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Flame Retardants and Heat Release
by
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(Fire and Materials Journal, 2015)

Flame retardants and heat release: review of traditional studies on products and on groups of polymers

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SUMMARY

This is part of a project considering whether flame retardants affect polymer heat release, a critical issue to assess whether adding flame retardants decreases fire hazard. The work investigated the following. (1) Fire properties affecting fire hazard, confirming that heat release rate is the key fire property most strongly influencing fire hazard. (2) Ways to assess heat release and whether full-scale fire heat release rate can be predicted from small-scale test results, confirming that cone calorimeter and Ohio State University data are adequate to predict full-scale heat release. (3) Analysis of key 1988 NBS/NIST study comparing the fire hazard of flame retarded products versus non-flame retarded products for the same application. This confirmed that the study demonstrated that flame retardants lower fire hazard and that the levels of additives in the flame retarded products used were not excessive. (4) Review of studies investigating effects of flame retardants on various polymeric systems. The overall conclusion is that flame retardants does indeed improve fire safety (when used appropriately) primarily because they decrease heat release. Part 2 of the project (separately) considers the key polymers that need to be potentially flame retarded and reviews recent studies on effects of flame retardants on heat released by such polymers. Copyright © 2014 John Wiley & Sons, Ltd.

1. INTRODUCTION

Fire safety can be improved in one of two ways, or via a combination of both, as shown later. This work will address exclusively passive fire protection.

- Passive fire protection. This means using materials and products with superior fire performance so as to either minimize the probability of ignition or, if ignition does occur, minimize the damaging effects of the resulting fire.
- Active fire protection. This means relying on fire detection and suppression systems (such as smoke alarms and sprinklers). Fire detection systems alert the occupants (and/or first responders, such as fire fighters) while fire suppression systems extinguish the fire.

Flame retardants are materials that can be incorporated into combustible materials to improve their fire performance. It has been shown in many studies that flame retardants can be effective in having effects such as making materials or products less easily ignitable and/or reducing flame spread and they are extensively used to help materials and/or products meet certain fire test requirements. In view of the fact that there is no fire if ignition does not occur, a delay in ignition will improve fire safety. However, because fire hazard assumes that ignition has occurred, it is important to also study the effects of flame retardants on fire hazard, with an emphasis on the key property of heat release, as explained later.

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Fire risk is the combination of fire hazard and of the probability of fire occurring. Fire hazard is defined as 'the potential for harm associated with fire'. Fire risk is defined as 'an estimation of expected fire loss that combines the potential for harm in various fire scenarios that can occur with the probabilities of occurrence of those scenarios'. It is essential to understand that it is possible to have high fire hazard but low fire risk because the probability of such a fire is low.

Most, if not all, solid combustible materials (plastics, wood, textiles, rubbers, and so on) are polymeric (meaning that they have a complex chemical structure, with repeating units). Many polymeric materials, whether natural or synthetic, have poor fire performance in the absence of added flame retardants. That is particularly important for those polymers that are in widest use, such as polyolefins (polyethylene or polypropylene), polyurethane, polystyrene, polyethylene terephthalate, nylon, and cotton. When a polymer is used in applications where fire safety is an important consideration, the lack of intrinsic fire safety must be addressed for ensuring passive fire protection. The following are examples of different approaches:

- adding flame retardants (i.e., using additive flame retardants),
- creating new polymers with better fire performance though syntheses of variations of the polymer (i.e., using reactive flame retardants),
- blending or otherwise compounding it with other polymers with better fire performance (i.e., creating blends or mixtures), and
- encapsulating the polymer or separating it from the potential exposure to the heat insult.

This study is looking primarily at the first aspect, namely additive flame retardants and fire hazard, mainly because more information is available on them. Information on direct comparisons of heat release between a flame retarded system with reactive flame retardants and the equivalent non-flame retarded materials is rarely published. Typical applications where fire safety can be critical are upholstered furniture, mattresses, wire and cable, interior finish, insulation, appliance and computer housings, among others.

