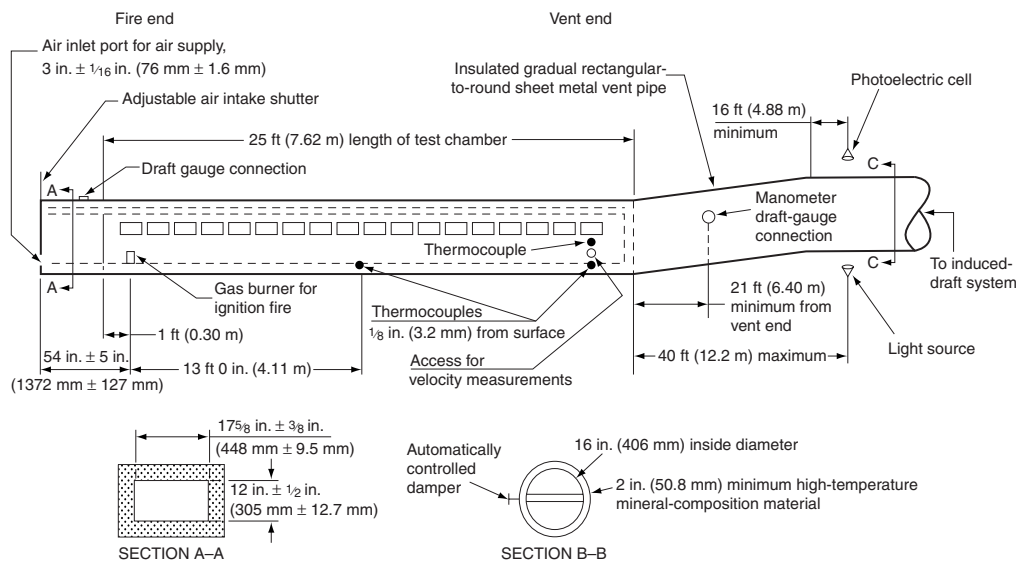


Figure 5.5 Schematic of ASTM E84 test



Figure 5.6 ASTM E84 test flame

Table 5.3 Classification for code use of materials tested in the ASTM E84 test		
	FSI	SDI
Class A	≤ 25	≤ 450
Class B	$26 \leq \text{FSI} \leq 75$	≤ 450
Class C	$76 \leq \text{FSI} \leq 200$	≤ 450
Plenum materials	≤ 25	≤ 50

Although the deficiencies of this test are well known, it is a popular procedure given the widespread regulatory applications in North America. It should be pointed out that it can yield misleading results with materials that have been developed ‘to pass the test’, rather than engineered for good fire performance (e.g., by testing at less than full width or by testing with water in the specimen). Many of the deficiencies are being corrected by the issuance of mandatory specimen preparation and mounting practices, together with changes that try to ensure consistency in test specimens. Typical changes involve ensuring consistent ‘system’ testing (as opposed to individual components) so that the appropriate combinations are assessed. The test has been shown to misrepresent the fire performance of many thermoplastic materials and floor coverings. One problem is that since the sample is sited on the ceiling of the tunnel, some products (typically incorrectly flame retarded thermoplastics) tend to drip or melt away from the flame source and thus do not propagate the fire.

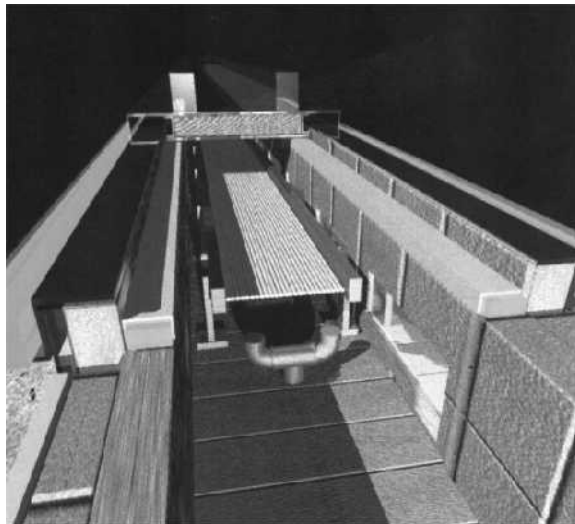


Figure 5.7 Mounting of wires and cables in the NFPA 262 test

The Steiner tunnel now has several variations applicable to individual products: NFPA 262 [3], used for wires and cables in plenums and previously known as UL 910 [60], UL 1820 [61], used for pneumatic tubing, UL 1887 [62], used for plastic sprinkler pipes and UL 2024 [63], used for communications raceways. The mounting of products in these tests is very different from the mounting methods in the ASTM E84 test, and **Figure 5.7** shows an example for wires and cables in NFPA 262. The products are not mounted on the ledges of the tunnel, but in special trays. These tests are all used to regulate the amount of flame spread and the smoke developed by products for various applications with stringent fire-performance requirements. The smoke-test results in all of these standards are based on actual measurements of optical density (OD) in the exhaust and not on relative indices (see **Table 5.4**).

Table 5.4 Classification for products tested in variations of the ASTM E84 test			
	Flame spread (m)	Average OD	Peak OD
NFPA 262*	≤ 1.5	≤ 0.15	≤ 0.50
UL 1820	≤ 1.5	≤ 0.15	≤ 0.50
UL 1887	≤ 1.5	≤ 0.15	≤ 0.50
UL 2024	≤ 1.5	≤ 0.15	≤ 0.50
* The pass/fail criteria are not included in NFPA 262, but in the code or standard that requires cables to meet this test			

The Steiner tunnel test can also produce wrong results for thin materials [64], particularly when they are tested using ‘chicken wire’ (formally known as ‘poultry netting’) for specimen support, which absorbs much of the heat generated by the test specimen (see examples in **Table 5.5**).

Table 5.5 Potential effect of using chicken wire on ASTM E84 test flame-spread index		
	FSI data	
	With poultry netting	Without poultry netting
Material 1	20	340
Material 2	25	310
Material 3	55	105
Material 4	15	45

5.5 Full-scale Tests Measuring Heat Release and Smoke Release

The ultimate measure of fire performance of a material or product is, of course, the way in which the end product reacts in a real fire. The best approximation of this fire performance will be found with room sized fire tests in which products can be tested in end-use configurations, or as close to such as possible. The single most important fire property is the rate of heat release, since its peak value will determine the peak intensity of a fire [65–67]. The fire science community has understood this concept only since the 1980s.

An empirical ‘rule’ discovered in the 1970s has helped to show the way ahead: the rate of heat release of the majority of combustibles is proportional to the level of consumption of oxygen (the proportionality constant is $13.1 \pm 0.3 \text{ kJ O}_2/\text{kg fuel}$) [68, 69]. This was accompanied by an improvement in oxygen measurement techniques, so that oxygen gas (O_2) can be determined with paramagnetic analysers at an accuracy of 0.001% O_2 . Thus, the almost insurmountable problem of ensuring adiabaticity is now replaced by a much simpler problem: ensuring complete capture of the fire effluents of the fire (or of a known representative fraction).

In the late 1970s and 1980s, several tests were developed in which products are burnt in a simulated end-use environment and in which heat release is measured together with other properties, including smoke obscuration. These are dynamic tests, involve continuous measurements and give a realistic appraisal of the fire performance of the product. These tests, generally known as room corner tests, involve a lined room (NFPA 265 [16], NFPA 286 [18], UL 1715 [17], ISO 9705 [20] or ASTM E2257 [19]) with different ignition sources or scenarios. A slightly smaller scale option involves the testing of whatever product or portion of a product is of interest, by placing it on a ‘furniture calorimeter’ (NFPA 289 [22]).

The room corner tests are now being used in the newest editions of all codes, as alternatives to replace the ASTM E84 Steiner tunnel test, thus generating more useful results. **Figure 5.8** shows a room corner test layout. The standard room used for most of these tests is the same size: $2.4 \text{ m} \times 3.7 \text{ m} \times 2.4 \text{ m}$ high, with a door in the centre of one of the shorter walls and a hood/vent and outlet outside the door: NFPA 265, NFPA 286 and ISO 9705 (identical to ASTM E2257). UL 1715 is slightly different because there are only three walls (no wall with door). Smoke release, together with heat release, is measured in the duct.

NFPA 265 applies to textile and expanded vinyl wall coverings and uses a $30 \text{ cm} \times 30 \text{ cm}$ square gas burner that starts at 40 kW for 5 minutes and then increases to 150 kW for 10 minutes. The burner is placed near a corner (opposite the door), 55 mm

away from each wall. Three walls are lined, but the ceiling is not lined and the test does not apply to ceiling coverings. The smoke pass/fail criterion (in the codes and not the test method) is 1,000 m². NFPA 286 is very similar, but has the following differences: the ignition source starts at 40 kW for 5 minutes and then goes to 160 kW for 10 minutes, with the burner flush against the corner. In this way, the burner flame reaches the ceiling and the test is applicable to any interior finish material. Three walls and the ceiling are lined. The code uses the same pass/fail criterion for smoke. ISO 9705 differs from NFPA 286 in the intensity of the burner (which is placed at the same location): 100 kW for 10 minutes and then 300 kW for another 10 minutes. The European Union (EU) uses this test for building products as a ‘referee test’, and smoke is a recommended measurement. UL 1715 uses a wood crib, and smoke measurement is qualitative.

NFPA 289 is a generic ‘furniture calorimeter’ test that is valid for any item, product or individual fuel package. The item is placed on a load cell, directly under the hood, and smoke release is measured in the hood.

There remains, however, a problem with such large-scale tests: their cost. It is desirable to find smaller scale tests, the results of which can serve as reasonable predictors of real-fire performance and which can be used as input into fire models for assessment of fire hazard or fire risk.

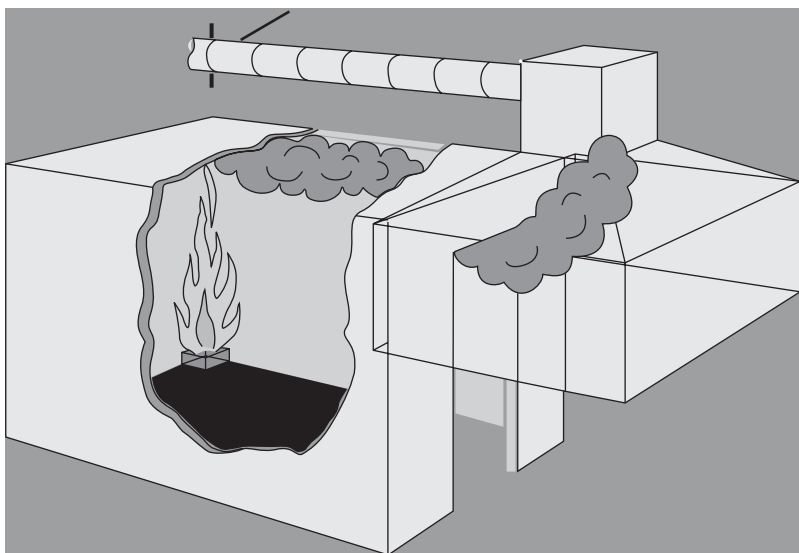


Figure 5.8 Room corner test layout

5.6 Specialised Full-scale Tests Measuring Heat and Smoke Release on Specific Products

A number of individual products have already had specialised tests for heat and smoke release designed for them, especially upholstered furniture (ASTM E1537 [21] and California Technical Bulletin (CA TB) 133 [70]), mattresses (ASTM E1590 [71], CA TB 129 [72], CA TB 603 [73] and 16CFR1633 [74]), stacking chairs (ASTM E1822 [23]), foam displays (UL 1975 [24] and NFPA 289) and electric and optical fibre cables (ASTM D5424 [25], ASTM D5537 [26], UL 1685 [27], IEC 60332-3 [28] and the Fire Performance of Electrical Cables Project (FIPEC) test, EN 50399-2 [75]).

The tests for upholstered furniture, mattresses and stacking chairs are all very similar and are based on the same concept: they require the item for testing to be placed on a load cell near one of the corners of a standard room and away from the door (or they permit a furniture calorimeter). A variety of burners and heat source intensities are used, and the details are indicated in each standard.

The tests for foam displays place the display on a load cell, using either a wood crib ignition source (340 g, UL 1975) or a gas burner (NFPA 289), with heat and smoke release measured in the exhaust duct above the load cell in these furniture calorimeter tests.

In the area of electric cables, low flame spread is a frequent requirement. The National Electrical Code (NEC) [76], contains requirements in terms of flame spread for both electrical and optical fiber cables and subdivides them into four categories:

1. Minimal improved fire performance is required for cables that need to be listed as 'being suitable for use in dwellings and for use in raceways' and as 'being resistant to flame spread' by testing the cable to a small vertical single cable test, namely the vertical wire flame test in UL 1581 [77]. This has no smoke component.
2. Somewhat better fire performance is required for cables that need to be listed as 'suitable for general purpose use, with the exception of risers, ducts, plenums, and other space used for environmental air' and as 'being resistant to the spread of fire' by testing the cable (in a grouped configuration) to a vertical cable tray flame test (20 kW), in which the cables are not allowed to spread fire to the top of the 2.4 m tray in UL 1685 [27], with two options: UL and CSA (a name which is based on the fact that the test was originally developed by the Canadian Standards Association). The CSA option is a somewhat more severe test for the same application - the cables are also in a grouped configuration with a 20 kW flame (but with the burner pointing at a 20 degree angle upward), and the cable loading is designed to make the test tougher to pass. Both of these tests have smoke components, and the NEC includes a voluntary smoke requirement.

3. The next level up in fire performance is required for cables that need to be listed as 'capable of preventing the carrying of fire from floor to floor' or riser cables. Such cables must pass the requirements of UL 1666 [78], whereby cables in a grouped configuration are exposed vertically, in a two-storey facility, to a 145 kW flame. There are no smoke requirements.
4. The toughest requirement for flame spread and smoke release is for cables that are to be used in plenums. They must be listed as 'low smoke' and comply with the requirements of NFPA 262 described earlier.

In Europe, traditionally, the fire performance of cables is assessed by an alternate vertical cable tray flame spread test, IEC 60332-3 [28], which is similar to the North American vertical cable tray tests (same ignition source but a longer cable tray; 3 m high), but slightly less severe. In the late 1990s, a European project developed a first attempt at a classification method for fire performance of cables, the FIPEC project [79]. This was an important development, as the test method, a variation of the IEC 60332-3 vertical cable tray test, also incorporates heat and smoke release and is being used for the European classification of cables. It should be noted that vertical cable tray tests use compartments with different sizes than furniture tests (**Figure 5.9**).

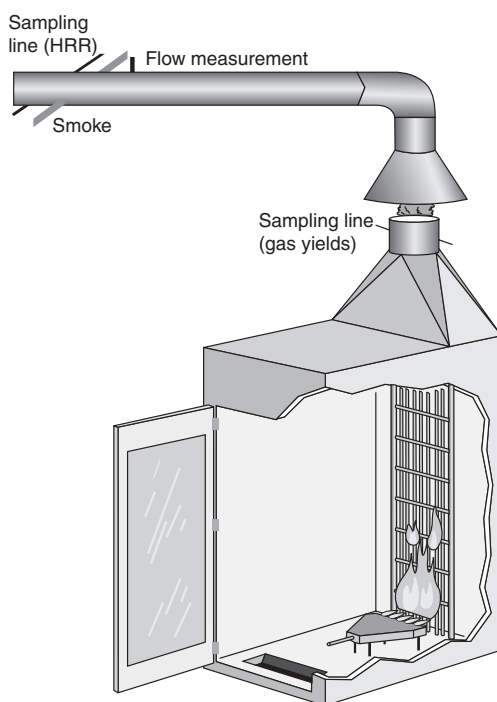


Figure 5.9 FIPEC Cable tray test

These tests are very valuable in that they are specific to the product involved, but, again, involve high cost.

5.7 Small-scale Tests Measuring Heat and Smoke Release

In fact, it has been shown that heat release is the most important property in a fire, as the peak heat release rate is the answer to the key fire question: ‘How big is the fire?’. When a product burns, it will spread the fire to nearby products only if it gives off enough heat to ignite them. Moreover, it has to give off that heat fast enough that it is not ‘lost’ while travelling through the colder air that surrounds a product that is not burning. Therefore, the fire hazard is dominated by the rate of heat release [67, 80, 81]. In fact, heat release rate has been shown to be much more important than either ease of ignition, smoke toxicity or flame spread in controlling the time available for potential victims of a fire to escape [65].

In view of this, smoke obscuration is best measured with small-scale tests that can fulfill four basic criteria, as follows [57]:

1. The tests must measure fire properties so that they can be used for purposes other than simple rankings or pass/fail criteria.
2. The tests must measure fire properties of considerable fire hazard interest, principally, the rate of heat release.
3. The tests must have been proven to give results that are representative of the corresponding property in a full-scale scenario.
4. The tests must allow calculations to compensate for complete sample consumption characteristic of small-scale tests.

Probably the only tests in existence to fulfill these requirements are based on heat release calorimetry. They are the cone calorimeter [82, 83], the Ohio State University (OSU) calorimeter [84] and the FM Global calorimeter [85].

In the late 1960s, Professor Edwin Smith at the OSU developed the first bench-scale test instrument to measure heat release: the OSU heat release rate calorimeter (ASTM E906 [34]). The OSU calorimeter exposes a 150 mm × 150 mm test specimen vertically and assesses heat release by measuring temperature increases with a thermopile. The test is most often used for the Federal Aviation

Administration (FAA), at an incident heat flux of 35 kW/ m². The FAA does not have pass/fail criteria for smoke based on this test, but the standard and the apparatus allow the measurement of smoke release, with detectors in the exhaust duct.

In parallel with the OSU calorimeter development, Tewarson (FM Global) created the 'Factory Mutual fire propagation apparatus' (ASTM E2058) [42]. One specific application of this apparatus is the use for materials in cleanrooms, NFPA 287 [43]. This instrument is used for assessing heat release and fire propagation. Heat release is assessed by measurement of carbon oxide generation instead of temperature increases with a thermopile. The protocol utilises three small-scale tests (designated as ignition, combustion and fire propagation). Ignition and combustion tests are conducted with horizontal test specimens (normally approximately 100 mm²), and fire propagation tests are conducted with vertical test specimens (approximately 300 mm high x 100 mm wide x 13 mm thick). Ignition tests assess time to ignition and critical ignition flux. Combustion tests assess chemical and convective heat release, and they are conducted at an incident heat flux of 50 kW/m². Fire propagation tests are also conducted at an incident heat flux of 50 kW/m², as well as at an oxygen level of 40%, in order to differentiate between the flame heat transfer characteristics of burning materials, in the absence of any imposed, high-intensity radiant flux [86]. Based on the results of these tests, a fire propagation index (FPI) can be determined for each material tested, which represents the ease/difficulty of fire propagation on the surface of the material beyond the ignition zone, under simulated flame heating conditions expected in large-scale fires. Experience indicates that non propagating materials have FPI values at or below 6.0. Materials that meet the flammability protocol criteria require high heat fluxes to be ignited; once ignited, these materials can burn locally in the ignition area, but they are not likely to propagate a fire beyond the ignition zone. The test also contains smoke measurement devices, as well as corrosion probes for assessing smoke corrosivity.

In the early 1980s, Babrauskas at the NIST developed a new fire test method to measure heat release rate, the cone calorimeter (ASTM E1354 [29], NFPA 271 [30], ISO 5660 [33, 34]) (Figure 5.10), based on the oxygen consumption principle [87] (Figure 5.10). This fire test instrument can also be used to assess a number of other fire properties, including the smoke released. Fire test results from this instrument correlate with those from full-scale fires for a variety of products, including upholstered interior finish, furniture, mattresses and electric cables [88-90]. In order to obtain the best overall understanding of the fire performance of materials, it is important to test the materials under a variety of conditions. Therefore, tests intended to evaluate the fire performance of a material are often conducted at a variety of incident heat fluxes, in order to compare a broad range of fire test conditions [91].



Figure 5.10 Cone calorimeter test. Reproduced with permission from Fire Testing Technology Limited, East Grinstead, West Sussex, UK

Several cone calorimeter applications standards have been issued by the ASTM: ASTM E1474 (upholstered furniture and mattress components and composites [35]), ASTM F1550 (same as ASTM E1474 but in a ‘vandalised’ mode, intended especially for detention occupancy applications [38]), ASTM E1740 (wall coverings, [36]), ASTM D6113 (electric cables and cable insulation materials [37]) and ASTM D5485 (corrosive atmospheres from the same electric cable materials [48]). The same test is also used for qualification of materials in the cleanrooms used in semiconductor fabrication facilities (UL 2360 [31]).

There are eight main differences between the cone and the OSU calorimeters:

1. The cone uses the oxygen consumption principle. It is not adiabatic, but allows easy observation of the burning process. The OSU was designed as adiabatic, and sample burning visibility is minimal. The apparatus can be modified to allow heat release measurement by O_2 consumption, but not easily.
2. The cone is normally used with horizontal samples, whereas the OSU is normally used with vertical samples. Samples can, however, be burnt in the cone vertically and horizontally in the OSU - the latter leads to larger irreproducibility because of makeshift radiation reflection.

3. The radiant source in the OSU is a set of four glow bars, sited directly across from the horizontal sample. Soot particles and smoke must make their way through a 'chimney' between the burning sample and the heat source, creating some afterburn. There is a truncated conical radiant heater in the cone, which generates a uniform energy distribution. Smoke is captured with minimal losses or afterburn.
4. The OSU has a flame igniter and the cone a spark igniter. Thus, the OSU ignition source is more powerful and more localised. The heat flux of the actual sample is larger in the OSU than the cone if both radiant heaters are calibrated to the same value. Therefore, samples may ignite in the OSU but not in the cone. Fire models are more likely to require data without 'hot spots', but the OSU is better at modelling impinging flames. This can be easily altered for either instrument.
5. The cone has a load cell to measure mass continuously, but the OSU does not. This is very important to calculate fire properties (including smoke released) on a mass lost basis. The OSU can be modified to incorporate a load cell, but not easily.
6. The cone uses a laser for measuring smoke obscuration, whereas the OSU uses a white light. Results from both measuring systems are virtually equivalent if scanning times are small (≤ 3 s). The white light is more similar to what the human eye sees, but it needs more maintenance (very infrequent cleaning is needed for the laser). Alternative obscuration sensors can be installed in either apparatus.
7. The sample size is somewhat different: approximately 100×100 mm in the cone and approximately 150×150 mm in the OSU. This will make no major difference to the results and is simply a consequence of the geometry.
8. The incident air flow rate is much higher in the OSU than in the cone, because of the geometric apparatus design.

In both apparatuses, as well as in the FM calorimeter (developed by FM Global), the incident air composition can be changed to simulate the vitiated atmospheres prevalent in intense fires; the nitrogen content of the air can be increased relatively easily. High incident air flow rates make it inconvenient (although not impossible, in the cone) to increase the oxygen content of the atmosphere. The FM calorimeter can easily operate at high oxygen levels. This is of interest with products destined for use in outer space, but it also simulates reradiation due to the burning sample.

In the three tests mentioned previously (OSU, FM and cone), smoke release can be assessed on the same test specimen as heat release, resulting in more realistic smoke results. Smoke obscuration is normally reported in the OSU by calculating rate of

smoke release and integrating this parameter to obtain total smoke released. In the cone, the normal way of reporting obscuration is the average extinction area, which measures smoke obscuration per unit mass.

In order to compensate for the complete consumption of the sample in small-scale smoke and heat release tests, it is possible to calculate derived combined heat/smoke magnitudes of smoke obscuration. An attempt has been made to compare smoke chamber test results with those of full-scale tests and small-scale heat-release test smoke obscuration results (cone and OSU) [92, 93]. The results indicate a lack of correlation between the smoke chamber test results and those of any of the other three tests. Moreover, the results also showed a fair predictability of combined heat/smoke parameters from the cone or the OSU to full-scale results for a variety of plastics. Work has also shown both reasonable correlation between such cone calorimeter parameters and smoke measured in full-scale vertical cable tray fire tests of cables and between results in the cone and the OSU [93]. All this suggests that the best way of measuring smoke obscuration in a meaningful way for full-scale fires, without conducting full-scale tests, is by using a small-scale heat-release test such as the cone calorimeter and compensating for incomplete burning of fire-retardant materials by using the combined heat/smoke magnitude concept.

However desirable and predictive bench-scale tests are, they are often unable to deal with physical phenomena such as joints, multiple layers and product irregularities. Intermediate-scale calorimeter (ICAL) tests have been developed to generate data similar to those from bench-scale heat release tests, but on a scale that is more likely to allow the use of test specimens that are representative of real-scale products. The ICAL (ASTM E1623 [44]) and the single burning item (SBI) (EN 13823 [94]) are North American and European versions of this concept. In the ICAL, flat specimens (1 x 1 m vertically) are exposed to a radiant heat source (a vertical gas fired panel) at an incident heat flux ranging up to 50 kW/m². The results obtained include heat and smoke release. In North America, this test is extensively used as a predictor of full-scale fire performance, but not for regulatory purposes. In the EU, the SBI test (**Figure 5.11**) was developed with the objective of using it to regulate building products. In this test, there are two test specimens, 1 m and 0.5 m x 1.5 m high, in a corner, and they are exposed to a 30 kW propane gas burner. Determinations are made of ignitability, flame spread, heat release, smoke release and flaming droplets. Key parameters are fire growth rate index (FIGRA) and smoke growth rate (SMOGRA). FIGRA is 'the maximum of the function of heat release rate *versus* time', starting at the time to ignition and describing the fire growth rate. SMOGRA is 'the maximum of the function of smoke production rate *versus* time', also starting at the time to ignition and describing the growth rate of smoke production. These parameters include the concepts of heat or smoke release and time to effect, so that a material or product that takes a long time to generate very high heat or smoke release will be

assessed to have better fire performance than an alternate one that reaches the same heat or smoke value rapidly. The SBI test is one of a battery of regulatory tests the European Commission uses for building product regulation (interior wall and ceiling finish and insulation), but not floor coverings, electric cables or pipes.