This work presents information on a few key studies that investigated the potential effects of using flame retardants (whether additive or reactive) in order to improve the fire performance, with an emphasis on heat release, of polymeric materials. Such analyses will be primarily based on individual polymers. One portion of this study involves a new discussion of an essential study conducted at NBS (precursor of NIST) in 1988 analyzing the effects of flame retardants on the fire performance of five important consumer products: TV cabinet housings, business machine housings, upholstered chairs, cable arrays, and laminated circuit boards. This particular study has been misinterpreted recently.

A separate publication will review recent studies of heat released by individual polymers before and after the addition of flame retardants [1].

2. HEAT RELEASE RATE AND FIRE HAZARD

Until relatively recently, heat release rate measurements were seen by some people as just another piece of data to gather. In fact, the importance of heat release as a fundamental fire safety property is still not a full part of the public understanding of fire safety. However, fire scientists have now concluded that heat release is much more than a set of data. It has been shown by multiple analyses of fire hazard that heat release rate is the most important fire property and that the peak heat release rate is the numerical indicator of the intensity of a fire [2–8]. Key studies have demonstrated that heat release rate is much more critical than either ignitability (whether expressed as time to ignition or minimum heat flux for ignition) or smoke toxicity in affecting the probability of survival in a fire, as shown later in this work [2].

The key demonstration that heat release rate is much more important than other fire properties in terms of fire hazard can be seen from Table I [2]. In the work, a simple analysis was made (using the fire hazard zone model HAZARD I) where the authors considered variations on a fire scenario in which a single upholstered chair burns in a small room with a single doorway opening. They calculated the hazard for the scenarios in terms of the predicted time to lethality. Fire properties of the burning chair in the base case were taken directly from typical such fire properties in the NIST data base. In order to assess the relative importance of several factors, the authors studied the following variations:

Table I. Effect of individual variables on fire hazard, example of chair [2].

Scenario	Predicted time to lethality (s)
Base case	Greater than 600
Double heat release rate	180
Double material smoke toxicity	Greater than 600
Halve time to ignition	Greater than 600

(1) base case, that is, a single burning chair in the room,
(2) the same chair with double the heat release rate,
(3) the same chair with double the smoke toxicity of the materials, and
(4) the same chair with half the time to ignition for the burning chair (from 70 to 35 s).

The authors considered the predicted temperatures and the levels of carbon dioxide in the compartment's upper layer. They chose carbon dioxide (instead of other gas species) because it has been shown that the carbon dioxide concentration is representative of the type and shape of the concentration-time curves for other gases. The results demonstrated that, as expected, changing the heat release rate has a much greater effect on fire hazard than changing the time to ignition or the smoke toxicity. The authors note that, of course, a significant improvement in time to ignition can lead to the absence of a fire; however, that affects fire risk and not fire hazard, because fire hazard presupposes that ignition has occurred. The effects of the changes in the three variations from the base case can be seen in Table I. The conclusions of this work is that doubling the heat release rate reduces the predicted time to lethality from greater than 600 s (the total simulation time) to about one third of that time, roughly the same time as the calculated time to incapacitation for all other scenarios. On the other hand, the effects of similar changes in time to ignition and in smoke toxicity have a negligible effect on predicted time to lethality. Note, that it is, of course, not always possible (or perhaps never possible) in practice to change one of the three variables (heat release rate, time to ignition, and smoke toxic potency) completely independently, without affecting the others. However, that in no way affects the data analysis and conclusions.

In simpler terms, heat release rate is critical because, as the heat release rate becomes larger, more materials will ignite and burn and will propagate the fire. On the other hand, if heat release rate remains small, it is possible (or even likely) that the next product will not ignite and that the fire will be confined to the area (or even the object) of origin. Thus, a higher heat release rate will promote faster flame spread. On the other hand, neither increased smoke obscuration nor increased smoke toxicity will cause a fire to become bigger.

It is essential to understand the concept that heat release rate if the most important fire safety property because a distinction needs to be made between (a) the reason a fire becomes big and results in large losses (including fire fatalities, fire injuries, and significant property loss) and (b) the actual 'cause of death' for a fire fatality. The two are different.