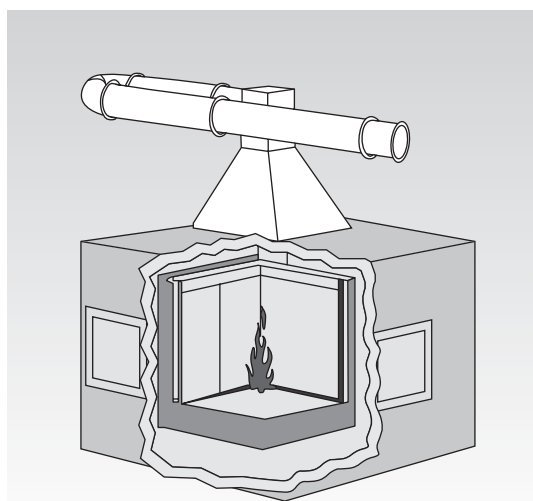


Figure 5.11 SBI test. Reproduced with permission from Fire Testing Technology Limited, East Grinstead, West Sussex, UK

5.8 Smoke Toxicity Tests

All of the previous comments addressing smoke obscuration are equally valid for combustion products, especially since it has now been demonstrated fairly conclusively that smoke toxicity is a minor aspect of fire hazard [65]. In fact, fire statistics and studies of fire fatalities have shown that (1) most fire victims die when fires have become large and have grown beyond the room of fire origin; and (2) fire fatalities can be correlated to the amount of carbon monoxide (CO) generated in fires [95-97]. This is very important, as CO is generated by all combustibles and, in fires that extend beyond the room of fire origin, its yield is 20% of the burnt mass, irrespective of what is burning [98-101]. Thus, fires resulting from materials with better fire performance tend to generate less fire hazard, even if they generate more toxic gases or more smoke per unit mass burnt [102].

Toxic potency of smoke is a quantitative expression relating smoke concentration and exposure time to adverse effects, usually lethality, on a test animal. It has to be

stressed that toxic potency of smoke is heavily dependent on the conditions of smoke generation, which affect both quality and quantity of smoke. During the 1970s and early 1980s, many smoke toxic potency test methods for smoke were developed, but most of them were never standardised and have fallen into disrepute. The tests differed in many respects, including: fire model, being static or dynamic, use of animals or analytical tools, animal model for bioassay and end point, and led to large ranking variations for the smoke of various materials, including one study [103] that showed that the material ranked most toxic by one protocol was ranked least toxic by another protocol! Neither of those protocols is in common use now. Toxicity of smoke is a function of composition, which depends both on what is burnt and on how it is burnt. Thus, if the composition of the smoke generated by any material in different tests varies broadly, so will its toxic potency. In fact, the toxic potency of the smoke of most ordinary materials (whether natural or synthetic) is very similar [104]. The difference between the smoke toxic potencies of almost all combustible materials is less than 1 order of magnitude. Thus, relative toxicity rankings are heavily dependent on the exact composition of the smoke being tested, i.e., on the test protocol, and are of little interest from the viewpoint of fire hazard assessment.

Many gases other than CO are given off in fires, but CO is the overwhelming hazardous toxicant in a fire. Peak concentrations [56] of various gases found by firefighters equipped with gas sensors were: 7,450 ppm CO, 100 ppm acrolein, 280 ppm hydrogen chloride (HCl) and 10 ppm hydrogen cyanide (HCN).

The overall smoke toxicity can also be calculated in more detail as a fractional effective dose (FED) using the formula shown in **Equation 5.1** [105].

$$\text{FED} = \sum_1 \sum_2 [C_i \cdot \Delta t] / (Ct)_i \quad (5.1)$$

In Equation 5.1, $\sum_1$ (from 1 to n) corresponds to the summation of the effects of each one of n toxic gases, and $\sum_2$ (from t_1 to t_2) corresponds to the summation of the relative concentration-time effects of the toxicants at each individual time increment (usually 1 minute). C_i is the average concentration (in ppm) of the toxic gas 'i' over the chosen time increment Δt , and concentration time $(Ct)_i$ is the specific lethal exposure dose (Ct product, in ppm * min). FED can be determined for each toxic gas (from 1 to n) at each discrete increment of time. The time at which their accumulated sum exceeds the lethal toxic dose represents the time available until lethality sets in with the actual concentrations measured. With this analysis, smoke toxicity depends both on the concentrations of toxic gases and on the intrinsic toxic potency of each component of smoke. This analysis is also based on the concept that the effects of both asphyxiant gases and irritant gases are a function of their dose (i.e., concentration and duration of exposure) and not simply of their concentration (as shown in studies of baboons and rats).

Typical lethal toxic potencies (in volumetric units of parts per million, ppm, for 30 minute exposures) for the major toxicants are shown in Table 5.6.

Table 5.6 Typical lethal toxic potencies for the major toxicants	
Gas	LC ₅₀ (ppm)
CO	4,000-5,100
HCN	150-200
HCl	3,700
Hydrogen bromide	3,000
Hydrogen fluoride	2,500-2,900
Acrolein	90-200
O ₂ (oxygen depletion)	54,000
LC ₅₀ = Lethal concentration of a chemical in air that kills 50% of the test subjects in a given time, typically 30 minutes	

The main direct cause of death in fires has always been toxicity of combustion products; however, fire victims usually die only when fires have become very large (very high heat release). Smoke contains mainly two types of toxic gases, asphyxiants and irritants, but the individual toxic gas associated with the largest fire hazard is CO.

Therefore, the use of actual smoke toxicity tests has decreased dramatically and there is now in North America typically just one standard smoke toxicity test: ASTM E1678 [46], also known as NFPA 269 [47]. This test exposes materials to radiant heat in a closed environment and uses rodents (rats) as the endpoint of a bioassay. It is rarely used, since the similarity of all toxic potencies has been demonstrated and there is no need to conduct animal experiments to perform unnecessary tests. The key need for the test, however, is for those instances when new materials are being developed, so as to ensure that unusual toxicants with very high toxic potencies are not generated.

5.9 Smoke Corrosivity Tests

Smoke corrosivity needs to be assessed by exposing metallic targets, such as circuit boards, to the smoke from various materials to assess their relative corrosivity. ASTM D5485 [48] is a test that does this by using the fire model from the cone calorimeter and diverting a portion of smoke and sending it across to a desiccator that contains

the metallic targets. A target is composed of two circuit elements. One circuit element is unprotected and is used for measuring corrosion. The other circuit, with a protective coating, is used as a reference. This compensates for change in electrical resistance due to change in temperature. Both elements of the target are part of a bridge circuit and are exposed to the combustion products. Most other tests used for smoke corrosivity are actually tests for measuring acid gas or conductivity, which are (erroneously) believed to be adequate surrogates for smoke corrosivity.

References

1. ASTM E84, *Standard Test Method for Surface Burning Characteristics of Building Materials*.
2. UL 723, *Test for Surface Burning Characteristics of Building Materials*.
3. NFPA 262, *Standard Method of Test for Flame Travel and Smoke of Wires and Cables for Use in Air-Handling Spaces*.
4. ASTM E162, *Standard Test Method for Surface Flammability of Materials Using a Radiant Heat Energy Source*.
5. ASTM E1317, *Standard Test Method for Flammability of Marine Surface Finishes*.
6. ASTM E1321, *Standard Test Method for Determining Material Ignition and Flame Spread Properties*.
7. ISO 5658, *Reaction to Fire Tests - Spread of Flame, Part 2: Lateral Spread on Building and Transport Products in Vertical Configuration*.
8. ASTM E662, *Standard Test Method for Specific Optical Density of Smoke Generated by Solid Materials*.
9. ASTM E1995, *Standard Test Method for Measurement of Smoke Obscuration Using a Conical Radiant Source in a Single Closed Chamber, With the Test Specimen Oriented Horizontally*.
10. NFPA 270, *Standard Test Method for Measurement of Smoke Obscuration Using a Conical Radiant Source in a Single Closed Chamber*.
11. ISO 5659-2, *Plastics - Smoke Generation - Part 2: Determination of Optical Density by a Single-Chamber Test*.

12. IEC 61034, *Measurement of Smoke Density of Cables Burning under Defined Conditions.*
13. ASTM E648, *Standard Test Method for Critical Radiant Flux of Floor-Covering Systems Using a Radiant Heat Energy Source.*
14. NFPA 253, *Standard Method of Test for Critical Radiant Flux of Floor Covering Systems Using a Radiant Heat Energy Source.*
15. ISO 9239-1, *Reaction to Fire Tests for Floorings - Part 1: Determination of the Burning Behaviour Using a Radiant Heat Source.*
16. NFPA 265, *Standard Methods of Fire Tests for Evaluating Room Fire Growth Contribution of Textile Coverings on Full Height Panels and Walls.*
17. UL 1715, *Standard for Fire Test of Interior Finish Material.*
18. NFPA 286, *Standard Methods of Fire Tests for Evaluating Contribution of Wall and Ceiling Interior Finish to Room Fire Growth.*
19. ASTM E2257, *Standard Test Method for Room Fire Test of Wall and Ceiling Materials and Assemblies.*
20. ISO 9705, *Fire Tests - Full-Scale Room Test for Surface Products.*
21. ASTM E1537, *Standard Test Method for Fire Testing of Upholstered Furniture.*
22. NFPA 289, *Standard Method of Fire Test for Individual Fuel Packages.*
23. ASTM E1822, *Standard Test Method for Fire Testing of Stacked Chairs.*
24. UL 1975, *Standard for Fire Tests for Foamed Plastics Used for Decorative Purpose.*
25. ASTM D5424, *Standard Test Method for Smoke Obscuration of Insulating Materials Contained in Electrical or Optical Fiber Cables when Burning in a Vertical Cable Tray Configuration.*
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6 Methods for Reducing Visible Smoke in Specific Polymer Systems

6.1 General Comments

Smoke is broadly defined by an American Society for Testing and Materials (ASTM) terminology committee as ‘the airborne solid and liquid particulates and gases emitted when a material undergoes combustion or pyrolysis’, and, more precisely, should include the quantity of air that is entrained or otherwise mixed into the emitted mass [1]. Some dictionaries define smoke as only the visible part, so the word is, unfortunately, somewhat ambiguous.

Elsewhere in this volume, the subject of smoke toxicology and corrosivity is discussed, which includes the invisible part of the smoke. However, in the present chapter, we will address only *visible smoke* since fire standards for materials are generally based only on that portion of smoke measured by optical absorption in the visible region. Visible smoke is usually expressed as optical density D measured by attenuation of a light beam passing for a specified distance, and expressed by the common logarithm of the ratio of the initial flux I_0 to the transmitted flux I ($D = \log_{10}[I_0/I]$). A 2009 overview of test methods for both the visible and the invisible components of smoke has been presented by Underwriters Laboratories (UL) authors [2].

In the United States, much of the smoke testing is done using the ASTM E84 [3] tunnel (Steiner tunnel) test for materials that must comply with building codes. Because of the expense and large samples required for the ASTM E84 test, there has been much effort to use the cone to make predictions of ASTM E84 surface burning characteristics, including smoke. Some difficulties have been summarised by Hirschler [4]. The reproducibility of the Steiner tunnel test is mediocre at best, and the precision is particularly poor for smoke testing. The cone is a small-scale test, and smoke is a property that is based on a combination of intrinsic smoke per unit area or mass (which small-scale tests assess) and the amount of material burnt (which small-scale tests don’t assess). The predictability of the cone with regard to smoke is less satisfactory than with regard to heat release. Therefore, it is likely that when a comparison of smoke between borderline candidate materials is made based on cone results, the information may be insufficient to make fail-safe decisions.

The effort to lower smoke generation at the same time as improving flame resistance can be a balancing act. Flame retardants acting in the flame zone can interfere in the combustion efficacy of the volatile species and may cause more airborne soot particles to be formed. Formulation studies to reduce smoke and flammability have been discussed by Innes [5], who emphasises the importance of the interactions. Efforts to use statistical and graphical methods to find optima of flammability and smoke in acrylonitrile-butadiene-styrene (ABS), brominated additive and several metal hydroxide systems are described by Hirschler [6], who also discusses the hypotheses regarding visible smoke (soot) control.

The contradiction between the rate of smoke formation and the net (accumulated or integrated) amount of smoke often leads to confusion. For example, in a testing configuration where burning is driven by continued application of heat from an external source, as in the cone calorimeter, both the rate of smoke formation as well as the total smoke collected or integrated will be worsened by the flame retardant. However, in a test where the ignition source is removed after ignition and the sample is then allowed to burn at its own rate or self extinguish, the *total* smoke may be less with the flame retardant present simply because less material was burned.

Whether or not the increased smoke production is viewed as a real problem may depend on whether the test scenario is ignition by a small flame, applied temporarily, or whether the plastic is subjected to an ongoing fire in which other materials are burning.

The best solution to the smoke problem is to keep the material from burning at all. However, if the material does burn, a significant decrease in rate of mass burning, decrease in rate or distance of flame spread and decrease in rate of heat release is likely to correlate roughly with a decrease in rate of smoke release, whereas a decrease in amount of material burned is likely to correlate roughly with total smoke accumulation.

One generality about visible smoke is worth noting: aromatic polymers tend to produce more visible smoke than aliphatic polymers. Polyvinyl chloride (PVC) is an aliphatic polymer, but tends to produce aromatic fragments when it pyrolyses, it thus produces heavy visible smoke. Aromatic plasticisers also add to the smoke, as do the volatile compounds from the usual antimony oxide (ATO) synergist.

6.2 Smoke and Decomposition/Combustion Products from Polyvinyl Chloride

The flame and smoke retardance of PVC was reviewed in 1997 by Nass and Heiberger [7] in a four volume set of books. This topic was addressed in a book edited by Grossman covering the formulation of PVC [8]. In 2005, Levchik and Weil

published an update of the literature (basic studies and as patents) on flame retardancy and smoke suppression of PVC [9]. An overview was given in 2006 by Shen [10]. The fire performance of PVC was further reviewed by Hirschler [11] in 2005 from the standpoint of standards, test methods and test performance of PVC.

When PVC is heated to combustion such as by flame exposure, it cracks out hydrogen chloride (HCl), a gas which is usually released into the surrounding space. If there is a suitable reactant such as calcium carbonate or hydrotalcite in the formulation, the HCl may react with it and be neutralised. When HCl is emitted, it does not travel far. Its concentration quickly declines as it is absorbed on surfaces, as discussed in the present volume in Chapter 4. The relative importance of HCl as a fire hazard in comparison to carbon monoxide (CO), the usual toxic combustion product, is addressed in **Chapters 2 and 4**.

PVC is widely used in building construction, as door and window frames, sidings, insulation (vapour barriers), conduits, wires and cables, and wall coverings. It has satisfactory light and heat stability for these uses. To increase its usable temperature range, it can be blended with ABS, acrylonitrile-styrene-acrylate copolymer or styrene-maleic anhydride, which will usually increase smoke. To make it a softer plastic, PVC can be blended with plasticisers, a major topic discussed next. In terms of the flame spread test, ASTM E84 (Steiner tunnel) [3] used for building code requirements in the United States, some rigid PVC formulations can achieve a flammability rating of Class A, i.e., a flame spread index (FSI) less than 25, compared to the reference for red oak flooring, which is rated at 100. However, the smoke developed index (SDI) of many rigid PVC formulations tends to be poor, and smoke suppressant additives may be needed, as discussed next.

PVC compounds (semi-rigid and flexible) are now extensively used for cable jackets and even primary electrical insulation. Such compounds can be used for the relatively demanding plenum cable applications, where they must meet the requirements of the UL 910 test, recently replaced by the National Fire Protection Association (NFPA), NFPA 262 test (previously known as the UL 910 test) [12], which assesses both flame propagation and smoke emission. This use was developed in the last two decades and has advantages in relative cost (compared to fluoropolymers) and ease of processing. The major disadvantage has been smoke obscuration, and that has been met by improved additive systems. Flexible PVC systems with flame-retarding and smoke-retarding additives are discussed next.

6.2.1 Antimony Oxide and Related Products: Effect on Smoke in Halogen-containing Polymers

ATO is not a flame retardant by itself, but is a powerful synergist with halogens, such as in PVC. A typical usage range is 2 to 8 phr. It reacts with HCl or hydrogen bromide (HBr), or possibly directly with some organohalogen compounds, to form antimony

trichloride or antimony tribromide, which volatilise at fire exposure temperatures and act as powerful flame chemistry inhibitors. This generally results in increased smoke including soot and antimony-containing particulate matter, and incomplete combustion products such as CO.

Some alleviation of smoke may be accomplished by use of sodium antimonate, but this is a more costly additive. It is mainly used in polyester thermoplastics for which antimony trioxide has some destabilising effect [13].

Some ATO combinations with other inorganic additives are sometimes found to be better on smoke, but good comparison data is scarce. For example, Thermoguard® CPA, now marketed by Chemtura, is a mixture of ATO, possibly with barium sulfate and zinc sulfide. This has long been on the market and is often lower in cost than pure ATO in PVC. Its zinc sulfide content provides some flame-retardant synergism and smoke reduction, and this inexpensive white pigment is sometimes used by itself for this purpose.

Several proprietary combinations of ATO with zinc oxide and/or magnesium hydroxide, molybdenum compounds and other minerals are made and sold by Marshall Additive Technologies, previously under the Charmax trade name, now under the name of C-Tec®. For example, C-Tec® FRZ30S and FRZ20S are 40% and 23% ATO combinations with zinc oxide and other metal oxides. Compounders frequently find that such combinations improve flame and smoke results and may reduce cost [14]. Results are formulation dependent.

ATO in PVC tends to increase the total smoke relative to the weight of plastic burned in small-scale tests, but it is important to note that total smoke may be lower in a large-scale test such as ASTM E84 tunnel [3] or in a real fire because the flame-retardant synergist effect of the ATO may lower the amount of polymer burned or the mass-loss rate of burning. This viewpoint regarding smoke in fires is discussed by Hirschler [6].

6.2.2 The Effect of Chlorinated Paraffins and Related Chlorine Additives on Smoke

The chloroparaffins as a class are old, but they are still widely used. The liquid ones are secondary plasticisers in PVC, rubber and various thermoplastics. In PVC, they can partially replace the low-flammability phosphate plasticisers, with reduction of cost. Chloroparaffins are useful in formulating PVC for low smoke. The originally marketed chloroparaffins had limited thermal stability, but modern grades from Dover Chemical, such as DG50 (chlorinated paraffin; $C_{14}H_{24}Cl_6$), have much better

stability and freedom from aquatic toxicity as the result of the use of longer-chain, mainly unbranched paraffins, chlorination to higher levels of chlorine content, and the addition of effective stabilisers [15].

Polychlorinated polyethylenes such as Tyrin® (Dow) can be blended with rigid PVC to provide improved low temperature impact, ductility, tensile strength and weatherability, and the smoke from such blends is reduced while flame retardancy is retained [16].

6.2.3 Use of Alumina Trihydrate for Reducing Smoke in Polyvinyl Chloride

Plasticised PVC, plasticised by phthalate esters tends to produce a high smoke level, which can either be aggravated or reduced by other additives. The smoke emission is made worse by the presence of ATO, as discussed previously, but can be reduced by adding aluminum trihydrate (ATH), either ground or precipitated [17]. To reach the same flame retardancy, the ATH percentage must be much higher than the percentage of ATO. Some data suggest a favourable synergism between ATH and ATO for both reducing the level of smoke and slowing down the rate of smoke release [18]. Huber Corporation has published data in their trade literature that shows an optimum ratio of ATO and ATH in the range of 1:10 to 1:15.

6.2.4 Magnesium Hydroxide and other Magnesium Compounds for Reducing Smoke in Polyvinyl Chloride

Magnesium hydroxide is generally more effective than ATH as a smoke suppressant in PVC, with some exceptions [17]. Magnesium hydroxide is basic and scavenges hydrochloric acid and thus reduces the corrosivity of the smoke. Combinations of ATH and magnesium hydroxide are often preferred because of water-release endothermicity over a broader temperature range or over a longer time - such combinations are often considered synergistic.

A variety of magnesium hydroxide, Huber's Vertex® 100, has been claimed to have unique particle characteristics that give it enhanced flame and smoke-suppressant properties, compared to the usual grades of magnesium hydroxide or ATH [17]. Martinswerk [18] developed proprietary technology for surface-treating magnesium hydroxide with polysiloxanes to improve smoke and flame retardancy, as well as mechanical properties in various polymers.

A natural mineral Ultracarb® (Minelco) or Marshall Additive Technology's HM-C9, which is a mixture of basic magnesium carbonate (hydromagnesite) and huntite

(a magnesium calcium carbonate), has been used for a long time as a smoke suppressant in flexible PVC, usually at 5-20% together with alkyl diphenyl phosphate plasticisers [19, 20]. In an optimisation study, this mineral was shown to be useful for compounding low-smoke ATO-free vinyl formulations plasticised by phosphate and tetrabromophthalate plasticisers. It was also found that blends of the mineral with calcium carbonate afforded flame-retardant plasticised PVC formulations with reduction of HCl fume release on fire exposure.

A zinc oxide-magnesium oxide product, Chemtura's Ongard® 2, has been marketed for many years as a smoke and flammability suppressant for PVC, especially with alkyl diphenyl phosphate plasticisers. Another application shows the combination of Ongard® 2 at 2 phr with ATO at 2 phr in rigid PVC pipe [21].

Hydrotalcite (magnesium aluminum hydroxycarbonate) has been shown to not only capture HCl and to act as a PVC-stabilising additive, but also to suppress smoke [22]. Moreover, the further addition of zinc oxide improves the action of the hydrotalcite; optimal formulations have 3% hydrotalcite and 2% zinc oxide [23].

6.2.5 Molybdenum Compounds in Polyvinyl Chloride

Molybdenum compounds are regarded as outstandingly effective additives for low-smoke PVC formulations. A leading additive of this group is ammonium octamolybdate (AOM). Mode-of-action studies have shown that the action of the molybdates is in the condensed phase, not the gas phase, since most of the molybdenum is found to remain in the solid residue. It is believed that the molybdates reduce smoke by catalysing the formation of *trans*-olefin structures from *cis*-olefin structures in the dehydrochlorinated PVC, which reduce the tendency of the unsaturated decomposed PVC chain to cyclise to benzene, toluene and related soot-forming aromatic compounds [24].

Zinc and calcium molybdates are effective smoke suppressants for PVC and are sold by Sherwin Williams as Kemgard® formulations. Kemgard® 911C, a zinc molybdate on talc, is efficient as a smoke suppressant, as shown in a wire-insulation blend of chlorinated polyethylene and PVC [25]. Kemgard® MZM, a zinc molybdate-magnesium oxide complex, is a newer product that combines good smoke suppression with improved dynamic stability in rigid PVC. Kemgard® HPSS is a basic zinc molybdate/magnesium hydroxide combination that is efficient as a smoke suppressant and provides flame retardancy with early charring and late burnoff of the char; it also shows good dynamic stability in flexible PVC [26, 27]. Efficacy advantages of these products relative to AOM have been claimed [28]. Combining a molybdenum smoke suppressant with various plasticisers and stabilisers has been studied in a statistical

design for plenum jacket applications; the molybdenum compound shows a small destabilising effect, whereas the phthalate plasticiser and hydrotalcite (magnesium aluminum carbonate) show stabilising effects [29].

Various proprietary combinations of AOM with zinc oxide and/or magnesium hydroxide and inorganic components are available in the C-Tec® LSZ series from Marshall Additive Technologies, previously under the Charmax trade name. Combinations of this sort are intended to afford favourable smoke properties in PVC at reduced cost compared to the use of the molybdenum compound by itself.

Physical mixtures of molybdenum trioxide with copper, iron and tin oxides are also reported to provide low smoke, although there may be a discoloration problem. Molybdenum oxide, copper oxides and ferric oxide have been shown by cone calorimetry to lower the rate of heat release while increasing char [30], but only molybdenum oxide seems to have a retarding effect on dehydrochlorination [31]. Besides the isomerisation effect mentioned previously, it has also been proposed that some of the smoke-lowering action of molybdenum may be in the flame phase, perhaps as a result of formation of a vapourised molybdenum carbonyl.

Melamine octamolybdate has long been used as an alternative to AOM for smoke reduction of PVC. It has lower water solubility than AOM and, therefore, may show better electrical resistance under hot, wet conditions, which is obviously important for power cable applications. Discoloration in PVC caused by melamine octamolybdate or other molybdenum smoke suppressants can be avoided by adding a basic compound such as magnesium hydroxide or a basic zeolite [32].

6.2.6 Copper Compounds as Smoke Suppressants in Polyvinyl Chloride

Copper salts, particularly copper oxalate together with a molybdate, were used and patented as smoke suppressants by BFGoodrich [33]. More recently basic studies were conducted by Starnes and co-workers [34], and some synthetic work was done to combine copper and molybdenum in single compounds. It is not evident whether commercial use is made of copper compounds as smoke suppressants in PVC at the present time. Coloration of the plastic is one problem.

6.2.7 Borates as Smoke Suppressants in Polyvinyl Chloride

These additives are well known and used in PVC to partially replace ATO and have the advantage of anti-afterglow action and lower smoke. The most frequently used zinc borate (ZB) is $2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 3.5\text{H}_2\text{O}$ (Firebrake® ZB made by Rio Tinto

Minerals, formerly Borax and Luzenac, and also available from Marshall Additive Technologies as C-Tec® ZB400 and ZB800). This zinc borate loses its 14% water of hydration in the range of 300-450 °C. Other zinc borates that are sold and used in PVC (with higher activity claimed due to higher zinc oxide ratio (ZnO) include $\text{ZnO} \cdot \text{B}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ and $2\text{ZnO} \cdot 2\text{B}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ (Chemtura's ZB223; Marshall's C-Tec® CT ZB200). The latter is also called zinc metaborate. These higher ZnO/ B_2O_3 compounds are believed to be mainly used in flexible PVC. Occasionally a destabilising effect is seen with zinc borate in PVC and is probably related to the ZnO content. Addition of more stabiliser will usually help. The action of the zinc borate is almost certainly in the promotion of crosslinking and charring, along with formation of a low melting glass, which together with other fillers such as ATH forms a barrier. There is also a 'heat sink' and fuel dilution effect when water of hydration is released from the zinc borate hydrates. Most of the boron and zinc content stays in the char, but there may be some vapour phase action from volatilised zinc chloride.