In order to understand this, it is important to review the concept of flashover, defined by the Life Safety Code as 'A stage in the development of a contained fire in which all exposed surfaces reach ignition temperature more or less simultaneously and fire spreads rapidly throughout the space.' In actual practice, fire statistics classify any fire that goes beyond the room of origin as a 'flashover fire' [9], because typically additional details are not available and because a fire that has gone beyond the room of origin has clearly been a very large fire. Thus, it should be noted that future descriptions in this work will talk about 'flashover fires' when the fire is either known to have gone to flashover or known to have gone beyond the room of origin, without distinction. In the USA, the vast majority of fire fatalities occur away from the room of fire origin (i.e., have been classified as flashover fires because they extended beyond the room of origin [9]).

At the moment when fires go to flashover, the concentration of combustion products (i.e., toxic gases) accelerates significantly, so that there is both a quantitative and a qualitative difference in the toxicity of the atmosphere as soon as the fire becomes a flashover fire. That is one of the key reasons why the toxicity of a fire atmosphere is much more toxic after flashover [7,9].

On the other hand, the 'cause of death' (in the USA) is usually listed as 'the effects of smoke inhalation'. This means that the listed 'cause of death' is, more often than not, the direct result of insult by smoke and toxic gases, while the actual cause of death is that the fire became large (typically a flashover fire) because the heat release rate was large. Thus, the size of the heat release rate is the best predictor of the fire hazard that caused a fire to become big. If a fire stays small (i.e., has a low heat release rate), it is unlikely to lead to significant numbers of fire fatalities. Thus, the relative toxicity of the gases emitted in fires (smoke emissions) plays a small role in fire hazard. For the reason indicated earlier, the examples shown in this work will primarily address heat release.

In some publications, it is stated that smoke toxicity is a measure of fire hazard: that is incorrect. The literature shows that the principal toxicant dominating smoke toxicity is carbon monoxide, found in all fires. In that connection, it is worth looking at toxic potency of smoke data, and Figure 1 illustrates that the toxic potency of the smoke of virtually all individual polymers is within such a narrow band (in toxicological terms) as to be almost indistinguishable [10]. In particular, this work showed that the smoke toxicity of all polymeric materials (including those releasing irritants) can be assessed together based on the lethal effective dose and that there is no need to introduce the flawed concept of fractional effective concentration (which assumes that victims are *instantly* incapacitated when a certain concentration of an irritant is reached). The latter concept is used by some toxicologists as a way to deal differently with polymeric materials containing heteroatoms, such as halogens or nitrogen. While academically potentially interesting, the technical literature and the practical reality of fires show that this is a flawed concept for predicting human survivability in fires. The work mentioned earlier [10] reviewed toxicity studies, including some performed by exposure of animals and people, in the late 19th century and early 20th century, to irritant gases alone or by their exposure to smoke containing them. The critical issue found was subject behavior and whether
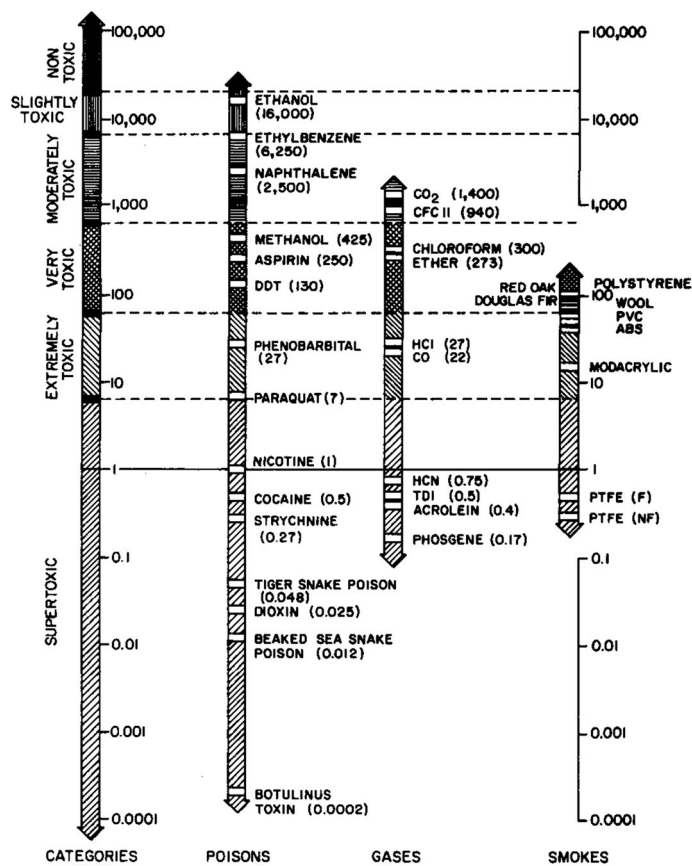

Figure 1. Levels of smoke toxicity (in orders of magnitude) [10].

incapacitation or lethality occurred eventually. It was found that rats and baboons were not incapacitated at huge concentrations of irritants (and in fact sometimes, they died a long time after exposure, but they were able to perform the escape functions that they were taught to do, to escape from their exposure). Moreover, the volunteer humans were also neither incapacitated nor killed. This showed that irritants do not usually cause incapacitation, even at concentrations that may eventually kill the victims.

3. USE OF THE CONE CALORIMETER AS A FIRE HAZARD PREDICTIVE TOOL

The cone calorimeter is a specialized piece of fire test equipment that is used to assess heat release data, as well as ignitability, mass loss, and smoke released by burning materials. There have been a large number of studies that have demonstrated that the cone calorimeter (ASTM E1354 [11]) can be successfully used for many products to predict full-scale (or at least relatively large scale) fire performance of the corresponding products. The most widely studied products are wires and cables, upholstered furniture, mattresses, wall linings, and aircraft panels.

The fire performance of wire and cable products is probably the one that has been investigated most extensively, usually in comparison with vertical cable tray tests, such as the UL 1685/CSA FT4 test [12–14]. One study looked at materials used in cable jackets and insulations, where a variety of different polymers were included. Tests were conducted in the cone calorimeter and in a vertical cable tray test [15]. The results showed that there is excellent correlation (Figure 2) between the cone calorimeter peak heat release rate (on the one hand) and tray cable heat release rate and tray cable char length (on the other hand). Tray cable char length was assessed because it is the typical property measured in tray cable tests. In particular, both ways (cable tray char length and cable tray heat release) of assessing the fire performance of the cables at a larger scale indicate the same trend. In fact, whichever way the data are analyzed, there is a steady increase in cable tray heat release with cone calorimeter heat release at low heat release values and then a leveling off of cable tray heat release (which in the cable tray test is a result of the full consumption of the cables). Similar information was also obtained by another study [16], which focused exclusively on PVC-based cables. These two studies are part of a series of studies, summarized in subsequent work [17], that have established that the cone calorimeter is fully suitable as a predictive tool for electrical cables (see, e.g., Figures 3–5). The figures show how predictions can be made from cone test results. This is important because it allows trends obtained in cone calorimeter tests to be indicative of trends in full-scale fire tests with cables.

A similar type of prediction results from analyzing data from the cone calorimeter on tests of upholstered furniture composite tests [18]. The Association of Contract Textiles/Decorative Fabrics Association (ACT/DFA) study was intended to investigate whether the cone calorimeter could be
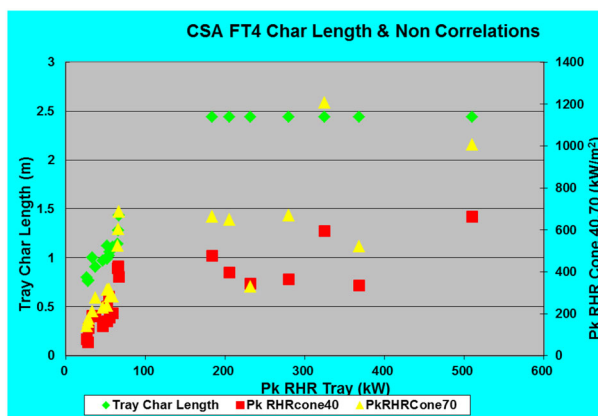
Figure 2. Char length for cables in the vertical cable tray test (UL 1685/CSA FT4) and peak heat release rate in the cone calorimeter as a function of cable tray peak heat release rate [13].