As mentioned previously, zinc borate can suppress afterglow (smoldering) by altering the surface morphology of the char. Boron inhibits carbon combustion by occupying some of the reactive sites on the graphite lattice, and other sites are inhibited by phosphorus [35]. Used alone, zinc borate is a less effective flame retardant in plasticised PVC than ATO, but combinations are better than either one alone for flame retardancy (Figure 6.1) and are also extremely effective for smoke reduction (Figure 6.2).

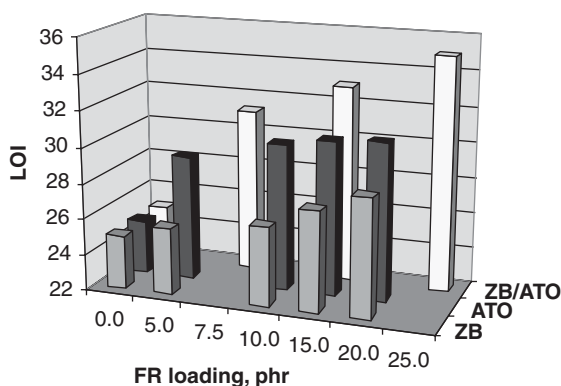


Figure 6.1 Oxygen index of flexible PVC with ATH, ATO, ZB and their blend 1:1. FR = fire retardant, LOI = limiting oxygen index, phr = parts per hundred rubber. Based on data from K.K. Shen in the *Proceedings of the SPE Conference - Vinyltec 2006*, Atlanta, GA, USA, 2006 [10]

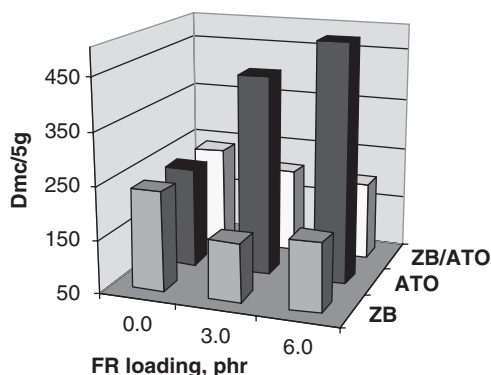


Figure 6.2 ASTM E662 smoke (flaming) test results from flexible PVC with ATH, ATO, ZB and their blend 1:1. Dmc = corrected specific optical.

Based on data from K.K. Shen in the *Proceedings of the SPE Conference - Vinyltec 2006*, Atlanta, GA, USA, 2006 [10]

Depending on the fire-standard targeted and other additives in the formulation, partial or complete replacement of ATO by zinc borate may offer a reduction in formulation cost and substantial benefits in smoke reduction. Also, zinc borate show synergistic flame-retardant effects with ATO, particularly with ATH, magnesium hydroxide or calcium carbonate [37]. Synergism or at least favourable additive effects are also seen in smoke reduction by use of zinc borate in combination with other smoke-lowering additives such as zinc stannates.

6.2.8 Zinc Stannates as Smoke Suppressants in Polyvinyl Chloride

Zinc stannate and zinc hydroxystannate are colorless, water-insoluble salts that are effective smoke suppressants and flame-retardant synergists in PVC. (The stannates are available from Marshall Additive Technologies as C-Tec[®] CT-ZST and CT-ZHS, respectively. Cost has slowed the use of these compounds. Zinc hydroxystannate performs well as a flame retardant and smoke suppressant in PVC at ~3 phr and does not spoil colour or stability [38, 39]. Zinc stannate was similar as a smoke suppressant, but was less effective as a flame retardant. Alcan researchers found that a mixture of zinc stannate and zinc hydroxystannate was more effective than either one separately as a smoke suppressant [40, 41]. These tin compounds are believed to have mostly, but not exclusively, condensed phase action and function as Lewis acids [42].

For partial or even complete replacement of ATO, the stannates are claimed to provide good flame retardancy with lower visible smoke and lower CO production [43–45]. Excellent flame and smoke performance was provided by an optimal combination

of dodecyl diphenyl phosphate, a brominated aromatic ester (likely to be dioctyl tetrabromophthalate), ATH, zinc stannate, AOM and ATO. Good smoke results were also reported by Alcan investigators from combinations of zinc stannate and AOM [46]. Zinc stannates can allow the reduction or elimination of the associated smoke suppressant AOM, which was in 2009 more costly than the stannates.

Tin dioxide supported on calcium carbonate has been shown by Chinese workers to be an effective smoke suppressant additive for semi-rigid PVC [47]. Merely adding the two materials separately did not give the same result.

6.2.9 Zinc Sulfide as a Smoke Suppressant in Polyvinyl Chloride

Zinc sulfide is an inexpensive white pigment that has smoke suppressant action in PVC. By itself, it is not very flame-retardant, but it can be used in place of about half the ATO in a PVC formulation, retaining the flame-retardant properties [48]. A zinc sulfide-barium sulfate mixture ('lithopone', also an inexpensive white pigment) can be purchased separately and used as a partial replacement for ATO.

6.2.10 Calcium Carbonate as a Smoke Suppressant in Polyvinyl Chloride

Calcium carbonate is usually considered to be an inert, low-cost filler with feeble flame and smoke-retardant properties. When it is heated to 1150 °C, carbon dioxide (CO₂) is released endothermically, but this chemistry is at too high a temperature to help retard burning of the polymer. Calcium carbonate usually gives poor performance in the ASTM E84 tunnel [3]. Of course, calcium carbonate does dilute the flammable material. During burning, calcium carbonate (especially the higher surface-area grades) can also react with and neutralise HCl and can thereby reduce smoke corrosivity, besides providing some stabilising function. This method for decreasing HCl emissions from hot PVC relies on the high surface area of the calcium carbonate and its good dispersion. The more easily dispersed stearic acid surface-treated calcium carbonate is readily available.

Recent Huber studies show that calcium carbonate-ATH combinations can have a favourable balance of cost and efficacy in flame retardancy and smoke suppression [49]. The practical usefulness of such interactions has been discussed by Innes [50].

6.2.11 Low Flammability Plasticisers: Phosphate Esters and their Smoke Effects

In flexible PVC, the major source of fuel and smoke generation is almost always the plasticiser. Less flammable plasticisers such as polymeric plasticisers or built-in

plasticising co-monomers can minimise this problem, but are less efficient or more costly. A tetrabromophthalate ester such as the bis(2-ethylhexyl) ester can be used as a flame-retardant plasticiser, especially in situations where a high degree of fire retardance is required (e.g., railroad coach cables), and it is possible to formulate for low smoke, but tetrabromophthalates provide only mediocre plasticisation.

The frequently used approach to achieving acceptable flammability and smoke is the use of organophosphate esters as part of the plasticiser system. It is not typical to use organophosphates entirely, because they are substantially more costly than nonphosphate plasticisers and are less efficient plasticisers. The organophosphates are much less combustible than the ordinary phthalates. They have lower heats of combustion and have some moderate retardancy. The organophosphate plasticisers, commonly blended with dialkyl phthalates, are used in PVC films, cables, belts and vinyl-coated textiles.

The use of organophosphates in flame retardancy has a long history, predating commercialisation of PVC and going back to cellulose nitrate and cellulose acetate. The use in PVC began in the 1930s. The first phosphate used was tricresyl phosphate, originally made from mixed *o,m,p*-cresol. It was discovered between 1930 and 1940 that the *ortho*-cresyl isomer caused tricresyl phosphates to be neurotoxic, so once this was established, only *m,p*-cresol was used to make cresyl phosphates. The molecular basis of the neurotoxicity has been shown to relate to the ability of the *ortho*-cresyl phosphate structure to be bio-oxidised to a bioreactive cyclic phosphate [51].

Cresyl-diphenyl-phosphate is often preferred over tricresyl phosphate in Europe and Asia because of its greater efficiency and lower cost, although it is also more volatile. In most US markets, however, it is less often used because of this volatility and concern over its slightly greater toxicity [52].

Tricresyl phosphate replacements have evolved by substituting the cresol (which has become increasingly costly) with a synthetic isopropylphenol-phenol mixture to produce a mixed triaryl phosphate, most commonly approximating diphenyl-isopropylphenyl-phosphate. Although one study showed the *ortho*-isopropylphenyl isomer to be the best from a stability standpoint [53], the commercial products appear to be a mixture of isomers. The isopropylphenyl phenyl phosphates with lower and higher levels of isopropyl substitution have been sold as flame-retardant PVC plasticisers, such as Akzo Nobel's (now Israel Chemical's) Phosflex® 21P, 31P and 41P or FMC's Kronitex® 50 (similar to cresyl diphenyl phosphate in physical properties) and Kronitex® 100 (similar to tricresyl phosphate in physical properties). FMC triaryl phosphate products are now made and sold by Great Lakes Chemical (now Chemtura) as Reofos® 50, 65 and 95 (from isopropylphenols) and Pliobrak® CDP, TCP and TXP (from cresols and xylenols). Certain products of the Bayer (Lanxess) Disflammol® family are of this type.

The triaryl phosphates are more costly and somewhat less effective as plasticisers than the common dialkyl phthalate plasticisers. Plasticised PVC usually has severe price constraints, so compounders of inexpensive plasticised PVC will typically use mostly the dialkyl phthalate, mixed with no more of the triaryl phosphate than is needed to comfortably pass whatever flammability requirements must be met.

6.2.12 Low Temperature Lower-smoke Alkyl Diphenyl Phosphate Plasticisers

The triaryl phosphates impart undesirable stiffness to plasticised PVC at low temperatures and are not the optimum phosphates for low smoke. In the 1950s, Monsanto developed 2-ethylhexyl diphenyl phosphate (now Santicizer® 141) and isodecyl diphenyl phosphate (Santicizer® 148). Along with Santicizer® 2148, believed to be a longer *n*-alkyl variant of Santicizer® 148 with even lower smoke and better low-temperature plasticising properties, these are now available from Ferro Corporation. Products similar to Santicizer® 141 and 148 were later available from Akzo Nobel (now ICL-IP) as Phosflex® 362 and 390, respectively. Octyl (probably 2-ethylhexyl diphenyl phosphate) has been available from Bayer (now Lanxess) as Disflammol® DPO. These partially aliphatic phosphates are more plasticising than the triaryl phosphates. Uses are in tarpaulins, automobile seating, flooring, conveyer belts and cable sheathing, especially plenum cable jacketing. They also are said to have advantages in weathering, gelling properties and resistance to saponification (e.g., by alkaline detergents). They are somewhat less effective than the triaryl phosphates from a flammability standpoint, but distinctly better in smoke evolution [54].

A patent from Teknor-Apex [55] shows the use of pentaerythritol ester plasticisers (Hercoflex®) in combination with isodecyl diphenyl phosphate and a tetrabromophthalate plus ATH and Charmax® (Marshall Additive Technologies C-Tec®) LSZ4A in low smoke formulations for wire and cable insulation. Data in this patent show that lowering the tetrabromophthalate and raising the ATH level is favourable to low smoke in a wire and cable insulation formulation.

6.2.13 Smoke Considerations in Calendered Vinyls

For thin PVC films such as those used in laminates, ATO is commonly used, but when it is the only flame-retardant synergist, visible smoke is too high for many applications. Alumina trihydrate, magnesium hydroxide and zinc borate are usually added to lower smoke. As an alternative to ATO, phosphate-ester plasticisers are used, again often with ATH and/or magnesium hydroxide. The combination of ATO and phosphate plasticisers is usually inefficient because of antagonism due to the

formation of antimony phosphate, an inert ceramic-like material. The phosphate plasticiser alternative to ATO has been preferred during periods when the ATO price is very high. As discussed previously, for minimising smoke, the alkyl diphenyl phosphates have been preferred.

Different applications have different requirements. Some typical or ‘starting point’ formulations are listed next.

Wall covering must often pass the ASTM E84 tunnel class 1 requirement (less than 450 rating in regard to smoke-developed index) [3]. Many wall coverings are based on PVC, and these typically meet the flame developed index (FDI) requirements and smoke limits for this application [56] (Table 6.1).

Table 6.1 Typical vinyl formulations for wall covering	
Component	phr
PVC	100
Diisodecyl phthalate	26
Phosphate ester	20
ATO	2–4
ZB	5–10
ATH	10–15
Calcium carbonate	40
Stearic acid	0.3
Stabiliser	3–5

6.2.14 Smoke Considerations in Plenum Wire and Cable

In the United States, communication, alarm and signaling wires and cables are often used in plenums (concealed spaces serving also for air distribution). Wiring in plenums, if not very fire-resistant and if it emits very low smoke, can result in fire and smoke spreading rapidly through a building, with the smoke often escaping notice until a dangerous point is reached. Very stringent fire and smoke standards, based on the NFPA 262 tunnel test [12], must be met wherever wire and cable are exposed, i.e., not enclosed in metal conduits. Vinyl formulators have been under pressure to achieve flame and smoke levels that are competitive with costly fluoropolymer wire and cable constructions. PVC formulations have been developed to meet the plenum requirements; an early example is a 1993 patent by Belden Division of Cooper Industries [57] (Table 6.2).

Table 6.2 PVC formulation for plenum cables	
Component	Parts (by weight)
PVC (Geon 30)	100
Santicizer® 2148 phosphate plasticiser	30
Diocetyl tetrabromophthalate	20
Epoxidised soybean oil	3
ATH	30
AOM	30
Zinc molybdate	10
Tribasic lead sulfate	7
Stearic acid	0.5
Paraffin wax	0.5

A formulation was developed by Teknor Apex for low-smoke PVC wire and cable use, in place of the more costly AOM, or the alternative smoke suppressant Charmax LSZ4A (Marshall Additive Technologies C-Ted® LSZ4A), which has a low level of AOM plus other possibly synergistic ingredients [58] (Table 6.3).

Table 6.3 Wire and cable formulation with lower cost smoke suppressant	
Ingredient	Amount (by weight)
PVC resin	100
Pentaerythritol ester plasticiser (Hercoflex® 707)	31
Calcium carbonate	10
Calcined clay (Engelhard SP33)	5
ATH (Alcoa C710B)	60
Basic lead heat stabiliser	7
Stearic acid lubricant	0.25
Antimony trioxide	5
Brominated phthalate (Chemtura DP45)	10
Long-chain alkyl diphenyl phosphate (Santicizer 2148)	5
Zn-Mo complex (Charmax LSZ4A, now C-Tec® LSZ4A)	10
Zinc borate (Climax ZB467)	2

Cables with this composition passed the UL 910 tunnel test [59] and had an oxygen index of 46.

Some alloys of PVC with thermoplastic elastomers have been found to have flame and smoke properties that pass requirements for plenum use and that can compete with fluorinated ethylene propylene (FEP) coatings to meet present codes and standards (currently in a state of flux). Some cable constructions use a PVC sheath over FEP insulation, with a low-smoke PVC formulation. Some patents show cables made with non flame retarded insulation encased in sheaths or jackets with improved fire performance properties, such as polytetrafluoroethylene or low smoke highly fire retarded PVC-based materials, for example, a patent by Belden [60] describes proprietary low-smoke PVC jacket formulations from AlphaGary and Gitto Global. Patents disclose a further range of technology for solving cable requirements by means of construction using layers with different properties.

Polymer-blend formulations for plenum use based on ATH and a huntite-hydromagnesite mineral were published in 1999 by Brown (Alcan) [61] (Table 6.4).

Table 6.4 Polymer-blend formulations for plenum cable			
Component	A (phr)	B (phr)	C (phr)
PVC	100	100	100
Elvaloy® HP-441 (DuPont ethylene-acrylate-CO)	15	15	15
Dodecyl diphenyl phosphate plasticiser	10	10	10
Diocetyl tetrabromophthalate plasticiser	25	25	25
Alumina trihydrate	40	40	40
Huntite/hydromagnesite mix	10	10	10
Hindered phenolic stabiliser (Ciba)	4	4	4
Tribasic lead sulfate stabiliser	3	3	3
Antimony trioxide, e.g., synergist	3	3	3
AOM, antismoke	25	-	10
Zinc stannate, e.g., synergist and antismoke	-	25	15
Cone calorimetry data at 40 kW/m²			
Time to ignition (s)	897	705	never
Peak rate of heat release (kW/m ²)	35	35	-
Average specific extinction area (m ² /kg)	433	342	-

Formulations A, B and C are said to be good starting points for formulation development. The test results imply a possible synergism of AOM and zinc stannate. Other published formulations show chlorinated PVC as a helpful component for plenum wiring to meet smoke and flame requirements. Lead stabilisers in all of the previous formulations have now, in most cases, been replaced by non lead alternatives.

Studies at DuPont have shown that their ethylene-acrylate-CO copolymers (DuPont's Elvaloy® HP products, in particular ECR-742 and ECR HP-441) used as resin modifiers in PVC compounds can substantially reduce smoke without loss of strength, elongation, flexural modulus or brittle point [62]. These formulations are suggested for plenum cable.

Some multicomponent blend formulations were developed for cable insulation and jackets at Furon Company, using a mixture of PVC, chlorinated PVC (CPVC), ethylene acrylic elastomer, polycaprolactone (probably a compatibiliser), alkyl diphenyl phosphate and trimellitate plasticisers and a combination of flame and smoke suppressants (Table 6.5).

This patent disclosed much useful information on the effect of composition changes on flammability, smoke and mechanical properties.

There has long been an ongoing competition in the plenum cable market between fluoropolymers such as those made by DuPont, and vinyls compounded for low smoke and high fire performance. Teknor Apex are wire and cable compounders who have made hybrids of plasticised PVC, fluoropolymers and polyacrylate compatibilisers [66]. Kroushl [67], discusses that polyvinylidene fluoride-PVC blends have been commercialised but are limited by cost.

A challenging smoke standard exists for cable jackets. These often must pass the 'limited smoke' requirements contained in the two versions of the UL 1685 vertical cable tray test [68] for flame spread and smoke release (usually in rail and ship applications). Formulations generally will be based on high loadings of ATH, often with zinc borate as a sintering agent to aid barrier formation.

6.2.15 Coated Textile Applications

The flame and smoke performance of PVC textile coatings was reviewed in 2006 by Munro [69]. Flame retarded PVC-coated fabrics frequently have a two-layer coating, an inner vinyl layer plasticised with a triaryl phosphate or, for lower smoke, alkyl diphenyl phosphate with a phthalate ester, and, in some cases, a chloroparaffin that acts as a secondary plasticiser. The outer layer may be plasticised with a phosphate together with a non volatilising polymeric or oligomeric ester plasticiser. Such formulations may also contain ATO (possibly inefficient when used with a phosphate), zinc borate or ATH. Sometimes, an acrylic topcoat is also applied.

Table 6.5 Wire and cable jacket formulations for plenum applications [63]		
Component	Wire Insulation (parts by weight)	Jacketing (parts by weight)
Geon® 86 × 1 PVC	70	65
Temprite® 674 chlorinated CPVC	30	35
Vamac® G ethylene acrylic elastomer	20	45
Isodecyl diphenyl phosphate plasticiser	8	13.0
Titanium dioxide pigment	2	5.0
Pol-U® molybdenum oxide composition	4	6.0
Micral® 932SP or CM hydrated alumina	20	110.0
H(DYT) D80 dibasic lead phthalate	12	8.0
II(TBS) D80 tribasic lead sulfate	0.30	-
Antimony trioxide	4.0	5.0
ZB223 (ZB; 2ZnO·2B ₂ O ₃ ·3H ₂ O)	-	8.0
Irganox® 1010 hindered phenol antioxidant	0.30	0.3
Calcium stearate	1.50	0.50
Structol® TR016 lubricant	1.0	-
Jayflex® triisononyl trimellitate plasticiser	8.0	8.0
P-tone® 700 high molecular weight (M _w) caprolactone polymer	20	20.0
Zerogen® 10 SP magnesium hydroxide	20	-
Physical Properties		
Oven ageing ICEA S-19-81*, 7 days/121 °C	Passes 90 °C rating	Passes 90 °C rating
Tensile retention (%)	112%	140%
Elongation retention (%)	86%	50%
Flammability/Smoke		
LOI (oxygen gas %) (ASTM D2863) [64]	44.0	61.0
D _m Smoldering (ASTM E662) [65]	105	95.5
D _m Flaming (ASTM E662) [65]	154	103.5

Decabromodiphenyl ether (usually with antimony trioxide) is cost effective in flexible PVC textile backcoating. However, its tendency to bloom (come to the surface), and towards photodiscoloration, and environmental worries tend to restrict its use. Some of the other polybrominated additives that are used in coated textiles are hexabromocyclododecane, tetrabromobisphenol A bis(dibromopropyl ether), poly(pentabromobenzyl acrylate) and proprietary bromine-containing blends such as ICL-IP SaFRon and TexFRon additives. These are generally used with antimony trioxide synergist and thus may be expected to increase smoke somewhat.

6.2.16 Vinyl Flooring

Vinyl sheet flooring typically has two vinyl layers on fibrous backing, the lower layer being PVC, usually with a phosphate (triaryl or alkyl diphenyl) and, typically, butyl benzyl phthalate plasticiser (specifically chosen to resist heelmarks). The upper layer (wear layer) typically has a low level of plasticiser such as a phthalate so that it does not need a flame-retardant phosphate. Often, vinyl tile flooring needs no flame retardant or smoke suppressant because of the high filler level, which is typically calcium carbonate and/or clay, and its low level of plasticiser. An acrylic or urethane topcoat is used in some cases, but may have a somewhat unfavourable effect on fire performance. The rather erratic flame and smoke requirements for vinyl flooring have been reviewed by one of the manufacturers [70].

6.2.17 Polyvinyl Chloride from a Safety and Environmental Point of View – the Role of Smoke

PVC is often opposed by environmental activists who claim that it produces especially toxic smoke (amongst many other faults that they note). It is well-established that CO is the main lethal gas in combustion products, and that the toxicity of fire gases is dominated by CO. Animal experiments have shown that the inhalation toxicity of HCl is in the same range as that of CO. However, HCl and HBr have a unique ability amongst the major combustion gases to have their concentration decay quickly with distance from the fire since they react or are absorbed by surfaces. In room-corner burns (Factory Mutual), visual obscuration caused by burning PVC was less than that found with wood. These relationships are discussed in **Chapter 4**.

PVC, along with other halogenated materials, has been under many years of attack by environmental activists. Their arguments, in addition to the one just discussed, are summarised by a Greenpeace author with emphasis on PVC [71]. Some have to

do with by-products of production, biodegradation, difficulties of incineration and recycling (although some PVC is recycled [72]), or concern about dioxin production in incineration. However, incineration in modern permitted incinerator-scrubber systems has been shown to produce little or no dioxins [73]. Disposal by burning in smelters and cement kilns is possible, but must be well-monitored. The EPA has noted that the largest source for dioxins is now forest fires.

PVC has advantages over other commodity plastics properties in regard to ignitability, flame spread and ease of extinguishment. Thus, PVC is less likely to be a source of fuel and generator of smoke than are many other plastics. The heat release of rigid and semi-rigid PVC is very low compared to other plastics. PVC with conventional phthalate plasticiser is higher than unplasticised PVC in terms of its heat release, but where fire and smoke behaviour is important, low flammability and low smoke plasticisers are available and have been discussed previously.

Several significant European and Australian studies on the environmental impact of PVC, including official ones, found it to be quite acceptable or even advantageous from an environmental standpoint [74]. Some of the more objectionable additives, such as cadmium and lead stabilisers, have been phased out. Even the phthalate plasticisers, which have some borderline toxicological concerns for use in toys, are being replaced. Data resources supporting the safe use of PVC are available on the Web [75, 76]. PVC as wire and cable insulation continues to be extensively used, but non halogen alternatives are coming into the market where 'green' marketing strategies are adopted. However, at the time of the present review, new manufacturing plants for PVC are being planned in the United States [77], Europe and Asia [78–80]. Efforts are made by the PVC industry, particularly in Europe, to meet the remaining environmental objections, such as the recyclability issue [81]. Usage has also been growing [82, 83].

6.3 The Smoke Problem with Styrenics

Styrenic polymers, both flame retarded and non flame retarded, burn with exceptionally dark, sooty flames. This is the result of incomplete combustion leading to fine black particles (soot). Flame retardants that retard complete oxidation of the fuel in the flame may mainly increase the CO/CO₂ ratio in the case of typical aliphatic polymers, but also may increase soot with aromatic polymers. However, if the flame retardant prevents or slows down ignition, or reduces the rate and amount of material burned, total smoke including soot may actually be lower. Some benefit has been reported in academic studies of the use of finely-divided high-surface-area silica, even as low as 3%, which appears to work by absorbing pyrolysates and then sintering to form a barrier [6]. Commercial applications of this silica approach are not known.

With styrenics, attempts have been made to reduce the smoke yield either by retarding the ignition or burn rate or causing self-extinguishment, or by specific smoke-suppressant additives. However, in contrast to PVC, for which commercially useful smoke-suppressing additives are available, there seems to be no effective smoke suppressant for styrenics on the market.