Predictions from Cone Calorimeter
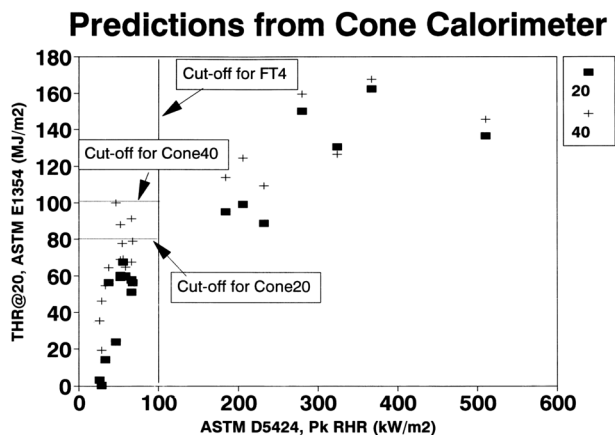
Figure 3. Comparison of flame spread in tray tests with char length and heat release rate [17].

ASTM D5424 and E1354 Cable Tests
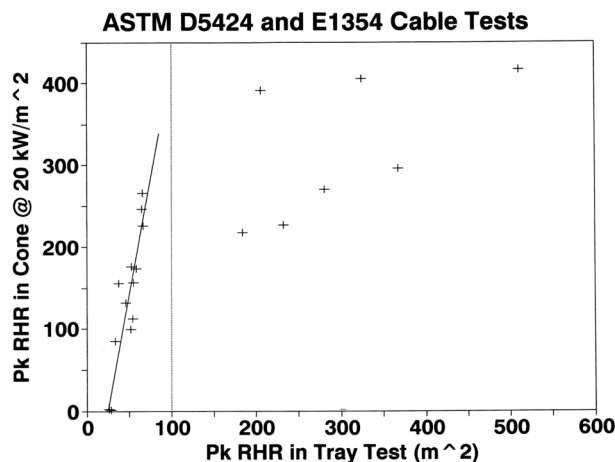
Figure 4. Comparison of peak heat release rate in cone and vertical cable tray test [17].

Predictions from Cone Calorimeter
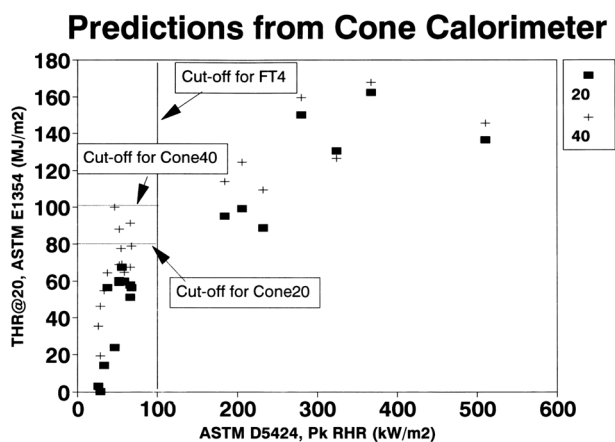
Figure 5. Indication of vertical cable tray test results predicted from cone test results [17].

used to predict CA TB 133/ASTM E1537 [19, 20] data. They chose 26 upholstery fabrics, representative of the most widely used compositions and weights, and conducted cone calorimeter tests, at an initial test heat flux of $35\,kW/m^2$, with tests in the horizontal orientation. They also ran

full-scale ASTM E1537 tests, using the California room. The data were not analyzed directly by ACT/DFA but were analyzed later by a different author [18]. The samples were prepared as recommended by the Combustion Behaviour of Upholstered Furniture (CBUF) project of the European Union (EU) [21]. The fabrics (with a very broad weight range) were all tested on a conventional slightly flame retarded polyurethane foam (complying with CA TB 117 [22]), weighing approximately 1.4 lb./ft^3, and an interliner, as well as on a highly flame retarded formulation containing high levels of melamine. The two interliners used were a polyaramid weighing approximately 2 oz./yd^2 and a coated glass weighing approximately 10 oz./yd^2. Soon after the ACT/DFA work was completed, NIST conducted a study with 27 fabric/barrier/foam systems that were tested in the cone calorimeter and in the CA TB 133/ASTM E1537 test [23]. The analysis of the ACT/DFA work [18] included consideration of the NIST results also.