Expanded polystyrene foam, a material widely used for insulation in buildings, refrigerators and the like, would seem to have a smoke problem, but this is avoided by preventing or retarding burning. For many codes, the values of the FSI and SDI by the ASTM E84 test [3] are required in order to get a classification. These values are measured in the 7.3 m 'Steiner tunnel'. The flame spread indices and smoke developed indices at a maximum thickness of 10 cm and density of 64 kg/m³ for class A are less than 25 and 450, respectively. For class B, the FSI must be less than 75 and the SDI also less than 450. These standards can be met if styrenic foam melts, flows and drips when exposed to fire, provided that the drips are non burning (no flaming drips). Melt-flow can even be enhanced for this mode of flame retardancy by adding small amounts of radical generators (peroxides or hindered hydrocarbons), which decrease M_w and thus reduce viscosity.

Because some pyrolysis to styrene monomer, dimer and volatile oligomer takes place, despite the flow of much of the molten polymer out of the fire zone, a vapour-phase flame retardant is generally required. The patent literature shows many brominated aliphatic compounds that can release flame-inhibiting HBr into the vapour phase at the fire temperature; such compounds are stable enough not to decompose at the processing temperatures for polystyrene foams. With sufficiently fast HBr release, a synergist such as antimony trioxide is not needed, and, indeed, such a solid might work against the melt-flow-drip part of the mode of action. Although the brominated flame retardants tend to increase smoke yield, their retarding action on burning usually allows for passage of smoke limitations, e.g., in the ASTM E84 tunnel classifications. In some cases, dripping is the mode of extinguishment.

Foamed polystyrene insulation in a marine application has evidently been linked to some unfavourable fire experiences and is advised against by the US Coast Guard for use in commercial fishing vessels such as in engine-box covers, as the foam might ignite in hot locations and rapidly spread fire and dense smoke [84].

With high-impact polystyrene and ABS, reasonably low smoke and a UL 94 V0 rating can be achieved with a cyclic chlorohydrocarbon additive, Oxychem's Dechlorane Plus®, chlorine content 65%. Like most halogen-containing flame retardants, it can be synergised with ATO, but low smoke results can be better achieved using ferric oxide or zinc oxide as synergists [85]. Combinations with chlorowax (70% Cl) are also useful.

6.4 Smoke Considerations with Textiles

Smoke is a consideration with wool upholstery such as that often used in aircraft. The Zirpro® finish developed by Benisek treats the wool with a soluble hexafluorotitanate or, better from a colour standpoint, a hexafluorozirconate. This treatment causes wool to form an intumescent char upon fire exposure, and the resultant extinguishment lowers the smoke. The competitive finish using tetrabromophthalic acid salts tends to yield somewhat more smoke upon burning, however, both finishes are used in aircraft seating [86] for which limited smoke emission is not a requirement.

6.5 Smoke Considerations with Polyurethanes

Expandable graphite, which creates a barrier upon exposure to flame, provides efficient smoke reduction in rigid polyurethanes (PU) foams and to some extent in isocyanurate foams [87]. Disadvantages are the adverse effects on the thermal insulation properties of the foam, but this is said to be slightly improved by addition of triethyl phosphate [88]. Other disadvantages are its black colour, electrical conductivity and granular texture.

Also, for non halogen applications of importance in Europe, high M_w finely-divided insoluble crystal type II (high M_w) ammonium polyphosphate (APP) (Clariant Exolit® AP 422 or Budenheim Iberica's FR Cros® 484) has been found effective in pentane-blown PU or polyisocyanurate foams. These demand enhanced flame-retardant additive levels to overcome the adverse flammability effect of the pentane. According to Clariant workers, APP, which works by a condensed-phase mechanism, provides lower smoke compared to halogen-containing foams of similar density [89]. APP is also useful in urethane elastomers and cast urethane resins at low levels of addition and generally results in low smoke.

Because of the relatively high water percentage used in spray-foam formulations, more urea groups are made at the expense of urethane groups - this tends to increase both flammability and smoke. An increased portion of polyester polyol at the expense of Mannich polyol and the use of a combination of Fyrol® PCF with triethyl phosphate tends to decrease smoke and aids in achieving a Class B result (up to 75 flame spread index) in the ASTM E84 tunnel test [3].

By use of certain polyols, a low smoke developed index can be reached even with a bromine-containing formulation [90]. It is also helpful to use a liquid phosphate such as Albemarle Saytex® RB-7980 (a blend of a brominated diol Saytex RB-79 with a liquid phosphate) in pentane-blown isocyanurate roofing foams. This may be a combination of the brominated diol Saytex RB-79 with tris(chloroisopropyl) phosphate, which was indicated by Albemarle to be a favourable choice for both

flame retardancy and smoke [91]. A flame- spread index of 23 (Class A) and a smoke developed index of 100 (ASTM E84 tunnel) could be reached at an isocyanate index of 350 using 25% Saytex® RB-79 and 25 parts of tris(chloroisopropyl) phosphate.

Polyols made from renewable agricultural products are increasingly used as ‘green’ ingredients in PU foams. A soy-oil-based polyol was claimed to be better in thermal stability and flame retardancy compared to a polypropylene oxide polyol in rigid PU foams [92] and may have an advantage of low smoke.

ATH can be added at quite high loadings in PU elastomers as the main or only flame retardant or can be used in combination with phosphorus additives. Besides retarding flame, ATH also suppresses smoke.

6.6 Smoke Considerations with Polycarbonates

Certain sulfonate salts, such as potassium perfluoroalkylsulfonates or potassium diphenylsulfone sulfonate, are effective at very low levels, even less than 1%, in polycarbonates to pass less stringent flammability requirements. Since they work by enhancing char and catalysing CO₂ evolution, they are favourable in regard to smoke. They may be used in combination with halogenated additives [93], such as a tetrabromobisphenol-A/bisphenol-A polycarbonate to meet more stringent flame retardancy with low smoke and low heat release. The cost can be kept relatively low by use of a combination of sodium trichlorobenzenesulfonate and a brominated polycarbonate additive. With this sulfonate as the only flame retardant, the chlorine percentage can be low enough so that the formulation is rated as non halogen by some classifications [94].

In polycarbonate-ABS blends, the styrenic portion of these blends causes high smoke evolution, but this is not a criterion in many of the uses of these blends, such as enclosures for office equipment.

GE Plastics has disclosed polycarbonate-polysiloxane copolymers and blends with additional polycarbonates [95], impact modifiers and polyether-polyimides [96]. Some of these blends, in particular the blends with polyether-polyimides and typical flame retardants, have quite low smoke [97, 98].

6.7 Smoke Considerations in Thermoplastic Polyesters

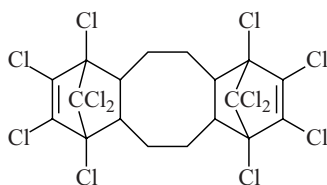
BASF phosphorus-flame-retarded polybutylene terephthalate (PBT), Ultradur® B4400, contains no halogen, antimony or red phosphorus. At 25% glass fibre content, it

achieves a UL 94 V0 rating at 1.6 mm and glow wire ratings of 960 °C at 1 mm, and has mechanical properties close to similar grades of halogen-flame-retarded PBT, but with lower density and better electrical tracking resistance. Smoke density is substantially lower than with halogenated PBT, and the smoke toxicity meets Airbus standards (which are based on emissions of individual gases, with emphasis on the halogenated ones). The details of the formulation are not published as of the date of this book, but BASF patents that may be relevant disclose the use of melamine cyanurate with phosphorus compounds such as resorcinol bis(diphenyl phosphate), calcium hypophosphite and triphenylphosphine oxide [99, 100]. A formulation with 15 wt% calcium hypophosphite and 10 wt% melamine cyanurate in glass filled PBT gave a UL 94 V0 rating [101] and would be favourable regarding smoke density.

Chemische Fabrik Budenheim has developed [102] a novel long-chain melamine polyphosphate (Budite® 3141), which is an effective flame retardant for PBT and polyethylene terephthalate. A 30% loading in glass-reinforced PBT provides an oxygen index of 28, a V0 rating of 1.6 mm, and low smoke evolution.

6.8 Smoke Considerations in Polyamides

Aliphatic polyamides tend not to be high smoke generators, but when halogen compounds are used as flame retardants, typically with a synergist such as antimony trioxide, more smoke is generated in a forced burning configuration. An early successful halogen additive, less conducive to smoke, is Oxychem's Dechlorane Plus®. This is a stable polycyclic polychlorinated compound with the following structure:



Its chlorine atoms are stable to hydrolysis and dehydrochlorination and it is high melting and stable for processing up to about 300 °C. Other advantages are: resistance to photodiscoloration, freedom from blooming (an advantage over decabromodiphenyl ether), higher comparative tracking index (CTI), low smoke on forced burning and even lower smoke with iron oxide or zinc oxide alternatives to ATO.

A typical addition level for use in non-glass-filled polyamide 6 is 20-25% plus about 5-10% ATO (see next) as synergist. Somewhat lower levels may suffice in non-glass-filled

polyamide 66. Somewhat higher levels are required, typically 25-35% Dechlorane Plus[®], in glass-reinforced polyamide 6 or 66. However, in reinforced polyamide 66, no ATO need be used, and in reinforced polyamide 6, about 2% ATO suffices [103], with smoke advantages. The synergism between Dechlorane Plus[®] and ATO in Nylon 6.6 was studied by Starnes [104]. If extremely low smoke is needed, it is preferable to substitute ATO with some other metal oxides, in particular iron oxide if the colour is not objectionable [105]. Combinations of Dechlorane Plus[®] with several other metal oxides, insoluble metal salts and polybrominated additives are reported to allow lower loadings [106]. If a CTI is crucial, adding zinc borate, zinc oxide and/or a zinc stannate borate mixture is helpful and these can be expected to also lower smoke [107, 108].

In filled polyamides, melamine cyanurate in combination with magnesium hydroxide may be found useful as a flame-retardant system with low smoke [109]. A melamine cyanurate variant, Ciba's MC-XL[®], which is said to have improved processability and to give less toxic and visible smoke, has been introduced for use in polyamides [110].

A DSM study of melamine polyphosphate in polyamide 66 confirmed the expectation of a large reduction in opacity and corrosivity of the smoke, with the polyphosphate additive compared to a halogenated additive [111, 112].

6.9 Smoke Considerations in Polyolefins

The aliphatic polyolefins tend to be quite flammable, but give rather low visibility smoke. As with other polymers, smoke is generally increased with halogen-antimony flame retardant systems, but some less so than with others.

Dechlorane Plus, discussed previously in connection with its largest use in Nylons, is still used substantially (its original use) in polyolefins, especially where low smoke is needed. A low-smoke system for use in ethylene-propylene-diene terpolymer (EPDM) as described by Markezich [113] contains 38.2% EPDM, 13.9% Dechlorane Plus[®], 5.1% ATO, 8.4% polyethylene, 9.1% 'others' (ZnO, stabiliser, wax, coupling agent, peroxide), 25.3% talc (zinc stearate-coated) and 0.05 iron compound (smoke suppressant). This system gave below one-half of the smoke density of the same formulation with decabromodiphenyl oxide instead of Dechlorane Plus[®]. This advantage may be explained by a mode of action of Dechlorane Plus[®] involving formation of char instead of smoke, in addition to providing flame inhibition, whereas brominated additives by contrast mainly cause flame inhibition with soot formation in the flame and give little char.

Chlorinated higher paraffins, such as 70% Cl content product made from C₁₄ chains and higher paraffins, may be used as an alternative to Dechlorane Plus[®]. Antimony

trioxide is typically used as a synergist at about one-quarter to one-third the level of the chloroparaffins. To avoid skin irritation from antimony trioxide, a concentrate in rubber or chloroparaffin may be used. The use of ATO generally increases smoke, and replacing part of the ATO by zinc borate to reduce smoke (and often to reduce cost) is a common practice.

Halogen-free phosphorus-based flame retardant systems for polyolefins tend to give little smoke. Many such systems are based on APP plus a char-former such as tris(hydroxyethyl)cyanurate (THEIC) or a less hydrophilic polymer made from THEIC. Typical APP-char-forming mixtures are Clariant's Exolit® AP 750 or AP 751 (preferred for talc or glass-reinforced polypropylene). Typical levels of addition are in the 25-30% range to reach V0 in polyolefins. The amount of smoke released is much less than that obtained with the halogen-antimony systems. A new APP with improved char-forming synergist, claimed to give very low smoke, has been introduced by Chemische Fabrik Budenheim and Budenheim Ibérica as Budit® 3167 [114].

Decabromodiphenyl ether plus ATO is often used to flame retard polyolefins and other hydrocarbon polymers such as natural rubber or EPDM, but tends to increase smoke. It has the advantage of low cost. Ethylenebis(tetrabromophthalimide) (Albemarle BT-93) is more expensive, but has better light and heat stability, less blooming tendency and sometimes less smoke.

The addition of a natural or synthetic zeolite in the 2-8% range is shown to reduce smoke as well as flame retard in a polyolefin containing a polybrominated additive and antimony trioxide [115].

6.10 Antimony Trihydrates and Magnesium Hydroxides in Elastomers: Low Smoke Formulations

Low smoke can almost always be achieved by high loadings of ATH or magnesium hydroxide(s) (MDH). Elastomers can tolerate ATH or MDH loadings of 60% or even higher without loss of useful properties, although hardness is obviously increased. ATH is substantially less costly than MDH, but limits processing temperatures to below about 200-220 °C. A combination of roughly equal amounts of ATH and MDH will often be found more effective in flame retardancy than either one alone, and a similar smoke benefit is possible but lacks published data. This apparent 'synergism' may simply be the result of the endothermic water release occurring over a wider temperature range.

ATH or MDH are often used with about 10% zinc borate. A low smoke formulation in EPDM with an oxygen index of 36 is given in **Table 6.6**.

Table 6.6 Low smoke EPDM formulation	
Component	Parts (by weight)
EPDM	100
Magnesium hydroxide	145
Zinc borate	10
DDPH (peroxide curing agent)	6
Triallyl cyanurate (crosslinker)	1
Wax	3

In a low-smoke formula, it is advantageous to avoid or minimise carbon black and petroleum oil, and to achieve a tight cure. Dispersion of the ingredients is important. Adding 1 phr of stearic acid helps dispersion and the oxygen index was raised from 24.5 to 34. Smoke data was not given in this case.

Calcium carbonate is also a useful and cost-saving additive in non halogen formulations where it acts mainly as a diluent. It is sometimes antagonistic in halogen-based systems. Favourable smoke suppression results are often seen, and, as hitherto mentioned, calcium carbonate can act as a hydrogen halide scavenger.

Ethylene acrylic elastomers can be flame retarded by high levels of ATH, and give unusually low smoke density as well as retain useful mechanical properties.

Polychloroprene (such as DuPont’s Neoprene) contains about 40% chlorine. Its main uses are in applications requiring high fire performance such as conveyer belts, mass transit vehicle interiors, electrical insulation and cable jackets [116] and detention centre upholstery . ATH or combinations of ATH and zinc borate help reduce smoke. A typical formulation [117] for polychloroprene is shown in **Table 6.7**.

If the formulation needs to be low enough in smoke, as now required, e.g., in some jurisdictions for mine conveyer belts, the ATO should be lowered from the level shown in **Table 6.7** and the zinc borate and/or ATH should be increased.

6.11 Smoke Considerations in Unsaturated Polyester Resins

Because of low cost and ease of fabrication, the most common unsaturated resin is a styrene-containing unsaturated polyester. Once they are ignited, unsaturated polyesters burn with copious production of black smoke, mainly because of the styrene units serving as crosslinks in the structure. The largest uses for unsaturated polyester resins where flame

Table 6.7 A flame-retardant polychloroprene formulation

Component	Parts (by weight)
Polychloroprene	75
Low M_w polychloroprene	25
Antimony trioxide	15
Zinc borate	10
ATH	30
Magnesium oxide	4
Hard clay	20
Carbon black	5
Ethylene thiourea (vulcanising agent)	0.5
N,N'-diphenyl- <i>p</i> -phenylenediamine	2

retardancy is required are ducts and other equipment in chemical plants and paper mills. They are also used in public transportation, aircraft parts, motor covers, belt guards, water-cooling towers and boats. Most of these products are fibreglass-reinforced. Because of very large applications where flame retardancy is not required, such as underground pipe, mine bolts and marine applications, the percentage of flame-retardant polyester resins relative to the total of all unsaturated polyester resins is perhaps less than 2% according to one market research study [118]. In low-cost formulations such as those used for bathtubs and shower stalls, ATH, gypsum and calcium carbonate at high loadings serve to provide both improved fire performance and low smoke.

The usual tests in the United States for unsaturated polyester and other composites used in construction are the ASTM E84 test [3] (a 25 foot tunnel described earlier that assesses flame spread and smoke release as indices and is required in many codes, the ASTM E162 radiant panel [119] (another flame spread test), the ASTM E662 test [65] (originally the National Bureau of Standards (NBS) smoke chamber) and the ASTM E1354 [120] (rate of heat release cone calorimeter, which gives rate of heat release, total heat release, and smoke formation). Fire and smoke tests are covered from an international viewpoint in a book by Troitzsch [121].

A statistical overview of the ASTM E84 test [3] as applied to glass-reinforced polyester laminates was presented by Stevens [122]. It was found that not only the flame spread index (FSI) but also the smoke developed index (SDI) greatly increased with panel thickness. Stevens also found that the cone calorimeter could be used to predict SDI within the range of materials he tested.

An excellent overview of the behaviour of glass-filled unsaturated polyester resins in the ASTM E84 tests, ASTM E662 smoke test [65] and various European and international tests, which compared brominated resin, non halogen resin with a high ATH loading, and a combination of bromine with ATH has been presented by Stevens [123]. Substantial differences between the tests were found. The non halogen resin with high ATH was the only formulation in this study to meet the recent European single burning item test.

At present, some flame retarded halogenated polyester resins are made based on tetrabromophthalic anhydride. The flame spread for these resins is substantially reduced compared to nonhalogenated resins, but the smoke is substantially higher for the halogenated resins [124]. ATO is usually added to those resins as a synergist, and most probably increases smoke.

ATO can be replaced, partially or completely, by zinc borate, and this usually reduces smoke, especially with polyester resins containing aliphatic halogens, such as the chlorendates used in Ashland's Hetron® resins, or with vinyl resins based on tetrabromobisphenol A [125]. Zinc stannate or zinc hydrostannate (Joseph Storey and Co. Ltd., or William Blythe Ltd., UK, Marshall Additive Technologies, US) have been shown to be able to replace antimony trioxide in unsaturated polyesters [126, 127] with reduction in smoke density [128]. With significantly higher prices of antimony trioxide, the use of zinc stannates (which are usually more expensive) may become more affordable.

Newer vinyl ester resins are available with a lower content of styrene, below 40%, driven by air pollution regulations that limit the emission of styrene vapours during fabrication. These also afford less smoke upon burning. One example is AOC Vipel® K022, which provides low styrene release during fabrication, an ASTM E84 flame spread index of 20 and an SDI below 450, with favourable corrosion resistance and mechanical strength. A significant use is in large entertainment structures in theme parks.

The most general way to lower smoke from unsaturated polyesters and related thermosets is to use substantial addition of ATH, which upon fire exposure releases water, dilutes the pyrolysis products that are burning and reduces flame velocity. Moreover, the ATH replaces combustible polymers with noncombustible inorganic materials, and, as the polymer is exposed to flame, the ATH, even after the water has been released, provides a noncombustible radiant-heat-reflective barrier and enhances the char. Comparison of ATH, silica [129] or a clay [130] at equivalent loadings in an unsaturated polyester showed a clear flame retardancy advantage for ATH and especially notable smoke reduction. Some surface-treated versions of ATH show improved fire and smoke properties [131–134]. Some precipitated and surface-coated ATH in Albemarle's Martinal® OL series have improved processing characteristics and

improved thermal stability [135]. Flame retarded formulations in polyester and vinyl ester resins have been found where excessive viscosity at high loadings of ATH can be achieved by using a specific size distribution (particularly bimodal). The addition of a few percent of a low viscosity flame-retardant liquid such as triethyl phosphate can also reduce viscosity of highly filled systems.

Very high loadings of ATH may reach an intractable viscosity, although larger particle size or use of a bimodal particle size distribution can help. Composites containing high levels of ATH such as 60 phr ATH show low smoke and may show initially adequate physical properties, but fatigue tests may show much shortening of the lifetime in which adequate physical properties are maintained [136]. A modified polyester resin developed by Curry (AOC) allows 150 phr ATH to be tolerated instead of the usual 60 phr, and these ATH-filled resins, particularly a halogen-free version, are very low in smoke and low in toxic combustion products (mainly CO) [137].

A study at Huber Corp. [138] using cone calorimetry in a neopentyl glycol-isophthalic bulk moulding compound compared ATH or ATH plus calcium carbonate with decabromodiphenyl ether plus ATO. The study found that decabromodiphenyl ether plus ATO gave a favourable effect on peak rate of heat release and effective heat of combustion, but no benefit in the time to peak rate or time to ignition. Moreover, adverse effects on smoke and CO yield were demonstrated, as would be expected from the mainly vapour-phase action of this additive combination. Further adding ATH to the decabromodiphenyl ether-ATO formulation gave a linear favourable increase for all parameters, except that maximum smoke (D_m) was not improved. On the other hand, ATH added as the sole flame retardant gave equal or better favourable effects on all parameters, except on the effective heat of combustion.

6.11.1 Low Smoke Polyester Resins by Replacement of Styrene

With ordinary unsaturated polyester resins containing styrene, smoke can be reduced as discussed previously by use of ATH as a flame retardant, but smoke often remains unacceptably high by some standards. When very low smoke is required, methyl methacrylate (MMA) can be used in place of styrene, usually only as a partial replacement. MMA usually slows down the cure.

Another approach to low styrene unsaturated polyester resins uses dicyclopentadiene as part of the crosslinking. A representative resin of this type is AOC Firepel® 133. Besides helping heat resistance, this monomer (probably because of increased crosslink density) permits lower levels of flame retardants than needed with high styrene

resins [139]. Some examples of Firepel® 133 formulations use 150 phr ATH and achieve very good flame retardancy and smoke.

6.11.2 Low Smoke Unsaturated Acrylate Oligourethane Resins with Alumina Trihydrate

The Modar® oligourethane unsaturated resins are different enough from other polyester resins to be called modified acrylic resins. They originated at ICI [140–142] and were acquired by Ashland in 1993. The Modar® resins, characterised by low viscosity and fast cure, are crosslinked with MMA or its blends with styrene. They have very favourable smoke properties. The Modar resins can be flame retarded by ATH at 100–160 phr to achieve good fire performance with very low smoke, for uses such as conduits, cable trays, switch boxes, architectural panels, fascia and trim (particularly in theme parks), doors, ducting, interior marine decking, and paneling for buses and passenger trains. They can be used for pultruded parts, which often have requirements for flame retardancy. Hernangil and co-workers [143] gives examples of optimised halogen-containing and halogen-free low viscosity formulations using Modar® 835 S resin.

At 160 phr ATH in Modar, a Class I in the ASTM E84 tunnel test [3] can be achieved and good performance is shown in the NFPA 286 room-corner test [144]. To assure maximum improved fire performance, an additional step, post-curing, is recommended. For exterior sheathing, it has been claimed that these systems can be formulated to pass the ASTM E119 [145] time-temperature fire-resistance test and ASTM E136 [146] noncombustibility tests.

6.11.3 Char-forming Low-smoke Additive for Unsaturated Polyester Resin Systems

Chemtura (previously Great Lakes Chemical) has offered for some years a char-producing organophosphate compound NH-1197 (CN-1197) for use in unsaturated polyester resins. NH-1197 is a bicyclic phosphate derived from pentaerythritol. This additive has found use particularly where low smoke is a requirement [147].

6.12 Inherently Low Smoke Phenolic Resins

Phenolic laminates, even without a flame retardant such as ATH, are difficult to ignite. They show very low flame spread rate, low heat release rate, and low smoke.

Typical values [148] for a paint-coated phenolic resin with 35% glass are an ASTM E162 [119] radiant panel index of less than 1 (far below the typical requirements, which are usually at around 25), ASTM E662 [65] specific optical smoke density of 0.6 in 1.5 minutes and a maximum density of smoke of 51 in 14 minutes. The NBS smoke chamber gas composition was found to be 100 ppm CO, 80 ppm SO₂ and zero HF, NO₂, HCl and hydrogen cyanide. The ASTM E84 [149] FDI was 5 (far below the Class A level of 25), and the smoke density was 10. The autoignition temperature was 475 °C by the ASTM D1929 test [150], and the oxygen index was above 55.

For very stringent fire- and smoke-avoidance requirements such as in Disneyland-type theme parks, a comparison of several thermoset laminates revealed that by far the best performance was shown by a phenolic glass laminate with 30% ATH [151]. This type of laminate is based on proprietary resol chemistry (control of water release) and shows high elongation, thus allowing it to overcome the brittleness usually found with phenolics. The laminate is sufficiently tough to function for helicopter landings. Using vacuum infusion, these laminates can be produced more rapidly than with the usual prepreg methods. In the ASTM E84 tunnel [3], an excellent flame spread index of 5 and a smoke developed index of zero can be reached. Phenolic composites have been widely used in Europe to meet tight flame and smoke requirements, e.g., in the London Underground, passenger ships and trains, buses, offshore oil platforms and theme parks [152]. Mould corrosion by the usually acid-curing catalyst can be avoided by using composite vinyl ester moulds, stainless steel or plated steel. It is very important that water release inherent in the curing process is sufficiently complete so that further water vapour evolution will not cause breakage of the thermoset when exposed to fire.

Reinforced phenolic resins meeting very demanding flame, smoke and toxic gas requirements such as the military standard MIL-STD-2031 [153] were developed for military applications, such as in submarines [154]. A patent application [155] shows the use of ATH to further improve fire behaviour and also the addition of a silicone for improved flexibility and impact resistance.

6.13 Low Smoke Epoxy Resins

Zinc borate is an effective smoke suppressant in halogen-flame-retarded epoxy resins, depending on the halogen source [156]. In Epon 828 with Oxychem's Dechlorane Plus (a polychlorinated polycyclic hydrocarbon), replacing ATO with zinc borate can give a 40% decrease in smoke. However, such smoke reduction is not observed when decabromodiphenyl oxide is the halogen source.

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7

Regulations, Codes and Standards Associated with Smoke

7.1 Background: Regulations, Codes and Standards

North American fire safety requirements, including smoke requirements, are based on an assortment of regulations, codes and standards and are not, and probably will never be, uniform. It is important, therefore, to start by defining the terms to be used and then discussing the various organisations involved:

1. Regulations are documents with the force of law that list general objectives and act as a framework for more detailed requirements. One example could be a national law requiring sprinkler protection of a certain type of occupancy.
2. Codes are documents connected with regulations, but which comprise more specific requirements and are valid for particular cases such as hospitals or schools. If they also offer practical solutions, they may be called codes of practice. An example associated with the national law above would be a building code detailing the layout of the sprinklers in each type of building.
3. Standards are documents referred to either in regulations or in codes that put forward special techniques to quantify results. Typical examples of standards are test methods and specifications. Examples associated with the national law above would be specifications describing sprinkler construction test methods assessing their effectiveness.
4. Specifications are documents that describe requirements for a particular material or product for use by a specific purchaser. These documents are often part of an open solicitation or of an agreement and can be between two parties or a generic request. An example associated with the scheme above could involve requirements for the type of sprinkler pipe and/or for the discharge density.
5. Guides are documents that explain the concepts associated with particular issues, such as test methods or properties. An associated example would be a guide explaining why sprinklers help in fires and what the effect of discharge density could be.

These definitions are so generic that they apply worldwide. In the European Union (EU), e.g., the way it works is that the European Commission issues the Construction Products Directive (CPD). Each of the individual member states (i.e., each country) is required to comply with European Commission Directives. The CPD contains 'essential requirements', including one associated with fire safety (and smoke is a component of fire safety). The government in each country issues regulations, adopts some requirements and incorporates the requirements, based on the CPD, into their own local codes. The codes can then reference national or international standards. European codes and standards, but not US ones, are issued by organisations associated with the governments of the individual countries.

In the United States, the federal government is entitled to regulate the fire safety of consumer products and of transportation vehicles, but rarely does. In fact, the fire safety of very few consumer products is being regulated via the federal government [with the Consumer Product Safety Commission (CPSC)], being the regulatory authority for consumer products). CPSC is governed by a set of commissioners appointed by the US president, with congressional approval. The only products CPSC regulates the fire safety of are the following: fabrics for wearing apparel, children's sleepwear, carpets and rugs, mattress sets and toys. In none of these cases is smoke regulated. CPSC has published a notice of its intent to regulate upholstered furniture (more details later), but smoke is also not included. By law, CPSC is required to regulate all consumer products that contain 'flammable fabrics' and is not permitted to regulate cigarettes. CPSC also regulates the use of hazardous materials, including flammable liquids and solids. The fire safety of mine conveyor belts is regulated by the Mine Safety and Health Administration (MSHA), subsidiary to the Department of Labor (responsible for the safety of miners). MSHA has instituted some requirements, in accordance with a 1969 Act, which then became the 1977 Federal Mine Safety and Health Act. There are, as of the end of 2009, no smoke requirements for mine conveyor belts, although that issue is under discussion. Various agencies are required to regulate the fire safety of transportation vehicles, and such regulations often contain smoke requirements (in the case of aircraft, ships and passenger trains, with voluntary guidelines for buses and underground rail). All other materials and products are regulated via the adoption by a state or local government of one of various codes (issued by private organisations) or (rarely) by their issuance of their own special regulations.

Canada has a system that is intermediate between the EU regulatory system (based on directives and/or regulations from the European Commission) and the US system (with codes and standards both developed by private companies and adopted, or not, by the various state and local governments). The National Building Code of Canada can be different from the building codes in the various provinces, and Canadian standards are issued by private companies.

In the United States, three major organisations develop codes: International Code Council (ICC), National Fire Protection Association (NFPA) and International Association of Plumbing and Mechanical Officials (IAPMO). ICC develops a full family of codes, including the following: International Building Code (IBC), International Fire Code (IFC), International Mechanical Code (IMC), International Wildland Urban Interface Code, International Residential Code (IRC), International Existing Building Code (IEBC) and the International Plumbing Code, which have been adopted widely throughout the country. NFPA also develops a full family of codes, with equivalent codes to most ICC codes. However, two NFPA codes (National Electrical Code (NEC) or NFPA 70 [1], and Life Safety Code, or NFPA 101 [2]) are unique and have no ICC equivalent. NFPA is also one of the premier developers of fire safety standards, including a few key ones: NFPA 90A (air-conditioning standard [3]), NFPA 13 (sprinkler standard [4]) and NFPA 130 (rail standard [5]). IAPMO develops two codes: Uniform Mechanical Code (UMC) and Uniform Plumbing Code (UPC). There is an agreement between NFPA and IAPMO that NFPA incorporates the UMC and UPC among its family of codes. Fire tests (standards) are developed primarily by the ASTM International (formerly American Society for Testing and Materials), and by NFPA, although FM Global (formerly Factory Mutual) and Underwriters Laboratories (UL) have also developed some widely used tests.

The individual states in America have always been entitled to issue their own regulation, as long as there is no contradiction with federal legislation, which is normally nonexistent. Thus, California has long had regulation for the fire performance of upholstered furniture and mattresses, based on requirements developed at the California Bureau of Home Furnishings and Thermal Insulation (CBHF) and this has, on occasion, been emulated by some other states.

7.2 Regulations

7.2.1 How Regulation for Fire Safety Works in the United States

As explained previously, the US system works primarily on the basis of ‘volunteers’ working within private codes and standards organisations to both develop new standards and also revise existing standards, which are then incorporated into new codes (or into revisions of existing codes). These people are called ‘volunteers’ because their participation in the process is neither funded by the codes and standards organisations within which they are active nor by the US government (unless they are government employees). Each code development organisation has a unique consensus process by which public proposals and comments are processed into new or revised documents. A successful process always consists of two stages before new documents or substantial revisions are approved.

The process of adoption of codes and standards is tightly controlled by each organisation so that no unfair advantage is provided to any individual interest and so that all concerns are addressed. For example, the ICC requires that 'Final Action' on all code changes be completed at a public meeting where the voting is restricted to public officials. In the case of organisations like ASTM International and the NFPA, voting membership in committees is strictly balanced by having representatives from producers or manufacturers and representatives from any other interests or stakeholders.

In some cases, standards that have been developed by trade associations, instead of having been developed by standards-making bodies, are included within codes. However, such types of standards have been frowned upon in recent years, and it is rare that they are newly included. They are, however, often 'grandfathered' in (i.e., allowed to remain because they have been in the relevant code or in its predecessor for years). Such standards must still comply with some consensus rules, and many of them tend to be eventually replaced by standards issued by the major standards-development organisations.

Fire safety of a variety of transportation vehicles (but not all) are covered by other federal government agencies mostly subsidiary to the Department of Transportation, including National Highway Traffic Safety Administration (NHTSA) for highway vehicles, Federal Aviation Administration (FAA) for aircraft, Federal Railroad Administration (FRA) for interstate and intercity trains), and United States Coast Guard (USCG) for ships. The Federal Transit Administration (FTA) has jurisdiction over US buses and underground fixed guideway vehicles, but has only issued old-fashioned guidelines and no requirements.

State and local authorities having jurisdiction are not permitted to issue regulation that conflicts with federal regulation, because of the issue of 'preemption'. In other words, a state or local authority is not allowed to require that a particular product be less safe than is required by the federal regulations. On the other hand, it is normally acceptable for a state or local jurisdiction to impose requirements that exceed those issued by the federal government. Therefore, as the information previously shows that there is little federal fire safety regulation, state and local authorities have wide opportunities for action.

7.2.2 Federal Regulations

In order for the federal (national) government to introduce a new regulatory requirement, there must be a 'demonstrated need'. After the need has been proven to the satisfaction of the government agency about to issue the regulation, a notice of proposed rulemaking (NPRM), is published in the Federal Register. This is required any time a regulatory agency of the United States Federal Government wishes to add, remove or change a rule (or regulation) as part of the rulemaking process.

The NPRM procedure is defined by the Administrative Procedure Act and was created by the US Congress to force agencies to listen to comments and concerns of those affected by the proposed regulation. The agencies mentioned previously (CPSC, FAA, FRA, NHTSA, USCG and MSHA) are all subject to these procedures, as is the Environmental Protection Agency. The NPRM is published in the Federal Register and typically gives 60 days for public comment from any interested party, and an additional 30 days for reply comments. Original comments may still be filed in the reply comments 'window'. In fact, complex regulation often winds up being preceded by an Advance Notice of Proposed Rulemaking. Each notice includes:

- A statement of the time, place and nature of the proposed rulemaking proceeding
- A reference to the authority under which it is issued
- A description of the subjects and issues involved or the substance and terms of the proposed regulation
- A statement of the time within which written comments must be submitted
- A statement of how and to what extent interested persons may participate in the proceeding

At least in theory, the relevant authority having jurisdiction must start by making a cost-benefit analysis that investigates the history of losses and assesses the benefits to result from the regulation. In fact, to some extent at least, local and state authorities must go through a similar process.

This complex set of rules, which can be derailed at many stages of the process, explains why federal regulations are rare in the area of fire safety, where the 'push' to introduce regulation is rarely front page news. Typically, changes in regulations follow flashy headlines, associated with a specific large fire loss.

7.2.3 State Regulations

It is rare for individual states to issue specific regulations associated with fire safety, but some states have done so. In particular, the CBHF issued a number of Technical Bulletins addressing various fire issues for furnishings. Some other states have also had regulatory activity, but none has been as proactive as California. In recent years, many US states have issued regulations governing the sale of so-called 'fire-safe cigarettes', namely cigarettes with a lower ignition propensity. The most typical (and important) way for individual states to apply fire safety regulations is by adoption of codes. Almost all US states have adopted a building code (often the IBC) and an electrical code (almost invariably the NEC) and often also a fire code (which could

be the IFC or NFPA 1 [6]) and the Life Safety Code (NFPA 101 [2]). US health care institutions, including all hospitals, follow the requirements of a private not-for-profit organisation called the Joint Commission, formerly the Joint Commission on Accreditation of Healthcare Organizations, which operates voluntary accreditation programs for hospitals and other health care organisations, and requires compliance with NFPA 101.

In the 1980s, New York State incorporated into its code (New York State Uniform Fire Prevention and Building Code), Article 15, Part 1120, a requirement for ‘Combustion Toxicity Testing’ [7], based on a smoke toxicity test developed at the University of Pittsburgh [8]. The test method was never standardised by either ASTM or NFPA because of severe concerns about its scientific validity [9–12]. The New York State regulation did not include pass/fail criteria and has since been rescinded.

7.2.4 Local Regulations

It is even less common in the United States for local jurisdictions to adopt specific regulations that differ from the federal (or state) requirements. An unusual requirement was put in place by the Department of Buildings in the city of New York for smoke toxicity testing, also based on the University of Pittsburgh test. This requirement, as opposed to the one in New York State, did have pass/fail criteria.

It is not unusual for cities, especially the larger ones such as Chicago or Los Angeles, to adopt a citywide code or set of codes. This can take place in different ways. The city of Los Angeles (USA), for example, has generally adopted its own building and fire codes, which are modifications of the applicable California code. On the other hand, the city of Chicago (USA), has issued its own independent building code. It is also not unusual for specific events or personalities to influence local bans on certain products. One example is a requirement in Chicago that all cables in plenums must be enclosed in metal raceways, whereas most codes and standards (including the NEC) require that cables be listed and fire tested for plenum use.

7.2.5 Regulations of Specific Items

The key items regulated are components in vehicles and items covered under the flammable fabrics act (but none of these are covered by smoke requirements).

NFPA has developed statistics that show average annual US vehicular losses (2002–2005): 306,800 fires, with 520 civilian fire fatalities, 1,640 civilian fire injuries and \$1.3 billion in total fire losses [13]. In structures over the same period, the numbers are: 388,250 fires, with 3,190 civilian fire fatalities, 13,500 civilian fire injuries, and \$6.3 billion in total fire losses, based on NFPA statistics. In fact, the data shows the number of

vehicular fires is over three-quarters of the number of structure fires. The heat release rate obtained from a burning automobile has been shown to be in the range of 1.5 to 8.0 MW, roughly the same order as heat released from a fully involved room in a home [14]. Unfortunately, most fires, fire fatalities and fire injuries occur in passenger road vehicles, especially cars, where there is no smoke regulation.

7.2.5.1 Aircraft

The FAA has developed a series of requirements for many of the materials and products contained in airplanes. Its regulations, contained in Federal Aviation Regulation, FAR 25.853 [15], cover four categories of aircraft: transport category airplanes (FAR Part 25) [16], small airplanes (FAR Part 23) [17], rotorcraft of all categories (FAR Parts 27 and 29) [18, 19] and engines and propellers (FAR Part 33 and 35) [20, 21]. All of the relevant fire tests are contained in the *Aircraft Materials Fire Test Handbook* [22], for which periodic updates are issued. The FAA has also published a notice [23] that advises the public that the FAA considers the material flammability tests described in the latest version of that document to be the preferred acceptable test methods for showing compliance with the relevant regulations. The required test methods (nonpropulsion) are described in Chapters 1 through 10 and Chapter 15, and they are acceptable methods for showing compliance with, or providing an equivalent level of safety to, the required regulations as outlined in the chapter. Although these test methods cannot - and do not - supersede any method specified by and described in the regulations, they represent an acceptable means of compliance with the relevant regulation and, in some cases, a preferred option over the specified method. However, the FAA will consider other alternative methods that demonstrate an equivalent level of safety on a case-by-case basis along with the necessary supportive data. Chapters 11 through 14 contain required test methods (propulsion), and they remain as the name indicates. The test methods described in Chapters 18 through 22 are nonrequired test methods; they are included in the Handbook for use as test methods applications where there currently are no requirements, and no process is required for their modification.

The only smoke test contained in the *Aircraft Materials Fire Test Handbook* is in Chapter 6. The test is based on the National Bureau of Standards (NBS), now the National Institute of Standards and Technology (NIST), smoke density chamber, which has also been standardised as ASTM E662 [24]. The test exposes a vertical test specimen approximately 75 mm × 75 mm to an initial test radiant heat flux of 25 kW/m² from a radiant heat burner for four minutes in the presence of an open flame pilot burner. The test applies to the same materials as the heat release rate test, namely the vast majority of nonmetallic materials contained inside the aircraft, typically vertical panels (which are often laminated and have multiple layers), ceiling and wall linings, luggage compartment racks, carts and so on. The test does not apply to foams and

fabrics for seats and draperies, windows, floor coverings (carpets), electrical wiring, insulation or firewalls. The acceptance criterion is an average maximum specific optical density of smoke (D_s) that does not exceed 200 (no units).

The fire safety requirements were obtained as a result of full-scale aircraft tests conducted by the FAA and by airframe manufacturers, which showed the key importance of heat release criteria for proper fire safety. The criteria were based on the concept of ensuring that, in a survivable postcrash scenario, aircraft evacuation can be completed in five minutes. Moreover, fires should not happen or should self-extinguish in hidden areas. The FAA was asked by the aircraft industry to add the smoke obscuration test, because that had been a test required by manufacturers in the past. The FAA does not have any regulatory smoke toxicity or material composition tests (because the research conducted showed that they were not needed), but some aircraft manufacturers and airlines do have such requirements. They are based on the use of Draeger tubes to assess the concentrations of individual toxic gases inside the smoke chamber. The concentration of each one of the gases assessed is divided by an assumed toxic potency for that gas, the ratios are then added and the result is compared with a predetermined pass/fail criterion. These values are almost completely arbitrary. The major standards are ATS 1000.001: Fire-Smoke-Toxicity Test Specification, Technical Specification (Airbus) [25] and BSS 7239 (Boeing) [26].

7.2.5.2 Ships

The USCG regulates all ships that moor in US ports (both on the exterior coasts and on rivers or lakes). The US is a signatory to the International Convention for the Safety of Life at Sea (SOLAS) and the USCG will enforce the corresponding regulations, which are issued by the International Maritime Organization (IMO).

All ships engaging in international trade and flying the flag of a country who signed the SOLAS convention must comply with the regulations of IMO detailed in the SOLAS book, periodically amended by 'Resolutions' of the IMO committees, and ratified by the signatory states. Details of fire and smoke issues are given in the IMO Fire Test Procedures Code (FTP), also reissued regularly. Some special vessels are regulated separately: high speed craft (never too far from shore) is regulated by the IMO High Speed Craft Code (HSC). This code applies to small vessels that operate at a minimum speed, carry a maximum number of passengers and make no overnight trips. The US is fairly unique in that many ships never leave inland waters, or simply hug coastal areas and often choose not to be covered by SOLAS. The USCG regulates every ship that uses US ports. The USCG thus enforces SOLAS or HSC requirements for ships that need to meet those rules, but it also has its own requirements for ships that sail in US waters only. Such ships must comply with the requirements laid out in US Federal Government - Coast Guard: Title 46, Shipping, Code of Federal

Regulations, Parts 1-199 [27], and in a Navigation and Vessel Inspection Circular (USCG Guide to Structural Fire Protection) [28]. With the instructions from the US federal government that standards should, whenever possible, be delegated to private organisations, the Coast Guard and NFPA agreed to develop a consensus code, NFPA 301, Code for Safety to Life from Fire on Merchant Vessels [29], for ships that do not sail in international waters. NFPA 301 references both SOLAS and HSC for the corresponding types of ships. The USCG has a policy of permitting ships to comply with NFPA 301 instead of its requirements, but this code is rarely used because it contains very onerous sprinkler requirements that exceed those of the USCG.

The IMO regulations, via the FTP code, cover reaction-to-fire requirements for cables (electric wires and cables), carpeting (floor coverings), deck coverings, fabrics, interior finish, mattresses and bedding, piping and upholstered furniture. They also cover fire resistance requirements for bulkheads, dampers, doors, windows and other divisions. For most applications, the building element or partition requires a specific fire resistance rating only, with no mention of smoke, but some applications require an A-60 Class, which means that the partition must prevent the passage of smoke, as well as flame, for one hour.

The fire safety philosophy used by SOLAS for materials and products in ships is based on the maximum use of noncombustible materials for shipbuilding (often described as ‘steel or equivalent’) while also severely limiting the amounts of combustible materials allowed as furnishings and contents. Smoke requirements apply to a number of products, and those products must be tested to International Organization for Standardization, ISO 5659-2 [30], equivalent to ASTM E1995 [31] or NFPA 270 [32], which is similar to the traditional smoke chamber except that the radiant heater is a conical heater, the specimen is exposed horizontally and the initial test heat flux is at 25 kW/m² (flaming and nonflaming) and at 50 kW/m² (nonflaming only). The smoke acceptance criterion is an average maximum specific optical D_s (no units) that does not exceed, in any condition:

1. 200, for materials used as surface of bulkheads, linings or ceilings
2. 400, for materials used as primary deck coverings
3. 500, for materials used as floor coverings
4. 400, for materials used as plastic pipes or electric cables

In every case, a set of seven gas concentrations cannot be exceeded: 1450 ppm carbon monoxide, 600 ppm (hydrogen chloride, hydrogen bromide, hydrogen fluoride), 140 ppm (hydrogen cyanide), 350 ppm (NO_x) and 120 ppm (SO₂).

The HSC code has deviated considerably from this concept by developing heat release and smoke release criteria for ‘fire restrictive materials’, which are combustible but have excellent fire performance, as assessed by a very severe room-corner heat release fire test, ISO 9705 [33], where the gas burner is initially operated at 100 kW and then raised to 300 kW. The rationale for this change in philosophy has been the fact that composites and other materials with excellent fire performance are much lighter than steel and can permit the ships to travel much faster.

The USCG regulations include reaction-to-fire requirements for the same products as the FTP code, but the tests required are usually more realistic and/or more severe.

The US Navy also has its own set of requirements for military ships and for submarines. It has, for some time now, been pursuing a similar type of approach to the HSC Code approach [34]. In this case, there is an additional advantage in moving away from steel products: the alternative materials are much less detectable by enemy radar.

NFPA 301 has much more restrictive reaction-to-fire test requirements for furnishings and contents than SOLAS. It also includes smoke requirements for insulation (as well as pipe and duct insulation and other coverings) in concealed spaces. The requirements are a flame spread index (FSI) of 25 and a smoke developed index (SDI) of 50 when tested in the Steiner tunnel test, ASTM E84 [35]. Electric and optical fibre cables are also required to be tested, with the minimum requirements being a vertical cable tray test (UL 1685 [36], CSA mode [a name which is based on the fact that the test was originally developed by the Canadian Standards Association]) or a plenum test (NFPA 262 [37]), both of which also require smoke testing. There are no smoke toxicity requirements in NFPA 301. However, the latest edition of NFPA 301 (2008) [29] permits the omission of many, if not most, of the reaction-to-fire requirements if the vessel is sprinklered or has a water-mist system installed. This means that the requirements can be omitted for passenger ships, as all Group I passenger vessels (i.e., those with either more than 3,000 day passengers or more than 300 overnight passengers), Group II passenger vessels (i.e., those with either more than 1,000 and under 3,000 day passengers or more than 150 and under 300 overnight passengers) and all passenger vessels with overnight accommodations for passengers must have a sprinkler or water-mist system to protect ‘all accommodation, service, and storage spaces’. This makes reaction-to-fire requirements for passenger ships mostly optional.

Electrical installations aboard US ships are also voluntarily regulated by a pair of Institute of Electrical and Electronic Engineers (IEEE) standards: IEEE 45 [38] and IEEE 1580 [39], which, in turn, address smoke in cable insulation and jacketing materials by referencing NES 711 [40], a variation of the traditional ASTM E662 smoke chamber [24], and in the cables themselves by referencing UL 1685 [36].

7.2.5.3 Trains and Underground Rail Vehicles

As a result of the 1973 Urban Mass Transportation Administration program to improve fire safety of public transport, *Guidelines for Flammability and Smoke Emission Specifications* for materials used in transportation vehicles were generated [41]. Although these guidelines have developed somewhat over the years, they are still based on the fire testing technology available in the 1970s, but the FRA has made regulations mandatory for trains connecting cities or crossing state lines [42, 43], while the FTA still uses them as guidelines for urban trains (including underground fixed guideway vehicles) and buses. **Table 7.1** shows the most recent FRA rulemaking to that effect. The table is the basis of the regulations for reaction-to-fire of materials and products. The two principal fire tests used are a radiant panel test for flame spread (ASTM E162) [44] and a static smoke obscuration test (ASTM E662 [24]); this test is the key smoke test used. The table contains detailed instructions and pass/fail criteria for all types of materials and products in trains (except for wire and cable products, which were eliminated between the 1999 and 2002 editions). So as to handle fire hazard assessment from a more balanced point of view, FRA now permits approvals to be based on the use of alternative approaches to the prescriptive table, using heat release for hazard assessment, but this approach does not include any smoke requirements. Both ASTM and NFPA have developed standard documents that address the way to do this: ASTM E2061 [45] and NFPA 130 [5]. Both consider critical the reaction-to-fire properties of wire and cable products, and the use of these documents is prevalent whenever a specifier (usually a local transportation authority) wants to exceed FRA regulations or is not bound by them (e.g., outside of the US). ASTM E2061 is a guide on how to assess fire hazard in rail transportation vehicles, which gives detailed instructions and can be followed in two ways: by complying with a version of ‘the table’ or by analysing the fire hazard of the rail car with modern fire modelling technology. NFPA 130 is a standard with broader applicability because it includes the entire rail system, but also has both a version of ‘the table’ and a section on a performance-based approach. **Table 7.2** contains the rail vehicle materials requirements from NFPA 130-2010. This standard also requires that all cables meet flame spread (with a vertical cable tray test, UL 1685 [36], CSA mode, being the minimum acceptable) and smoke obscuration criteria. The standard requires wires and cables to meet either the UL 1685 or the NFPA 262 [37] plenum cable test, both requiring smoke measurements, just like shipboard cables in NFPA 301.

Table 7.1 FRA requirements for passenger rail materials (2002)					
Category	Function of material	Flammability		Smoke emission	
		Test procedure	Performance criteria	Test procedure	Performance criteria
Cushions, Mattresses	All ^{a-h}	ASTM D3675 [46]	$I_s \leq 25$	ASTM E662 [24]	$D_s (1.5) \leq 100$
					$D_s (4.0) \leq 175$
Fabrics	Seat upholstery, mattress ticking and covers, curtains, draperies, wall coverings and window shades ^{a-c, f-h}	14CFR25 Appendix F, Part I (vertical test) [59]	Flame time ≤ 10 s; Burn length ≤ 15 cm.	ASTM E662 [24]	$D_s (4.0) \leq 200$
Other Vehicle Components ^{i-l}	Seat and mattress frames, wall and ceiling panels, seat and toilet shrouds, tray and other tables, partitions, shelves, opaque windscreens, end caps, roof housings and component boxes and covers ^{a, b}	ASTM E162 [44]	$I_s \leq 35$	ASTM E662 [24]	$D_s (1.5) \leq 100$
					$D_s (4.0) \leq 200$
	Flexible cellular foams used in armrests and seat padding ^{a, b, d, f}	ASTM D3675 [46]	$I_s \leq 25$	ASTM E662 [24]	$D_s (1.5) \leq 100$
					$D_s (4.0) \leq 175$
	Thermal and acoustic insulation ^{a, b}	ASTM E162 [44]	$I_s \leq 25$	ASTM E662 [24]	$D_s (4.0) \leq 100$
	Heating, ventilation and air conditioning (HVAC) ducting ^{a, b}	ASTM E162 [44]	$I_s \leq 25$	ASTM E662 [24]	$D_s (4.0) \leq 100$

	Floor covering ^{l, m}	ASTM E648 [47]	CRF ≥ 5 kW/m ²	ASTM E662 [24]	D _s (1.5) ≤ 100
					D _s (4.0) ≤ 200
	Light diffusers, windows and transparent plastic windscreens ^{b, n}	ASTM E162 [44]	I _s ≤ 100	ASTM E662 [24]	D _s (1.5) ≤ 100
					D _s (4.0) ≤ 200
Elastomers ^{a, j, k}	Window gaskets, door nosings, intercar diaphragms, roof mats and seat springs	ASTM C 1166 [48]	Average flame propagation ≤ 10 cm.	ASTM E662 [24]	D _s (1.5) ≤ 100
					D _s (4.0) ≤ 200
Structural Components ^o	Flooring ^p , other ^q	ASTM E119 [57]	Pass		

I_s : Radiant panel index in the ASTM E 162 test method

CRF: Critical radiant flux in the ASTM E 648 test method

CFR: Code of Federal Regulations

^a Materials tested for surface flammability shall not exhibit any flaming running or dripping.