The full-scale testing for this furniture work was conducted using the standard mock-up cushions, constructed with thread recommended by the manufacturers of the interliners. There was no replication of full-scale work. Several predictive equations and approaches to fire safety correlations were investigated, including one proposed by NIST when they compared work in two standard rooms (California and ASTM) [24]. The NIST equation [24] assumed that the key cut-off, when the full-scale construction is a standard mock-up, should be for systems with a 3 min average cone calorimeter heat release rate of 160 kW/m^2; as shown later, that value is too high. However, a system was proposed [18] that resulted in better predictions. With that system, in some cases, the cone calorimeter erroneously labeled as unsafe systems (i.e., fabric/foam or fabric/barrier/foam combinations), which were found to be safe in full-scale testing, but in no cases did the cone calorimeter predict satisfactory performance for systems that failed large-scale tests. This was an improvement over the NIST recommendations [24]. When using the NIST suggestions, as expanded to more systems, eight systems (out of 27) were predicted to perform well (from cone calorimeter data) but actually had poor fire performance in the full-scale test. Four of the eight systems incorrectly predicted contained melamine foam (which was only adequately predicted in two of six systems). In the case of one system that performed badly (although the cone data did not predict that), the repeat full-scale test performed well. The results are partially invalidated by the fact that plastic (nylon) zippers were used in several systems, a construction feature known to make systems perform badly. As a summary of this analysis, the cone calorimeter correctly predicted whether 67 of the 78 ACT-DFA systems would cause a self-propagating fire (86%) and whether 19 of the 27 NIST systems would cause a self-propagating fire (70%). If the melamine foam systems are excluded, the analysis predicted adequately 49 out of the 52 ACT-DFA systems (94%) and 16 out of the 20 NIST systems (80%). The threshold value estimated by NIST (a 3 min average heat release rate of 160 kW/m^2) does not use the cone calorimeter as a direct predictor of full-scale heat release rate but rather as an indicator of the probability of a system to be made into a safe item of upholstered furniture. The results of this flawed 'correlation' are shown in Figure 6.
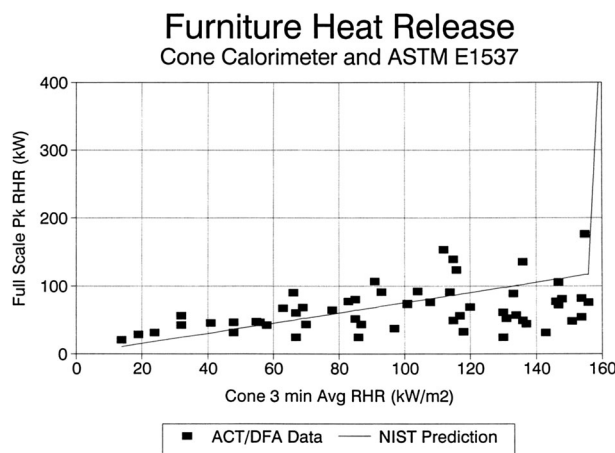

Figure 6. Prediction of CA TB 133 test results from cone calorimeter [17].

Figure 7 indicates that there is a 'safe zone' (based on heat release) for which furniture upholstery systems are likely to lead to safe constructions, within a reasonable probability.

The European study mentioned earlier (the CBUF project [21]) predicted that systems with average rate of heat release $\leq 65 \, kW/m^2$ would not cause self-propagating fires; all 12 systems complying with that criterion in the ACT-DFA study gave good full-scale results. The conclusion from the ACT/DFA work was that the cone calorimeter could be used as a surrogate test method to assess whether systems are likely to cause a self-propagating fire or whether they are safe. An important secondary finding was the realization that the fabric has a much greater effect in cone testing than in real-scale fires. The majority of predictive errors from the cone calorimeter are false positives, meaning materials that perform adequately in large-scale tests are falsely predicted to fail by cone data; these errors do not negatively affect fire safety.