^b The ASTM E662 [24] maximum test limits for smoke emission (specific optical density) shall be measured in either the flaming or nonflaming mode, utilising the mode which generates the most smoke.

^c Testing of a complete seat assembly (including cushions, fabric layers, upholstery) according to ASTM E1537 [49] using the pass/fail criteria of the California Technical Bulletin (CA TB) 133 [50], and testing of a complete mattress assembly (including foam and ticking) according to ASTM E1590 [51] using the pass/fail criteria of CA TB 129 [52] shall be permitted in lieu of the test methods prescribed herein, provided the assembly component units remain unchanged or new (replacement) assembly components possess equivalent fire performance properties to the original components tested. A fire hazard analysis must also be conducted that considers the operating environment within which the seat or mattress assembly will be used in relation to the risk of vandalism, puncture, cutting, or other acts which may expose the individual components of the assemblies to an ignition source. Notes 5, 6, 7, and 8 apply.

^d Testing is performed without upholstery.

^e The surface flammability and smoke emission characteristics shall be demonstrated to be permanent after dynamic testing according to ASTM D3574 [53], Test I2 (Dynamic Fatigue Test by the Roller Shear at Constant Force) or Test I3 (Dynamic Fatigue Test by Constant Force Pounding) both using Procedure B, except that the test samples shall be a minimum of 154 mm by 457 mm by the thickness of the material in its end use configuration, or multiples thereof. If Test I3 is used, the size of the indenter described in paragraph 96.2 shall be modified to accommodate the specified test specimen.

^f The surface flammability and smoke emission characteristics shall be demonstrated to be permanent by washing, if appropriate, according to FED-STD-191A Textile Test Method 5830 [54].

^g The surface flammability and smoke emission characteristics shall be demonstrated to be permanent by dry-cleaning, if appropriate, according to ASTM D2724 [55].

^h Materials that cannot be washed or dry-cleaned shall be so labeled and shall meet the applicable performance criteria after being cleaned as recommended by the manufacturer.

ⁱ Signage is not required to meet any flammability or smoke emission performance criteria specified in this Appendix.

^j Materials used to fabricate miscellaneous, discontinuous small parts (such as knobs, rollers, fasteners, clips, grommets, and small electrical parts) that will not contribute materially to fire growth in end use configuration are exempt from flammability and smoke emission performance requirements, provided that the surface area of any individual small part is less than 100 cm² in end use configuration and an appropriate fire hazard analysis is conducted which addresses the location and quantity of the materials used, and the vulnerability of the materials to ignition and contribution to flame spread.

^k If the surface area of any individual small part is less than 100 cm² in end use configuration, materials used to fabricate such a part may be tested in accordance with ASTM E1354 [56] as an alternative to both (a) the ASTM E162 [44] flammability test procedure, or the appropriate flammability test procedure otherwise specified in the table, and (b) the ASTM E662 [24] smoke generation test procedure. Testing shall be at 50 kW/m² applied heat flux with a retainer frame. Materials tested in accordance with ASTM E1354 shall meet the following performance criteria: the average heat release rate over the 180 s following ignition shall be ≤ 100 kW/m², and the average specific extinction area (σ_f) shall be ≤ 500 m²/kg over the same 180 second period.

^l Carpeting used as a wall or ceiling covering shall be tested according to ASTM E162 and ASTM E662 and meet the respective criteria of I_s less than or equal to 35 and D_s (1.5) less than or equal to 100 and D_s (4.0) less than or equal to 200. Notes 1 and 2 apply.

^m Floor covering shall be tested with padding in accordance with ASTM E648 [47], if the padding is used in the actual installation.

ⁿ For double window glazing, only the interior glazing is required to meet the requirements specified herein. (The exterior glazing is not required to meet these requirements.)

^o Penetrations (ducts, and so on) shall be designed against acting as passageways for fire and smoke and representative penetrations shall be included as part of test assemblies.

^p A structural flooring assembly separating the interior of a vehicle from its undercarriage shall meet the performance criteria during a nominal test period as determined by the railroad. The nominal test period must be twice the maximum expected time period under normal circumstances for a vehicle to stop completely and safely from its maximum operating speed, plus the time necessary to evacuate all the vehicle's occupants to a safe area. The nominal test period must not be less than 15 minutes. Only one specimen need be tested. A proportional reduction may be made in the dimensions of the specimen provided it serves to truly test the ability of the structural flooring assembly to perform as a barrier against under-vehicle fires. The fire resistance period required shall be consistent with the safe evacuation of a full load of passengers from the vehicle under worst-case conditions.

^q Portions of the vehicle body which separate major ignition sources, energy sources, or sources of fuel-load from vehicle interiors, shall have sufficient fire endurance as determined by a fire hazard analysis acceptable to the railroad which addresses the location and quantity of the materials used, as well as vulnerability of the materials to ignition, flame spread, and smoke generation. These portions include equipment-carrying portions of a vehicle's roof and the interior structure separating the levels of a bilevel car, but do not include a flooring assembly subject to Note 16. A railroad is not required to use the ASTM E119 test method [57].

Table 7.2 NFPA 130-2010 [12] requirements for passenger vehicle rail materials					
Category	Function of Material	Flammability		Smoke Emission	
		Test Procedure	Performance Criteria	Test Procedure	Performance Criteria
Cushioning	All individual flexible cushioning materials used in seat cushions, mattresses, mattress pads, armrests, crash pads and grab rail padding ^{a-c}	ASTM D3675 [46]	$I_s \leq 25$	ASTM E662 [24]	$D_s (1.5) \leq 100$ $D_s (4.0) \leq 175$
Fabrics	Seat upholstery, mattress ticking and covers, curtains, draperies, window shades and woven seat cushion suspensions ^{a-c, f-h}	14CFR25 Appendix F, Part I (vertical test)	Flame time ≤ 10 s; Burn length ≤ 15 cm.	ASTM E662 [24]	$D_s (4.0) \leq 200$
Other Vehicle Components	Seat and mattress frames, wall and ceiling lining and panels, seat and toilet shrouds, toilet seats, trays and other tables, partitions, shelves, opaque	ASTM E162 [44]	$I_s \leq 35$	ASTM E662 [24]	$D_s (1.5) \leq 100$ $D_s (4.0) \leq 200$

	windcreens, combustible signage, end caps, roof housings, articulation bellows, exterior shells, nonmetallic skirts, and component boxes and covers ^{a, b, i-k}				
	Thermal and acoustical insulation ^{a, b}	ASTM E162 [44]	$I_s \leq 25$	ASTM E662 [24]	$D_s (4.0) \leq 100$
	HVAC ducting ^{a, b}	ASTM E162 [44]	$I_s \leq 25$	ASTM E662 [24]	$D_s (4.0) \leq 100$
	Floor covering ^{k, l}	ASTM E648 [47]	$CRF \geq 5 \text{ kW/m}^2$	ASTM E662 [24]	$D_s (1.5) \leq 100$
	Light diffusers, windows and transparent plastic windcreens ^{b, i}	ASTM E162 [44]	$I_s \leq 100$	ASTM E662 [24]	$D_s (1.5) \leq 100$
					$D_s (4.0) \leq 200$
Elastomers ^{a, j}	Window gaskets, door nosings, intercar diaphragms, seat cushion suspension diaphragms and roof mats	ASTM C1166 [48]	Flame propagation $\leq$ ~~100 mm (10 cm)~~ 101.6 mm	ASTM E662 [24]	$D_s (1.5) \leq 100$
					$D_s (4.0) \leq 200$

Structural Components	Flooring ^{m, n} , other ^o	ASTM E119 [57]	Pass		
Wire and cable	Requirements not included by FRA - See description following notes				
I_s : Radiant panel index in the ASTM E 162 test method CRF: Critical radiant flux in the ASTM E 648 test method CFR: Code of Federal Regulations ^a Materials tested for surface flammability shall not exhibit any flaming running or dripping. ^b The ASTM E662 [24] maximum test limits for smoke emission (specific optical density) shall be based on both the flaming and nonflaming modes. ^c Testing of a complete seat assembly (including cushions, fabric layers, upholstery) according to ASTM E1537 [49] using the pass/fail criteria of CA TB 133 [50], and testing of a complete mattress assembly (including foam and ticking) according to ASTM E1590 [51] using the pass/fail criteria of CA TB 129 [52] shall be permitted <i>in lieu</i> of the test methods prescribed herein, provided the assembly component units remain unchanged or new (replacement) assembly components possess equivalent fire performance properties to the original components tested. A fire hazard analysis shall also be conducted that considers the operating environment within which the seat or mattress assembly will be used in relation to the risk of vandalism, puncture, cutting, or other acts which may expose the individual components of the assemblies to an ignition source. The requirements of notes 22, 23, 24, and 25 shall be met. ^d Testing shall be performed without upholstery. ^e The surface flammability and smoke emission characteristics shall be demonstrated to be permanent after dynamic testing according to ASTM D3574 [53], Test I2 or Test I3, both using Procedure B, except that the test samples shall be a minimum of 150 mm × 450 mm × the thickness used in end-use configuration, or multiples thereof. If Test I3 is used, the size of the indenter described in Section 96.2 of ASTM D3574 [58] shall be modified to accommodate the specified test specimen. ^f The surface flammability and smoke emission characteristics shall be demonstrated to be permanent by washing, if appropriate, in accordance with the manufacturer's recommended procedure. If a washing procedure is not provided by the manufacturer, the fabric shall be washed in accordance with ASTM E2061, Annex A1 [45].					

^g The surface flammability and smoke emission characteristics shall be demonstrated to be permanent by dry-cleaning, if appropriate, according to ASTM D2724 [55].

^h Materials that cannot be washed or dry-cleaned shall be so labeled and shall meet the applicable performance criteria after being cleaned as recommended by the manufacturer.

ⁱ Combustible operational and safety signage shall not be required to meet flame spread or smoke emission requirements if the combustible mass of a single sign does not exceed 500 g and the aggregate area of combustible signage does not exceed one square foot per foot of car length.

^j Materials used to fabricate miscellaneous, discontinuous small parts (such as knobs, rollers, fasteners, clips, grommets, and small electrical parts) that will not contribute materially to fire growth in end use configuration are exempt from flammability and smoke emission performance requirements, provided that the surface area of any individual small part is less than 100 cm² (16 in.²) in end use configuration and an appropriate fire hazard analysis is conducted that addresses the location and quantity of the materials used and the vulnerability of the materials to ignition and contribution to flame spread.

^k Carpeting used as a wall or ceiling covering shall be tested according to ASTM E162 [44] and ASTM E662 [24] and shall meet the respective criteria of $I_s \leq 35$, $D_s (1.5) \leq 100$, and $D_s (4.0) \leq 200$. (See Notes 1 and 2.)

^l Floor covering shall be tested with padding in accordance with ASTM E648 [47], if the padding is used in the actual installation.

^m Penetrations (ducts, and so on) shall be designed against acting as passageways for fire and smoke, and representative penetrations of each type shall be included as part of test assemblies. Fire resistance testing on assemblies shall be conducted in general accordance with ASTM E119 [57]. See corresponding section in NFPA 130 [5].

ⁿ See section on ASTM E119 [57] testing in NFPA 130 [5].

^o Portions of the vehicle body that separate the major ignition source, energy sources, or sources of fuel load from vehicle interiors shall have fire resistance as determined by a fire hazard analysis, acceptable to the authority having jurisdiction, that addresses the location and quantity of the materials used, as well as vulnerability of the materials to ignition, flame spread, and smoke generation. These portions include equipment-carrying portions of a vehicle's roof and the interior structure separating the levels of a bilevel car, but do not include a flooring assembly subject to the NFPA 130 section on fire resistance testing. In those cases, the use of the ASTM E119 [57] test procedure shall not be required.

Wires and cables are permitted if they have been listed by any of the following methods:

- (a) Tray cable, listed via UL 1581-1160 [60] (UL tray), plus low specific optical D_s via ASTM E662 [24] (specific optical D_s at 4 minutes into the test that does not exceed 200 in the flaming mode and 75 in the nonflaming mode)
- (b) Tray test, listed via UL 1581-1164 [61] (CSA tray), plus CSA ST1 low smoke, as shown in the CSA FT4 test protocol [62]
- (c) Tray cable, listed via UL 1685 [36], with limited smoke
- (d) Riser cable, listed via UL 1666 [63], plus low specific optical D_s via ASTM E662 [24] specific optical D_s at 4 minutes into the test that does not exceed 200 in the flaming mode and 75 in the nonflaming mode
- (e) Plenum cable, listed via NFPA 262 [37]

Wires and cables used for fire alarm systems and smoke alarms must comply with the above and one of the following:

- (a) Be capable of having 15 minute circuit integrity when tested in accordance with International Electrotechnical Commission, IEC 60331-11 [64]
- (b) Demonstrate that, if circuit integrity is tested during the vertical flame test, a current continues operating for at least 5 minutes during the test
- (c) Have fire alarm circuit integrity cable in accordance with NFPA 70 [1]

European trains have had their own unique requirements for many years, one of the most widely broad-based requirements being the British BS 6853 [65], which uses as its smoke test the so-called three metre cube test that is typically used for cables (IEC 61034) [66] (see next). The French requirements applicable to rail provide for two types of classification of material properties: ‘reaction to fire’ and ‘toxicity’ (which is actually a combination of smoke release and smoke toxicity). Acceptance criteria vary by application and depend on the results in both sets of tests. The ‘toxicity’ tests classify the materials on the basis of a combination of smoke emission and smoke toxicity of the material, with classifications in the range of F0 to F5. The F0 designation is reserved for items that are deemed to be noncombustible. These classifications are based on two tests: NF X 10702 [67], which is the same as the NBS smoke chamber, ASTM E662 [24], and NF X 70100 [68], which is an analytical toxicity test. The specific standard that is applicable to a particular material depends on its use (e.g., curtains, cushion covers) and, in addition, on the intended use of the cars. A further

complication is that the final test to be used depends in many instances on the results of earlier tests. It is also not clear at this point which standards are actually enforced. With this ambiguity in mind, the most stringent requirement for each test method will be cited in this report. The specification 'NF P 92507 - Classification of Materials' [69] provides the criteria that are applied to the results of the tests to determine the classification of the material.

The European Commission has mandated the identification of test methods for use in the classification of materials and products to be used in railway vehicles throughout the European member states. Thus, in the near future, national standards, including BS 6853 [65] and NF P 92507 [70], will be withdrawn and replaced by one standard, where the material fire safety requirements are contained in EN 45545-2 [71]. All smoke emission testing will be done using the ISO 5659-2 method [30], normally at 50 kWm² (nonflaming mode). Two parameters are used to quantify smoke emission: the specific optical D_s value, either at 4 minutes or at the maximum, and the French parameter (VOF4), which is the area under the D_s *versus* time curve during a four minute test period, intended to discriminate fast smoke production by integration under an already cumulative curve (in units of minutes). For rail flooring materials, smoke released is also assessed by ISO 5659-2 [34], but using the 25 kWm² (flaming mode).

7.2.5.4 Motor Vehicles

The statistics of fire losses in the US show that more than two-thirds of all fires in vehicles occur in road vehicles, and more than 95% of those occur in automobiles (a category that includes, of course, the popular private minivans and sports utility vehicles). In spite of this, the regulatory requirements are simply the very mild FMVSS 302 [72] flame spread test without any smoke testing.

7.2.5.5 Buses and School Buses

The authority having jurisdiction is NHTSA (and the FTA for buses), and the fire safety requirements for interior materials are contained in FMVSS 302 [72], again without smoke. It is intended that buses follow the same guidelines that trains and underground rail vehicles are required to follow, but, as explained previously, these are voluntary.

7.2.5.6 Mine Conveyor Belts

The fire safety of mine conveyor belts is covered by the MSHA. Regulation mandates the exclusive use of 'flame-resistant conveyor belts', without giving any test or

requirement details. The actual test used is a Bunsen burner type test, based on ASTM D635 (UL 94 HB) [73], which has been shown to be inappropriate for the associated fire hazard. Originally, large-scale tunnels were used to classify the flammability of conveyor belts, but those tunnels have since been destroyed. A final report was published in December 2007, recommending the replacement of the Bunsen burner test by a 'BELT' test for regulatory purposes [74]. The BELT test was developed by the US Bureau of Mines and is conducted in a 1.7 m long by 0.2 m² wide ventilated tunnel. The belt material sample size is 1.5 m long by 230 mm wide. The sample is ignited by applying a gas burner to the front edge of the belt sample with the flames distributed equally on the top and bottom surfaces of the sample. In June 2008, MSHA published in the Federal Register a Request for Information as to whether tests exist that can be used for assessing conveyor belt combustion toxicity and smoke density. The information collected will potentially result in developing additional requirements for mine conveyor belts.

7.2.5.7 Carpets

A number of local jurisdictions, including local transportation authorities, are concerned about the fire safety of carpets. There is usually no specific local regulation, but various specifications are put in place that have the same effect. Typically, such specifications require carpets to meet some smoke obscuration criterion, almost always based on testing via ASTM E662 [24].

7.2.6 Comparison with International Regulations

It is important to point out that the previously described regulations do not include any requirements in the US for construction products (building products) or for electrical wires and cables (or their optical fibre equivalents), other than in some transportation vehicles. As explained earlier, these requirements are contained in codes, which may be adopted into regulation. Most other developed countries have government-mandated regulation for such products.

In the case of the EU, the European Commission has developed 'directives', including one requiring 'safety in case of fire' [75]. The consequence of this was the development of a scheme for the classification of products [76], starting with construction products 'other than floorings', and 'floorings' (Tables 7.3-7.5). Basically, five tests are used: a noncombustibility test (EN ISO 1182 [77]), an oxygen bomb calorimeter (EN ISO 1716 [78]), an intermediate-scale heat release apparatus (the single burning item (SBI), EN 13823 [79]), a small ignitability apparatus (EN ISO 11925-2 [80]) and, for flooring, a flooring radiant panel (EN ISO 9239-1 [81]). Two of these tests include smoke measurements, namely EN 13823 (SBI) and EN ISO 9239-1 (the

latter a test very similar to the flooring radiant panel used in the US, ASTM E648 [47], except that the US version does not measure smoke). Every country (or member state) is entitled to choose the limits that apply to each application, but they should all, eventually, adopt the overall scheme. In order to help with the development and implementation of this scheme, the European Community has developed a ‘reference scenario’ fire test, namely the ISO 9705 room-corner test [33], and uses other tests as surrogates. **Table 7.3** shows the concept of what each class is intended to represent in the European Community standard testing approach. The specific classification schemes for construction products (excluding floorings) and for floorings are shown in **Tables 7.4** and **7.5**. Afterward, the European Commission addressed fire testing of linear pipe thermal insulation products [82], and, later, of electric cables [83], as shown in **Tables 7.6** and **7.7**. Electric cables are tested in this scheme by means of the FIPEC test [84], EN 50399 [85], which is a vertical cable tray test that includes measurements of heat and smoke release. It is of interest that, in every case, the criteria for smoke obscuration, smoke toxicity and smoke corrosivity are ‘additional declarations’, which are usually not required. The requirements are included as regulation by all European member states, with various implementation dates. The individual European countries have had different regulatory approaches to fire safety regulation, but most of them are in the process of being withdrawn.

Table 7.3 European Community Concept for Classes

Fire Class	Tests simulations		Time to flashover	Contribution to fire growth
A1	Fully developed fire in a room	Single Burning Item in a Room	No flashover	None
A2	Fully developed fire in a room	Single Burning Item in a Room	No flashover	None
B	Small fire attack on limited area	Single Burning Item in a Room	No flashover	Extra small
C	Small fire attack on limited area	Single Burning Item in a Room	After 10 minutes	Small
D	Small fire attack on limited area	Single Burning Item in a Room	2 - 10 minutes	medium
E	Small fire attack on limited area		Before 2 minutes	Large
F	No A1 through E			

Essential definitions for European Community regulations

Material: a single basic substance or uniformly dispersed mixture of substances, for example metal, stone, timber, concrete, mineral wool with uniformly dispersed binder, polymers.

Homogeneous product: a product consisting of a single material, having uniform density and composition throughout the product.

Non-homogeneous product: a product that does not satisfy the requirements of a homogeneous product. It is a product composed of one or more components, substantial and/or non-substantial.

Substantial component: a material that constitutes a significant part of a non-homogeneous product. A layer with a mass per unit area $\geq 1.0 \text{ kg/m}^2$ or a thickness $\geq 1.0 \text{ mm}$ is considered to be a substantial component.

Non-substantial component: a material that does not constitute a significant part of a non-homogeneous product. A layer with a mass per unit area $< 1.0 \text{ kg/m}^2$ and a thickness $< 1.0 \text{ mm}$ is considered to be a non-substantial component. Two or more non-substantial layers that are adjacent to each other (i.e. with no substantial component(s) in-between the layers) are regarded as one non-substantial component and, therefore, must altogether comply with the requirements for a layer being a non-substantial component.

For non-substantial components, distinction is made between internal non-substantial components and external non substantial components, as follows:

Internal non-substantial component: a non-substantial component that is covered on both sides by at least one substantial component.

External non-substantial component: a non-substantial component that is not covered on one side by a substantial component.

TABLE 7.4 European Community classes of reaction to fire performance for construction products excluding floorings, linear pipe thermal insulation products and electrical cables

Class	Test method(s)	Classification criteria	Additional classification
A1	EN ISO 1182 ^a [77] and	$\Delta T \leq 30 \text{ }^\circ\text{C}$ and	-
		$\Delta m \leq 50 \text{ \%}$ and	
		$t_f = 0$ (i.e., no sustained flaming)	

	EN ISO 1716 [78]	$PCS \leq 2.0 \text{ MJ/kg}^a$ and	-
		$PCS \leq 2.0 \text{ MJ/kg}^{b,c}$ and	
		$PCS \leq 1.4 \text{ MJ/m}^2^d$ and	
		$PCS \leq 2.0 \text{ MJ/kg}^e$	
A2	EN ISO 1182 ^a [77] or	$\Delta T \leq 50 \text{ }^\circ\text{C}$ and	-
		$\Delta m \leq 50 \text{ \%}$ and	
		$t_f \leq 20\text{s}$	
	EN ISO 1716 [78] and	$PCS \leq 3.0 \text{ MJ/kg}^a$ and	-
		$PCS \leq 4.0 \text{ MJ/kg}^b$ and	
		$PCS \leq 4.0 \text{ MJ/m}^2^d$ and	
		$PCS \leq 3.0 \text{ MJ/kg}^e$	
	EN 13823 (SBI) [79]	$FIGRA \leq 120 \text{ W/s}$ and	Smoke production ^f , and
		$LFS < \text{edge of specimen}$ and	Flaming droplets/ particles ^g
		$THR_{600s} \leq 7.5 \text{ MJ}$	
B	EN 13823 (SBI) [79]	$FIGRA \leq 120 \text{ W/s}$ and	Smoke production ^f , and
	And	$LFS < \text{edge of specimen}$ and	Flaming droplets/ particles ^g
		$THR_{600s} \leq 7.5 \text{ MJ}$	
	EN ISO 11925-2 [80] ⁱ Exposure = 30 seconds	$F_s \leq 150 \text{ mm}$ within 60 seconds	
C	EN 13823 (SBI) [79]	$FIGRA \leq 250 \text{ W/s}$ and	Smoke production ^f , and
	and	$LFS < \text{edge of specimen}$ and	Flaming droplets/ particles ^g
		$THR_{600s} \leq 15 \text{ MJ}$	
	EN ISO 11925-2 [80] ⁱ Exposure = 30 seconds	$F_s \leq 150 \text{ mm}$ within 60 seconds	

D	EN 13823 (SBI) [79]	FIGRA ≤ 750 W/s and	Smoke production ^f , and
	And		Flaming droplets/particles ^g
	EN ISO 11925-2 [80] ⁱ Exposure = 30 seconds	F _s ≤ 150 mm within 60 seconds	
E	EN ISO 11925-2 [80] ⁱ Exposure = 15 seconds	F _s ≤ 150 mm within 20 seconds	Flaming droplets/particles ^h
F	No performance determined		

a: For homogeneous products and substantial components of non-homogeneous products.

b: For any external non-substantial component of non-homogeneous products.

c: Alternatively, any external non-substantial component having a PCS ≤ 2.0 MJ/m², provided that the product satisfies the following criteria of EN 13823 (SBI): FIGRA ≤ 20 W/s; and LFS < edge of specimen, and THR_{600s} ≤ 4.0 MJ and s1 and d0.

d: For any internal non-substantial component of non-homogeneous products.

e: For the product as a whole.

f: In the last phase of the development of the test procedure, modifications of the smoke measurement system have been introduced, the effect of which needs further investigation. This may result in a modification of the limit values and/or parameters for the evaluation of smoke production.

g: d0 = No flaming droplets/particles in EN 13283 (SBI) within 600 s; d1 = No flaming droplets/particles persisting longer than 10 s in EN 13823 (SBI) within 600 s; d2 = not d0 or d1. Ignition of the paper in EN ISO 11925-2 results in a d2 classification.

h: Pass = no ignition of the paper (no classification). Fail = ignition of the paper (d2 classification).

i: Under conditions of surface flame attack and, if appropriate to the end-use application of the product, edge flame attack.

ΔT : Temperature rise
 Δm : Mass loss
 t_f : Duration of flaming
PCS: Gross calorific potential
FIGRA: Fire growth rate
 THR_{600s} : Total heat release
LFS: Lateral flame spread
SMOGRA: Smoke growth rate
 TSP_{600s} : Total smoke production
 F_s : Flame spread

TABLE 7.5 European Community classes of reaction to fire performance for floorings

Class	Test method(s)	Classification criteria	Additional classification
A1fl	EN ISO 1182 ^a [77] and	$\Delta T \leq 30$ °C and	-
		$\Delta m \leq 50$ % and	
		$t_f = 0$ (i.e. no sustained flaming)	
	EN ISO 1716 [78]	$PCS \leq 2.0$ MJ/kg ^a and	-
		$PCS \leq 2.0$ MJ/kg ^b and	
		$PCS \leq 1.4$ MJ/m ² ^c and	
		$PCS \leq 2.0$ MJ/kg ^d	
A2fl	EN ISO 1182 ^a [77] or	$\Delta T \leq 50$ °C and	-
		$\Delta m \leq 50$ % and	
		$t_f \leq 20$ s	
	EN ISO 1716 [78]	$PCS \leq 3.0$ MJ/kg ^a and	-
		$PCS \leq 4.0$ MJ/m ² ^b and	
	And	$PCS \leq 4.0$ MJ/m ² ^c and	
		$PCS \leq 3.0$ MJ/kg ^d	
	EN ISO 9239-1 [81] ^e	Critical flux ^f ≥ 8.0 kW/m ²	Smoke production ^g

Bfl	EN ISO 9239-1 [81] ^e and	Critical flux ^f ≥ 8.0 kW/m ²	Smoke production ^g
	EN ISO 11925-2 [80] ^h	F _s ≤150 mm within 20 s	-
	Exposure = 15 seconds		
Cfl	EN ISO 9239-1 [81] ^e and	Critical flux ^f ≥ 4.5 kW/m ²	Smoke production ^g
	EN ISO 11925-2 [80] ^h	F _s ≤150 mm within 20 s	-
	Exposure = 15 s		
Dfl	EN ISO 9239-1 [81] ^e and	Critical flux ^f ≥ 3.0 kW/m ²	Smoke production ^g
	EN ISO 11925-2 [80] ^h	F _s ≤150 mm within 20 s	-
	Exposure = 15 s		
Efl	EN ISO 11925-2 [81] ^h	F _s ≤150 mm within 20 s	-
	Exposure = 15 s		
Ffl	No performance determined		
a: For homogeneous products and substantial components of non-homogeneous products			
b: For any external non-substantial component of non-homogeneous products			
c: For any internal non-substantial component of non-homogeneous products			
d: For the product as a whole			
e: Test duration = 30 minutes			
f: Critical flux is defined as the radiant flux at which the flame extinguishes or the radiant flux after a test period of 30 minutes, whichever is the lower (i.e. the flux corresponding with the furthest extent of spread of flame)			
g: s1 = Smoke ≤ 750 %.min; s2 = not s1			
h: Under conditions of surface flame attack and, if appropriate to the end-use application of the product, edge flame attack			

Table 7.6 European Community Classes of Reaction-to-Fire Performance for Linear Pipe Thermal Insulation Products			
Class	Test method(s)	Classification criteria	Additional classification
A1 _L	EN ISO 1182 ^a [77] and	$\Delta T \leq 30$ °C and	-
		$\Delta m \leq 50$ % and	
		$t_f = 0$ (i.e. no sustained flaming)	
	EN ISO 1716 [78]	$PCS \leq 2.0$ MJ/kg ^a and	-
		$PCS \leq 2.0$ MJ/kg ^b and	
		$PCS \leq 1.4$ MJ/m ² ^c and	
		$PCS \leq 2.0$ MJ/kg ^d	
A2 _L	EN ISO 1182 ^a [77] or	$\Delta T \leq 50$ °C and	-
		$\Delta m \leq 50$ % and	
		$t_f \leq 20$ s	
	EN ISO 1716 [78] and	$PCS \leq 3.0$ MJ/kg ^a and	-
		$PCS \leq 4.0$ MJ/kg ^b and	
		$PCS \leq 4.0$ MJ/m ² ^c and	
		$PCS \leq 3.0$ MJ/kg ^d	
	EN 13823 (SBI) [79]	$FIGRA \leq 270$ W/s and	Smoke production ^e , and
		$LFS < \text{edge of specimen}$ and	Flaming droplets/particles ^f
		$THR_{600s} \leq 7.5$ MJ	
B _L	EN 13823 (SBI) [79]	$FIGRA \leq 270$ W/s and	Smoke production ^e , and
	And	$LFS < \text{edge of specimen}$ and	Flaming droplets/particles ^f

		$\text{THR}_{600\text{s}} \leq 7.5 \text{ MJ}$	
	EN ISO 11925-2 [80] ^h Exposure = 30 s	$F_s \leq 150 \text{ mm}$ within 60 seconds	
C_L	EN 13823 (SBI) [79]	$\text{FIGRA} \leq 460 \text{ W/s}$ and	Smoke production ^e , and
	And	$\text{LFS} < \text{edge of specimen}$ and	Flaming droplets/particles ^f
		$\text{THR}_{600\text{s}} \leq 15 \text{ MJ}$	
		EN ISO 11925-2 [80] ^h Exposure = 30 s	$F_s \leq 150 \text{ mm}$ within 60 s
D_L	EN 13823 (SBI) [79]	$\text{FIGRA} \leq 2,100 \text{ W/s}$ and	Smoke production ^e , and
		$\text{THR}_{600\text{s}} \leq 100 \text{ MJ}$	Flaming droplets/particles ^f
	EN ISO 11925-2 [80] ^h Exposure = 30 s	$F_s \leq 150 \text{ mm}$ within 60 s	
E_L	EN ISO 11925-2 [80] ^h Exposure = 15 s	$F_s \leq 150 \text{ mm}$ within 20 s	Flaming droplets/particles ^f
F_L	No performance determined		
a: For homogeneous products and substantial components of non-homogeneous products			
b: For any external non-substantial component of non-homogeneous products			
c: For any internal non-substantial component of non-homogeneous products			
d: For the product as a whole.			

e: $s_1 = \text{SMOGRA} \leq 105 \text{ m}^2/\text{s}^2$ and $\text{TSP}_{600\text{s}} \leq 250 \text{ m}^2$; $s_2 = \text{SMOGRA} \leq 580 \text{ m}^2/\text{s}^2$ and $\text{TSP}_{600\text{s}} \leq 1600 \text{ m}^2$; $s_3 = \text{not } s_1 \text{ or } s_2$.

f: $d_0 = \text{No flaming droplets/particles in EN13823 (SBI) within 600 s}$; $d_1 = \text{No flaming droplets/particles persisting longer than 10 s in EN 13283 (SBI) within 600 s}$; $d_2 = \text{not } d_0 \text{ or } d_1$. Ignition of the paper in EN ISO 11925-2 results in a d_2 classification

g: Pass = no ignition of the paper (no classification); fail = ignition of the paper (d_2 classification). Fail = ignition of the paper (d_2 classification)

h: Under conditions of surface flame attack and, if appropriate to end-use application of product, edge flame attack

Table 7.7 European Community classes of reaction to fire performance for electric cables

Class	Test method(s)	Classification criteria	Additional classification
A_{ca}	EN ISO 1716 [78]	$\text{PCS} \leq 2.0 \text{ MJ/kg (1)}$	
$B1_{ca}$	FIPEC ₂₀ Scenario 2 (5)	$F_s \leq 1.75 \text{ m and}$	Smoke production (2, 6) and Flaming droplets/particles (3) and Acidity (4) (8)
		$\text{THR}_{1200\text{s}} \leq 10 \text{ MJ and}$	
	And	Peak HRR $\leq 20 \text{ kW and}$	
		FIGRA $\leq 120 \text{ W/s}$	
	EN 60332-1-2 [86]	$H \leq 425 \text{ mm}$	
$B2_{ca}$	FIPEC ₂₀ Scenario 1 (5)	$F_s \leq 1.5 \text{ m; and}$	Smoke production (2, 6) and Flaming droplets/particles (3) and Acidity (4) (8)
		$\text{THR}_{1200\text{s}} \leq 15 \text{ MJ; and}$	
	And	Peak HRR $\leq 30 \text{ kW; and}$	
		FIGRA $\leq 150 \text{ W/s}$	
	EN 60332-1-2 [86]	$H \leq 425 \text{ mm}$	
C_{ca}	FIPEC ₂₀ Scenario 1 (5)	$F_s \leq 2.0 \text{ m; and}$	Smoke production (2, 6) and Flaming droplets/particles (3) and Acidity (4) (8)
		$\text{THR}_{1200\text{s}} \leq 30 \text{ MJ; and}$	
	And	Peak HRR $\leq 60 \text{ kW; and}$	
		FIGRA $\leq 300 \text{ W/s}$	
	EN 60332-1-2 [86]	$H \leq 425 \text{ mm}$	

D _{ca}	FIPEC ₂₀ Scenario 1 (5)	THR _{1200s} ≤ 70 MJ; <i>and</i>	Smoke production (2, 6) and Flaming droplets/particles (3) and Acidity (4) (8)
		Peak HRR ≤ 400 kW; <i>and</i>	
	<i>And</i>	FIGRA ≤ 1300 W/s	
	EN 60332-1-2 [86]	H ≤ 425 mm	
E _{ca}	EN 60332-1-2 [86]	H ≤ 425 mm	
F _{ca}	No performance determined		
FIPEC: Fire Performance of Electric Cables [84] 1. For the product as a whole, excluding metallic materials, and for any external component (i.e. sheath) of the product 2. s1 = TSP₁₂₀₀ ≤ 50 m² <i>and</i> Peak SPR ≤ 0.25 m²/s s1a = s1 and transmittance in accordance with EN 61034-2 ≥ 80% s1b = s1 and transmittance in accordance with EN 61034-2 ≥ 60% < 80% s2 = TSP₁₂₀₀ ≤ 400 m² <i>and</i> Peak SPR ≤ 1.5 m²/s s3 = not s1 or s2 3. For FIPEC₂₀ Scenarios 1 and 2: d0 = No flaming droplets/particles within 1200 s; d1 = No flaming droplets/ particles persisting longer than 10 s within 1200 s; d2 = not d0 or d1 4. EN 50267-2-3 : a1 = conductivity < 2.5 μS/mm <i>and</i> pH > 4.3 ; a2 = conductivity < 10 μS/mm <i>and</i> pH > 4.3; a3 = not a1 or a2. No declaration = No Performance Determined. 5. Air flow into chamber shall be set to 8000 ± 800 l/min FIPEC₂₀ Scenario 1 = EN 50399-2-1 [85] with mounting and fixing as below FIPEC₂₀ Scenario 2 = EN 50399-2-2 [85] with mounting and fixing as below 6. The smoke class declared for class B1_{ca} cables must originate from the FIPEC₂₀ Scenario 2 test 7. The smoke class declared for class B2_{ca}, C_{ca}, D_{ca} cables must originate from the FIPEC₂₀ Scenario 1 test 8. Measuring the hazardous properties of gases developed in the event of fire, which compromise the ability of the persons exposed to them to take effective action to accomplish escape, and not describing the toxicity of these gases.			

Until the new European Commission requirements fully come into effect, the traditional requirements for flame spread and smoke release for electrical and optical fibre cables will remain in use. In terms of smoke release, the test is the three metre cube, IEC 61034 [66], which is a static test.

7.3 Codes

7.3.1 International Codes Council Codes

As explained earlier, in the United States, there are three primary organisations that develop codes: ICC, NFPA and IAPMO; they are all private companies. All codes are revised by public proposals and consensus action every three years.

Until the mid 1990s, the United States had three regional code development companies: (1) International Conference of Building Officials (ICBO), which issued the Uniform Building Code, primarily used in the 25 states west of the Mississippi; (2) Building Officials and Code Administrators, which issued the National Building Code or NBC, primarily used in the Northeast and Midwest; and (3) Southern Building Code Conference International, which issued the Standard Building Code, primarily used in the Southeast. The three organisations chose to join up to form ICC to develop the ICC set of codes in a uniform fashion and to discontinue the old codes (also called the legacy codes). At least some of the legacy codes also had parallel documents dealing with the other issues that need codification, but not all of them had complete sets. The key codes issued by the ICC relevant to smoke testing are the following: International Building Code (IBC), International Fire Code (IFC), International Residential Code (IRC), International Mechanical Code (IMC) and the International Existing Building Code (IEBC).

7.3.1.1 International Building Codes

The IBC applies to the ‘construction, alteration, movement, enlargement, replacement, repair, equipment, use and occupancy, location, maintenance, removal and demolition of every building or structure or any appurtenances connected or attached to such buildings or structures’. However, the IBC does not apply to ‘detached one- and two-family dwellings and multiple single-family dwellings (townhouses) not more than three stories above grade plane in height with a separate means of egress and their accessory structures’, to which the IRC applies. The IBC does not apply to materials contained in plenums, which are addressed in the IMC.

Requirements for smoke obscuration testing in the IBC address only relatively few materials/products: interior wall and ceiling finish, insulation, signs, foam plastics, light transmitting plastics, thermal barriers, fire retardant treated wood, aluminum composite materials (ACM) and metal composite materials (MCM).

All wall and ceiling interior finish materials, as well as insulation (except for cellulose loose-fill insulation), must be tested for flame spread and smoke in accordance with the traditional Steiner tunnel test (ASTM E84 [35], a 7.3 m tunnel with the test specimen on the underside of the ceiling). The Steiner tunnel provides results as a FSI and a SDI. Whenever ASTM E84 is used for testing, the material or product must exhibit an SDI not exceeding 450, irrespective of the FSI requirements [which can be Class A (up to 25), Class B (> 25 and up to 75) or Class C (>75 and up to 200)]. As an alternative, all materials are permitted to be tested using a room-corner test for heat and smoke release (NFPA 286 [87]). There is clear evidence that the Steiner tunnel test is appropriate for some, but not all, materials and that NFPA 286 is a suitable test for any wall or ceiling interior finish material. Some materials (textile and expanded vinyl wall coverings) are permitted to be tested by using a less severe room-corner test (NFPA 265 [88]), but the room must also be sprinklered. The smoke criterion for both NFPA 286 and NFPA 265 is a total smoke release of no more than 1,000 m². Foam plastics are only allowed to be fire tested for interior finish use via the NFPA 286 test and not via ASTM E84, because of evidence that the Steiner tunnel test results are misleading. However, the foam plastic material itself must be tested to ASTM E84 and exhibit an FSI not above 75 and an SDI not above 450. Foam plastics are allowed to be used when covered by a thermal barrier (such as gypsum board). Thermal barriers (other than gypsum board) are required to have the system, (i.e., thermal barrier and foam plastic) tested using NFPA 286 (with the same smoke criteria as previously), although some other tests are also permitted for thermal barriers, without smoke testing. Very thin (< 0.9 mm thick) materials coated onto wall surfaces are exempt from fire/smoke testing because they are believed to be likely to produce insufficient heat or flames to cause serious problems. Very thick structural members are also exempt from fire/smoke testing because they are believed to be of low enough ignitability that they do not pose a serious hazard. Interior trim (which occupies less than 10% of a wall or ceiling surface) is tested by the same means as other interior finish, but is allowed greater leniency (and is not required to have smoke testing unless it is made of foam plastic). Recent trends have started incorporating specific mounting practices for the use of ASTM E84 with a variety of materials, such as wall coverings, to ensure adequate testing results.

Light transmitting plastics are required to be tested (when used in a variety of applications, including glazing, skylights, signs and so on) by three tests: ignitability in accordance with ASTM D1929 [89], flame spread in accordance with ASTM D635 [74] and smoke obscuration in accordance with either ASTM D2843 (Rohm and Hass

smoke chamber) [90] or ASTM E84 [36]. If they are tested to ASTM D2843, they must exhibit a maximum average smoke density rating not greater than 75, whereas they must exhibit an SDI of no more than 450 in the Steiner tunnel.

Some types of materials called out specifically are ACM, MCM and fire-retardant treated wood. The first two are factory-manufactured composite panels with metal skins bonded to both faces of a plastic core (often a foam plastic). They need to be tested just like interior finish, with the issues associated with individual testing of the foam plastic and potential requirements for use of a thermal barrier. Fire-retardant treated wood must be tested to an 'extended ASTM E84 test' (which is conducted for 30 minutes instead of the normal 10 minutes) and must have an SDI not exceeding 450, as well as some additional requirements not related to smoke.

7.3.1.2 International Fire Codes

The IFC applies to the following:

- Structures, facilities and conditions arising after the adoption of the relevant IFC edition
- Existing structures, facilities and conditions not legally in existence at the time of adoption of the relevant IFC edition
- Existing structures, facilities and conditions when identified in specific sections of the IFC
- Existing structures, facilities and conditions that, in the opinion of the fire code official, constitute a distinct hazard to life or property
- Conditions and operations arising after the adoption of the relevant IFC edition
- Existing conditions and operations

Smoke testing requirements in the IFC mirror those in the IBC.

7.3.1.3 International Residential Codes

The IRC applies to the construction, alteration, movement, enlargement, replacement, repair, equipment, use and occupancy, location, removal and demolition of detached one- and two-family dwellings and townhouses not more than three stories above-grade in height with a separate means of egress and their accessory structures. The

IRC is intended to provide minimum requirements to safeguard the public safety, health and general welfare through affordability, structural strength, means of egress facilities, stability, sanitation, light and ventilation, energy conservation and safety to life and property from fire and other hazards attributed to the built environment.

General requirements for residential construction tend to use, when they exist, the same tests as those used in the IBC, but with milder requirements. That is also valid for smoke testing.

7.3.1.4 International Mechanical Codes

The IMC regulates the design, installation, maintenance, alteration and inspection of mechanical systems that are permanently installed and utilised to provide control of environmental conditions and related processes within buildings. It does not regulate the installation of fuel gas distribution piping and equipment, fuel gas-fired appliances and fuel gas-fired appliance venting systems. Also, mechanical systems in detached one- and two-family dwellings and multiple single-family dwellings (townhouses) not more than three stories high with separate means of egress and their accessory structures are regulated by the IRC. Other exclusions are historical buildings and existing buildings.

The key provisions covered by this code are those for materials in ducts and plenums and for piping systems. Plenums are enclosed portions of the building structure that are not occupiable and that have been designed to allow air movement and serve as part of an air distribution system. These concealed spaces can move air (and smoke) easily between building compartments without the occupants being aware. Therefore, typically fairly severe requirements govern all materials permitted in plenums. The only materials permitted (by the IMC, the UMC and NFPA 90A) are: wires and cables that meet criteria based on the NFPA 262 [37] plenum-cable fire test or that are enclosed in noncombustible raceways; pneumatic tubing, based on UL 1820 [91]; sprinkler pipes, based on UL 1887 [92]; fibre optic raceway systems, based on UL 2024 [93] and combustible electrical equipment, based on UL 2043 [94], so that each one is covered by a special test for that product. The pass/fail criteria for the first four tests (all variations on the ASTM E84 tunnel) are: maximum flame spread of 1.5 m, maximum peak optical density of 0.5 and maximum average optical density of 0.15. In the case of UL 2043 (a furniture calorimeter) [94], the maximum flame spread is replaced by a maximum heat release rate of 100 kW. Foam plastic wall and ceiling insulation must meet the NFPA 286 room-corner test [87] or be covered by a thermal barrier or steel skin. All other materials, including pipe and duct insulation, must meet the requirements of an FSI of 25 and an SDI of 50 in the ASTM E84 Steiner tunnel test (a much more severe smoke criterion than that for non plenum areas, where the SDI is allowed to reach 450).

7.3.1.5 International Existing Building Codes

The provisions of the IEBC apply to the repair, alteration, change of occupancy, addition and relocation of existing buildings. This code contains relatively few fire safety provisions, unless a problem has been found and such provisions are deemed necessary by the code official for the general safety and welfare of the occupants and the public. However, when buildings are being renovated, the IEBC often requires that the provisions of either the IBC or the IFC apply.

7.3.1.6 Other International Code Council Codes

None of the other ICC codes contain any smoke testing requirements.

7.3.2 National Fire Protection Association Codes and Standards

NFPA is the second major developer of codes in the United States, and it also develops some key standards that are not codes but are used for regulation. This includes the NFPA 13 series of sprinkler standards (NFPA 13, 13D and 13R) [4], which form the bases for all the requirements for sprinkler installations in the United States (and probably worldwide), NFPA 130 (for trains and underground systems) [5], NFPA 99 [95] (which govern all health care occupancies, in conjunction with the Life Safety Code) and NFPA 90A (for air-conditioning, which regulates materials in ducts and plenums) [3]. NFPA documents are revised every three to five years, with the period being three years for all codes.

7.3.2.1 National Electrical Codes

The NEC (NFPA 70 [1]) regulates all electrical installations and also all electrical and optical fibre cables. Chapter 3 in the NEC describes wiring methods and materials. That includes Article 300, which is a type of general guide through the code with the requirements for many applications and materials (including plenums, ducts and other spaces used for environmental air, in section 300.22). NEC Chapter 3 allows optional marking of cables to criteria such as ‘limited smoke’, but does not include any smoke testing requirements. NEC Chapter 6 addresses special equipment, and the key article of importance to fire safety is article 645, on Information Technology Equipment, which regulates wiring in computer rooms. Of particular interest is the fact that it requires cables in ‘under raised floors’ to meet a vertical cable tray test and not the more severe plenum cable test, in spite of the fact that such locations are often deemed to be plenums.

NEC Chapter 7, dealing with ‘Special Conditions’, and NEC Chapter 8, dealing with ‘Communications Systems’, address the cables with highly improved fire performance

and smoke requirements. They are in articles 725 (Class 1, Class 2, and Class 3 Remote-Control, Signaling, and Power-Limited Circuits), 760 (Fire Alarm Systems), 770 (Optical Fiber Cables and Raceways), 800 (Communications Circuits), 820 (Community Antenna Television and Radio Distribution Systems) and 830 (Network-Powered Broadband Communications Systems). They require cables to comply with one of 4 tests. The most severe test is NFPA 262 [37], a cable fire test for flame spread and smoke conducted in a modified Steiner tunnel (88 kW), for which the requirements in the NEC are that the maximum peak optical density not exceed 0.5, the maximum average optical density not exceed 0.15 and the maximum allowable flame travel distance not exceed 1.52 m. The next test, in order of decreasing severity, is UL 1666 [63], known as the ‘riser cable test’, which requires that, when exposed to a 155 kW flame, the cable must be capable of preventing the carrying of fire vertically from floor to floor. The next rung in the severity scale is the vertical cable tray test, and there are two parallel tests, listing to both of which allows the cable to be used in the same application, even though the tests are not of equal severity; they are both contained within UL 1685 [36]. The concept in these cable tray tests is that the cable should not spread flame vertically beyond certain limits. The specimen is roughly 2.4 m high, and the requirement is that the char length (cable destruction) does not go all the way to the top (UL mode) or does not reach 1.5 m (CSA mode). The flame is approximately 20 kW, applied for 10 minutes, with the burner perpendicular to the cable tray (in the UL mode) and at a 20 degree angle (in the CSA mode). The NEC does not require smoke measurements for these tests, but UL 1685 has smoke pass/fail requirements, which are optional for the NEC. The fourth and minimal test in the NEC hierarchy is the small-scale Bunsen burner UL VW-1, vertical wire test [96], with only 500 W, which simply requires the wire not to burn all the way.

The NFPA Standards Council has stated that NFPA 90A [3] is responsible for requirements for all materials and products in ducts and plenums, but this has been very controversial because it means that the committee responsible for NFPA 90A (a small committee called Technical Committee on Air-Conditioning) mandates requirements for ducts and plenums in all the major NFPA codes (NFPA 70 [1], NFPA 101 [2] and NFPA 5000 [97]).

7.3.2.2 National Life Safety Code

The Life Safety Code (NFPA 101 [2]), in terms of the fire safety of products, addresses, in Chapter 10, interior finish, contents and furnishings. The occupancy chapters, Chapters 11-43, are the ones that reference where the requirements apply. The requirements for interior finish are very similar to those in the IBC and IFC. Each occupancy chapter makes an independent decision as to whether the corresponding committee wants to incorporate requirements for interior finish, but all of them do.

7.3.2.3 Uniform Fire Code

The UFC (NFPA 1) [6] is a blend of two documents, the NFPA Fire Prevention Code (also known as NFPA 1) and the UFC previously issued by the Western Fire Chiefs, which was a partner of ICBO when ICBO issued the Uniform Building Code. The purpose of the UFC, just like the IFC, is to prescribe minimum requirements necessary to establish a reasonable level of fire and life safety and property protection from the hazards created by fire, explosion and dangerous conditions. It applies to both new and existing conditions. The code applies also to vehicles and vessels when they are in a fixed location and are occupied as buildings. The code applies to buildings permitted for construction after the adoption of a particular edition of NFPA 1, but only with the provisions for new buildings. Buildings in existence or permitted for construction prior to the adoption of a particular edition of NFPA 1 must comply with the provisions for existing buildings. Repairs, renovations, alterations, reconstruction, change of occupancy and additions to buildings must comply with both NFPA 101 and the building code. Newly introduced equipment, materials and operations regulated by NFPA 1 need to comply with the requirements for new construction or processes. Smoke testing requirements in the UFC mirror those in NFPA 101 (from which most are ‘extracted’ verbatim), which are similar to those in the IBC and are virtually restricted to interior wall and ceiling finish.

7.3.2.4 National Fire Protection Association Building Code

The NFPA Building Construction and Safety Code or NFPA 5000 [97] is the alternate building code to the IBC. In structure, it is similar to the Life Safety Code (NFPA 101) [2] in that it starts with general requirements and then includes chapters on occupancies. It is also similar to the NFPA 1 [6] and the UFC in that, after Chapter 40 it has specific chapters on individual materials, such as plastics, wood, glass and gypsum board. It also contains a performance option alternative in Chapter 5.

With regard to smoke testing, NFPA 5000 [97] is very similar to the IBC.

7.3.2.5 Buildings of Historic or Cultural Interest

There are two codes addressing buildings of particular interest: NFPA 909 Code for the Protection of Cultural Resource Properties - Museums, Libraries, and Places of Worship [98] and NFPA 914 - Code for Fire Protection of Historic Structures [99]. The intent is for NFPA 909 to address buildings, new or old, that have cultural significance, either because of their contents (museums, libraries and the like) or because they are used for religious ceremonies. On the other hand, NFPA 914 deals with older buildings (or structures) that have some historic significance because of

some particular historic association with the building. In many countries, buildings or structures are entitled to be declared of historic significance if they are > 100 years old. However, not every structure that has survived for 100 years is of historic significance. Usually there is a need for the authority having jurisdiction to make a determination that the building or structure is associated with some historic event or represents some very unusual characteristic that makes it worth preserving (and often expending the necessary funds to update it for fire safety). Libraries, museums and places of worship that are housed in historic structures need to comply with the requirements of both NFPA 909 and NFPA 914. In the NFPA system, the three key codes - the building code, the life safety code and the fire code - all incorporate special considerations for historic buildings that comply with NFPA 914. On the other hand, only NFPA 5000 (the building code) [97] and NFPA 1 (UFC) [6] incorporate requirements for NFPA 909; they say that buildings, structures or spaces that are or contain cultural resource properties must be constructed in accordance with NFPA 909 [98]. In the ICC set of codes, there are no references to either of these codes because the concept of buildings of particular significance is not considered.

The requirements contained in both of these codes tend to represent a lower level of passive fire protection than in other buildings (especially for NFPA 914 [99]) because of the interest in preserving the historic 'look'.

7.3.2.6 Manufactured Housing

Manufactured homes are built and installed to the US Department of Housing and Urban Development's (HUD) Manufactured Home Construction and Safety Standards (MHCSS). The standards address structural, fire safety and energy-efficiency issues and require adequate ventilation. This regulation supersedes local and state building codes and is the current minimum standard that all HUD-code homes are required to meet. The NFPA periodically updates NFPA 501 - Standard on Manufactured Housing [100]. NFPA 501 is the standard currently approved by industry and other stakeholders, but has yet to be officially adopted by HUD. The NFPA standard does not have authority over the older MHCSS regulation but, rather, provides recommendations to HUD. In terms of fire safety, thermal insulation materials other than foam plastics must meet an ASTM E84 Class A requirement (i.e., FSI ≤ 25 and SDI ≤ 450) and loose-fill insulation must meet the same requirements as the building codes have, which are mostly based on smoldering tests (as the materials tend to be cellulosic). Foam plastic insulation must be treated as in the building codes as well: it cannot be used exposed (expensive foam that meets the NFPA 286 [87] test is not used in manufactured housing) and must meet an ASTM E84 Class B requirement behind the thermal barrier.

7.3.2.7 Air-Conditioning Standard

NFPA 90A [3] is a key document because it controls all of the fire safety requirements for ducts and plenums in the NFPA system. The requirements are basically very similar to those in the IMC and the UMC and will not be repeated here. However, it must be noted that NFPA 90A [10] also notes that electrical wires and cables listed to a more severe requirement, UL 2424 [101], can be used without further testing; this is very important because the UL 2424 requirement is based on ‘limited combustible’ cables that have a very low heat content (when tested to NFPA 259 [102]) and a very low smoke release (when tested to ASTM E84); they are almost invariably constructed of fluoropolymer materials, whereas other plenum cables tend to be constructed of fire-retarded materials. NFPA 90A also notes that electrical wires and cables and optical fibre cables installed in metal raceways or metal sheathed cable are not considered to be exposed to the airflow, and need not meet the requirements of NFPA 262 [37]. Plenum cables are permitted to be installed in three of the types of plenums covered by the standard: ceiling cavity plenums, raised floor plenums and air-handling room plenums, but not in apparatus casing plenums or in ducts. The materials of construction of the plenums themselves, and all other plenum or duct contents, must be made of ‘limited combustible’ materials. Finally, ducts and plenums are not permitted to be used for storage. It is worth pointing out that there has been much debate regarding the use of plenum cables, due to various attempts to replace them by cables complying with UL 2424. These efforts have all been unsuccessful.

7.3.2.8 Other National Fire Protection Association Codes and Standards

As discussed earlier, NFPA 130 [5] is another important document because it is used for regulation of train and underground systems, by authorities having jurisdiction over local rail systems in some US, Canadian and Asian systems. NFPA 130 also includes requirements for stations and trainways as well as rail vehicles. The key issues to be considered in stations are the same ones as in other assembly occupancies, namely electrical, interior finish, upholstered furniture, decorations and trash disposal. With regard to trainways, the standard looks at the effect of areas that are potentially concealed spaces and considers that factor.

7.3.3 International Association of Plumbing and Mechanical Officials Codes

Beyond the Western Fire Chiefs Association issuing the UFC, now NFPA 1 [6], another organisation was a partner to ICBO, namely the IAPMO who issued the UMC and the UPC. They continue to be so, but now have an agreement with NFPA so that the UMC and the UPC are NFPA’s equivalents to the ICC codes. The UPC has little, if any, importance with regard to fire or smoke issues.

7.3.3.1 Uniform Mechanical Code

The UMC applies to the addition to or erection, installation, alteration, repair, relocation, replacement, use or maintenance of heating, ventilating, cooling, refrigeration systems, incineration or other miscellaneous heat-producing appliances. It also covers design. In effect, there is a considerable amount of overlap with NFPA 90A [3] and it is very similar to the IMC.

7.4 Standards

7.4.1 Organisations and Committees Issuing Fire Standards or Standards with Fire Tests

As discussed earlier, fire test standards are developed primarily in the United States by ASTM International and by NFPA, although FM Global (formerly Factory Mutual) and UL have also developed some widely used tests. Within ASTM, the following committees have developed fire tests:

- ASTM E05: fire standards (primary fire standards development committee, with subcommittees on smoke and combustion products (which includes heat release), surface burning, combustibility, external fire exposures, furnishings and contents, transportation, large-scale tests and fire resistance)
- ASTM C16: Thermal insulation
- ASTM D07: Wood (primarily subcommittee D07.07)
- ASTM D09: Electrical and electronic insulating materials (primarily subcommittee D09.21)
- ASTM D13: Textiles (primarily subcommittee D13.52)
- ASTM D20: Plastics (primarily subcommittee D20.30)
- ASTM F15: Consumer products
- ASTM F23: Personal protective clothing and equipment (primarily subcommittee F23.80)
- ASTM F25: Ships and marine technology (primarily subcommittee F25.03)
- ASTM F33: Detention and correctional facilities (primarily subcommittee F33.05)

These same committees have also developed some specifications and practices that reference fire tests (and pass/fail criteria) and occasionally also contain some new fire tests. The NFPA Technical Committee on Fire Tests is the developer of all fire tests for NFPA. Two other international organisations are systematic developers of fire tests, most of which are primarily used in Europe: ISO and IEC. Within ISO and IEC, the key technical committees are the following:

- ISO TC92: Fire safety (with subcommittees on fire initiation and growth, fire containment (or fire resistance), fire threat to people and the environment (or smoke toxicity) and fire safety engineering)
- ISO TC61: Plastics (primarily subcommittee SC4)
- IEC TC20: Electric cables
- IEC TC89: Fire hazard testing

There is an agreement between ASTM Committee E05, the NFPA Fire Tests Committee and UL that duplication of fire test standards between those organisations must be minimised.

7.4.2 Standard Test Methods for Smoke Obscuration

Smoke obscuration (reduction in light transmitted) (discussed more broadly in **Chapter 1**) is a serious concern in a fire, because a decrease in visibility reduces the light available, thus hindering both escape from the fire and rescue by safety personnel. The main way in which a fire decreases visibility is through smoke emission. This decrease in visibility is the result of a combination of two factors: how much material is burnt in the real fire (which will be less if the material has better fire performance) and how much smoke is released per unit material burnt.

Despite the understanding that smoke obscuration ought to be measured in a large scale, or by a method that can predict large-scale smoke release, the most common small-scale test method for measuring smoke from burning products is the traditional smoke chamber in the vertical mode (ASTM E662 [24]). The test results are expressed in terms of a quantity called ‘specific optical density’, which is defined in the test standard. This test has now been shown to have some serious deficiencies. The most important problem is misrepresentation of the smoke obscuration found in real fires and for melting materials, such as thermoplastics [103-107]. When materials that melt or drip when exposed to flame are exposed vertically in the smoke chamber test, the molten portions will have escaped the effect of the radiant heat source [108]. This means that some of the material does not burn during the test (and does not give off smoke), suggesting a low test result. In a real fire, all of the molten material will

burn and generate smoke. If these dripping products are exposed horizontally, the entire sample will be consumed and much more smoke will be released. The problem associated with the spread of fire from the flaming melt that occurs when thermoplastic materials have not been properly fire retarded has recently been highlighted by NIST work [109]. An alternate fire test exists also that assesses smoke obscuration in a closed chamber, ISO 5659-2 [30], using a conical heater instead of the traditional ASTM E662 heater. The other alternate static smoke chambers are also used for smoke requirements, as discussed previously: ASTM D2843 [90], used for light transmitting plastics in US codes; NES 711 [40], used for cable insulation and jacket materials in ships; and IEC 61034 [67], used for cables in Europe.

The cone calorimeter (ASTM E1354 [56] or ISO 5660 [110, 111]) is a dynamic flow-through fire test, which can also be used to assess smoke obscuration. The rankings tend to be quite different from those found with any static smoke chamber and are much more realistic.

Beyond the small-scale test methods discussed previously, there are some larger-scale test methods that assess smoke. The key ones are the following: the ASTM E84 Steiner tunnel test [36], the various room-corner tests (NFPA 286 [87], NFPA 265 [88] and ISO 9705 [33]) and the furniture calorimeter (now standardised at NFPA as NFPA 289 [112]).

7.4.3 Standard Test Methods Associated with Smoke Toxicity

Toxic potency values are most often assessed from the most suitable small-scale smoke toxicity (discussed more broadly in **Chapter 2**) test (NIST radiant test, using rats as the animal model, but only for confirmatory purposes, standardised in ASTM E1678 [113] and NFPA 269 [114]). The results from this test have been well validated with regard to toxicity in full-scale fires. However, such validation cannot be done to a better approximation than a factor of 3 [115]. This is illustrated by the fact that the range of the toxic potency of the smoke of almost all materials is so small that it pales in comparison with the ranges of toxic potencies of typical poisons [116]. Consequently, all smoke is extremely toxic, virtually irrespective of the material that is burning. In spite of this, there are several so-called toxicity tests that are simply measurements of concentrations of materials (sometimes with some associated toxicity values), and they tend to be directed toward the elimination of some materials, such as halogenated materials.

There are generally no requirements based directly on smoke toxicity, but it is not uncommon to find requirements that state that a material should be ‘no more toxic than wood’ or that state that the concentrations of a number of toxicants (or of the combination of various toxicants with their assumed toxic potency) must not exceed certain limits, especially in the transportation arena.

7.5 Conclusions

This chapter describes the regulatory (and semi-regulatory) situation, particularly in North America, in the area of smoke testing. In recent years, the key areas where smoke testing is being used most extensively is that of interior wall and ceiling finish materials, insulation materials and products contained in plenums.

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8

Fire Hazard and Smoke Generation

Smoke is an important contributor to fire hazard. Once ignition has occurred, there are three main ways in which fire, regardless of the materials that are burning, can cause harm to people, property or operations. These are, in decreasing order of their importance to fire hazard:

1. Heat or flames spread from the item first ignited to other items, potentially resulting in thermal injury to people, destruction of property or loss of operations;
2. Smoke generation, which obscures vision and can inhibit both the escape of trapped victims and the action of firefighters; and
3. Toxic product generation (gases and particulates in smoke), which can be inhaled by victims and injure them.

However, the key issue in terms of fire hazard is to ensure that a fire remains small and does not become self-propagating. At the very least, it is critical to ensure that flashover does not occur. Flashover is that stage in the development of a contained fire in which all exposed surfaces reach ignition temperatures more or less simultaneously, allowing fire to spread rapidly throughout a space. Preventing flashover requires a good measure of heat release or of the potential for materials and products to release heat in a compartment.

The terms ‘fire hazard’ and ‘fire risk’ are often misunderstood; they have different meanings. Fire hazard is the potential for harm associated with fire, whereas fire risk is an estimation of the expected fire loss that combines the potential for harm in various possible fire scenarios with the probabilities of those scenarios actually occurring. Regarding the latter, what matters is what constitutes an acceptable level of risk, and different individuals or societies presented with the same risk situation may have different opinions on its acceptability. This issue will not be addressed here. Rather, this chapter will simply analyse the importance of smoke as a parameter in fire hazard.

In terms of flame spread and heat release, most materials that exhibit low heat release (and the associated low flame-spread values) do not result in flashover in a room-corner test and can usually be assumed to be safe. **Table 8.1** [1] presents the results of five series of tests that were conducted using room-corner tests and shows that, for 90% of the cases, low heat release is associated with low smoke release, and *vice versa*, so that high smoke release occurs with materials reaching flashover early in those tests. The most interesting phenomenon from the table, however, is that 10% of materials have a high smoke release and very low heat release rate. Analysing all the results mentioned previously, this indicates that:

- 1. Limits for smoke release need to be an integral part of the requirements; and
- 2. Most (but not all) materials performing well in a room-corner test also release low smoke.

Table 8.1 Results of several series of room-corner fire tests				
Room-corner test series	Number of materials tested	Materials reaching early flashover	Materials with adequate heat and low smoke	Materials with adequate heat and high smoke
SwRI [2]	10	1	8	1
EUREFIC [3, 4]	28	14	12	2
Single burning item [5]	30	12	15	3
Coast Guard [6]	9	3	5	1
BFGoodrich [7]	7	1	5	1
Overall	84	31 (37%)	45 (54%)	8 (9%)
SwRI: Southwest Research Institute				
EUREFIC: European Reaction to Fire Classification Project [3]				

National Fire Protection Association, NFPA 555 [8] is a guide that includes information on how to assess or predict heat release in actual fires. It discusses techniques for estimating the heat release rate for various individual items or products in a compartment, based on the results of direct measurements or predictions, since estimates of this rate are critical in predicting whether or not flashover is likely to occur in a compartment.

The American Society for Testing and Materials (ASTM) has also developed guides to assist in evaluating potential for flashover: ASTM E2061 (on rail-transportation

vehicles) [9] and ASTM E2280 [10] (on patient rooms in health care facilities). NFPA 555 [8] gives the following hierarchical order for preferred techniques for assessing the probability of flashover:

1. Full-compartment fire tests with all items contained in the compartment
2. Full-scale fire tests on individual items
3. Tests on large-scale mock-ups of individual items
4. Bench-scale tests with composite samples representing end-use assemblies
5. Bench-scale tests using individual materials
6. Estimation techniques for calculating the heat release rate in the compartment as determined from the results of tests, based on quantitative estimation techniques (preferred option) or relative estimation techniques (least preferred option)

As discussed, it has been shown that heat release techniques can be used to adequately predict the fire performance of several types of products in full scale. However, although the use of full-scale fire tests is the best ‘insurance’ that the test results will accurately indicate of fire performance, it is clear that predictive tests will be used with increasing frequency, as they are much more cost-effective.

The most common predictive models are correlative ones, based on comparing test results in both sets of tests and interpolating the expected test results from the material or product being investigated (which has not been tested in full scale). Such predictions are often very helpful when they are based on variations of a set of materials or products (such as the same material with different sets of additives). They are less helpful when they compare materials with different types of chemical composition, or try to extrapolate results based on data that are not bracketed by full-scale tests already conducted. Other models can be used that consider physical/theoretical aspects of the fire issue and yield results that are not (at least in concept) material-dependent. This approach is much more complex, but has been very successful for simple geometries, such as wall linings/interior finishes.

A common problem in fire testing is that most manufacturers develop materials, which will then become components of composites, products or assemblies. Manufacturers usually have limited control over the ultimate use of their materials, which are combined with other components. However, it is now clear that ‘the sum of the parts’ does not give, in fire testing, an adequate picture of the ‘whole’. Occasionally, an assembly, or composite system, will have better fire performance than expected from individual test results on the component materials. However, more often than

not, test results for individual materials may be adequate to meet the fire safety or smoke release requirements (irrespective of whether regulation is involved), but the combination of materials in a product may generate test results that would ‘fail’ the criteria. In such cases, testing of composite specimens simulating the product intended to be used is essential. Very often, it is not immediately apparent how to conduct testing so that the results are fully representative of the end use, which poses a dilemma for committees developing test methods. In both the European Union and North America, adequate mounting methods for complex products or assemblies are being developed to address this problem, and will then be incorporated into the relevant requirements. It is important to note that simple statements such as ‘testing in the composite form is required’, without further detailed explanations, are of little use and are likely to lead to misinterpretations.

With the preceding thoughts in mind, it is worth considering the importance of smoke corrosivity, smoke toxicity, and smoke obscuration to fire hazard.

Smoke corrosivity: This is a property protection issue and almost never a life safety issue. Smoke corrosivity, which is usually erroneously assessed by measuring acidity (based on pH or on conductivity), can be responsible for damage to essential (and costly) equipment and can cause serious business interruption. It will not cause high heat release because more smoke corrosivity will not make a fire more severe. In fact, ironically, if high acidity is a measure of smoke corrosivity and often results from the large release of acid gases (hydrogen chloride, hydrogen bromide or hydrogen fluoride), such gases serve as scavengers that cause fires to decrease in intensity. Efforts should nevertheless be made to decrease the potential for smoke corrosivity, but this should be done in such a way as not to increase fire hazard and cause additional life-safety concerns.

Smoke toxicity: As discussed previously (see **Chapter 2**), it is well known that about two-thirds of fire victims die of smoke inhalation rather than burns. However, it is also well known that most of these victims die in fires that have become large, with a heat release so high that typically the fire has left the compartment of fire origin. Seminal work by Babrauskas and Peacock [11] showed that whereas doubling the smoke toxicity of materials had no effect on the time to lethality, doubling the heat release rates of materials caused an almost four-fold decrease in the time to lethality. In other words, although smoke toxicity had almost no effect on fire hazard, heat release rate had a massive effect. Other key research has shown that the smoke toxic potency of the vast majority of materials is almost the same and falls within a small range. Efforts should rarely be made to decrease the potential for smoke toxicity, since such attempts are unlikely to have any effect on fire hazard.

Smoke obscuration: This is the key property: reduction in smoke obscuration is essential for fire safety. High smoke obscuration will more than likely result in

disorientation of fire victims (thus slowing down or even preventing their escape) and difficulties for potential rescuers (typically first responders), who may be unable to rescue victims (if they can't find them) and may even become victims themselves (if they become lost). However, reductions in smoke obscuration should be sought intelligently, in the following order:

1. Heat release rate should be minimised
2. Full-scale smoke release should be minimised
3. Small-scale smoke release should be assessed with tests that allow proper predictions of full-scale smoke release
4. High small-scale smoke release should be an indicator of potential concern to be assessed by full-scale tests or predictive models

In conclusion, smoke obscuration is an essential fire hazard property that must be addressed.

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A

bbreviations

2-MN	2-Methylnaphthalene
$2\text{ZnO} \cdot 2\text{B}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$	Zinc borate
ABS	Acrylonitrile-butadiene-styrene
Ace	Acenaphthene
Aceny	Acenaphthylene
ACM	Aluminum composite materials
AFNOR	Association Française de Normalisation
Ant	Anthracene
AOM	Ammonium octamolybdate
APP	Ammonium polyphosphate
ASTM	American Society for Testing and Materials
ATH	Aluminum trihydrate(s) (aluminium trihydroxide)
ATO	Antimony oxide
ATS	Airbus test specification
BaA	Benzo[<i>a</i>]anthracene
BaP	Benzo[<i>a</i>]pyrene
BbF	Benzo[<i>b</i>]fluoranthene
BgP	Benzo[<i>g,h,i</i>]perylene
BkF	Benzo[<i>k</i>]fluoranthrene
Br	Bromine
BSS	Boeing Specification Support Standard
CA TB	California Technical Bulletin
CBHF	California Bureau of Home Furnishings and Thermal Insulation
CFR	Code of Federal Regulations
Chr	Chrysene
Cl	Chlorine

CNET	Centre National d'Etudes Télécommunications
CO	Carbon monoxide
CO ₂	Carbon dioxide
COHb	Carboxyhaemoglobin
CPD	Construction Products Directive
CPSC	Consumer Product Safety Commission
CPVC	Chlorinated polyvinyl chloride
CRF	Critical radiant flux
CSA	Canadian Standards Association (CSA International)
Ct	Concentration time
CTI	Comparative tracking index
Cu	Copper
CuNi	Copper/nickel alloy
DahA	Dibenzo[<i>ab</i>]anthracene
DFIR	Douglas fir wood
DIN	Deutsches Institut für Normung
D _m	Maximum smoke density
D _s	Density of smoke
EPA	Environmental Protection Agency
EPDM	Ethylene-propylene-diene terpolymer
EU	European Union
EVA	Ethylene vinyl acetate
F	Fluorine
FAA	Federal Aviation Administration
FAR	Federal Aviation Regulation
FDI	Flame developed index
FED	Fractional effective dose
FEP	Fluorinated ethylene propylene
FIGRA	Fire growth rate
FIPEC	Fire Performance of Electrical Cables Project
Flu	Fluorine
Fluor	Fluoranthrene
FMVSS	Federal Motor Vehicle Safety Standards
FPA	FM Global fire propagation apparatus

FPI	Fire propagation index
FR	Flame (or fire) retardant
FR	Fire retardant/retarded
FRA	Federal Railroad Administration
FSI	Flame spread index
FTA	Federal Transit Administration
FTP	IMO Test Procedures Code
GWD	Generation without decay
H ₂ O ₂	Hydrogen peroxide
H ₂ S	Hydrogen sulfide
HBr	Hydrogen bromide
HCHO	Formaldehyde
HCl	Hydrogen chloride
HCN	Hydrogen cyanide
HCOOH	Formic acid
HF	Hydrogen fluoride
HIPS	High-impact polystyrene
HNO ₃	Nitric acid
HpCDD	Heptachlorodibenzodioxin
HpCDF	Heptachlorodibenzofuran
HSC	High Speed Craft Code
HUD	Housing and Urban Developments
HVAC	Heating, ventilation and air conditioning
HxCDD	Hexachlorodibenzodioxin
HxCDF	Hexachlorodibenzofuran
IAPMO	International Association of Plumbing and Mechanical Officials
IBC	International Building Code
ICAL	Intermediate-scale calorimeter
ICBO	International Conference of Building Officials
ICC	International Code Council
IEBC	International Existing Building Code
IEC	International Electrotechnical Commission
IEEE	Institute of Electrical and Electronics Engineers

IFC	International Fire Code
IMC	International Mechanical Code
IMO	International Maritime Organisation
IND	Indeno[123- <i>c,d</i>]pyrene
IRC	International Residential Code
I_s	Radiant panel index
ISO	International Organization for Standardization
LC ₅₀	Lethal concentration which results in death of 50% of the subjects tested after 30 minutes
LIFT	Lateral ignition and flame spread test
LOI	Limiting oxygen index
MCM	Metal composite materials
MDH	Magnesium hydroxide(s)
MHCSS	Manufactured Home Construction and Safety Standards
MMA	Methyl methacrylate
MSHA	Mine Safety and Health Administration
M_w	Molecular weight (weight average)
NAP	Naphthalene
NBC	National Building Code
NBS	National Bureau of Standards
NEC	National Electrical Code
NFPA	National Fire Protection Association
NH ₃	Ammonia
NHTSA	National Highway Traffic Safety Administration
NIST	National Institute of Standards and Technology
NO ₂	Nitrogen dioxide
NPRM	Notice of proposed rule making
O ₂	Oxygen gas
OCDD	Octachlorodibenzodioxin
OCDF	Octachlorodibenzofuran
OD	Optical density
OSU	Ohio State University
PAH	Polyaromatic hydrocarbons
PBDD	Polybrominated dibenzodioxins

PBDF	Polybrominated dibenzofurans
PBT	Polybutylene terephthalate
PCDD	Polychlorinated dibenzodioxins
PCDF	Polychlorinated dibenzofurans
PE	Polyethylene
PeCDD	Pentachlorodibenzodioxins
PeCDF	Pentobromodibenzofuran
Phen	Phenanthrene
phr	Parts per hundred rubber
PMMA	Polymethyl methacrylate
ppm	Parts per million
PS	Polystyrene
PU	Polyurethane(s)
PVC	Polyvinyl chloride
PVC-LH	Low halogen polyvinyl chloride
PVC-WR	Polyvinyl chloride for wires and cables
PVDC	Polyvinylidene dichloride
Pyr	Pyrene
RSR	Rate of smoke release
SBI	Single burning item
SDI	Smoke developed index
SMOGRA	Smoke growth rate
SO ₂	Sulfur dioxide
SOLAS	IMO International Convention for the Safety of Life at Sea
TCDD	Tetrachlorodibenzodioxin
TEF	Toxic equivalency factor
THEIC	Tris(hydroxyethyl) cyanurate
UFC	Uniform Fire Code
UL	Underwriters Laboratories
UMC	Uniform Mechanical Code
UPC	Uniform Plumbing Code
USCG	United States Coast Guard
ZB	Zinc borate(s)
ZnO	Zinc oxide

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