Similar work to the furniture work discussed earlier was also performed for mattresses [25], for a series of wall linings in Europe [26], and for a series of special wall linings, namely aircraft panels [27]. In the case of mattresses, the transition region in the cone calorimeter is still at roughly the same 3 min average value for heat release rate as for upholstered furniture: $100–200 \, kW/m^2$ average (3 min). The corresponding equation is similar to that for upholstered furniture. However, experience has shown that bedding (such as sheets and blankets) can substantially affect heat release from mattresses, particularly when the actual mattress has fairly poor fire performance. Thus, in general, tests with mattresses and bedding are of particular interest for systems with fairly high heat release rate values. With regard to wall linings, it is interesting to note that the aircraft cabin wall lining data and actual room wall lining data (from a European project using the ISO 9705 room–corner test [28]) can both be correlated with a simple empirical equation, a first order approximation for relative time to flashover in a room–corner scenario. This information was generalized in a study that addressed several different products [29]. The predictive equation for relative time to flashover based on cone calorimeter data at an incident heat flux of $50 \, kW/m^2$ suggests that time to flashover is proportional to the ratio of time to ignition to peak heat release rate, a ratio sometimes called the fire performance index or FPI [30]. An example using the aircraft panel and European wall lining data is shown in Figure 8 [29]. Figure 9 shows that the cone calorimeter can even be used to predict zones of flashover potential for wall and ceiling linings based on a fire model, such as the one by Karlsson [31] instead of a simple correlation like Figure 8.

It has also been shown that the computer model Conetools [32], developed at SP (in Sweden), serves as a useful means to predict ISO 9705 room–corner fire test results for wall linings from small-scale fire test results in the cone calorimeter (e.g., [33]). Additionally, the work just cited and other scientific work also showed [33, 34] that the use of the cone calorimeter and Conetools can, in a preliminary fashion, help to predict results for wall linings in the European regulatory single burning item test (SBI test, EN 13823 [35]).
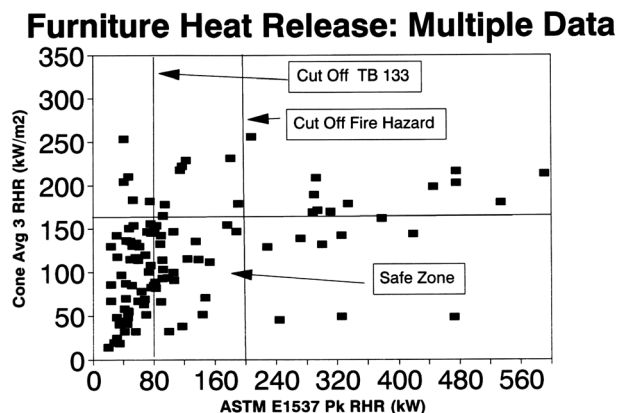
Figure 7. Predictions of full-scale furniture test data showing safe zone [17].
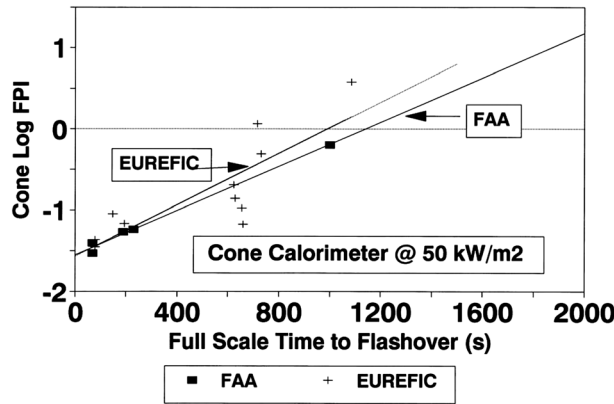
Figure 8. Comparison of wall linings (EUREFIC) and aircraft panels (FAA) full-scale test results with fire performance index predictions from cone calorimeter [28].
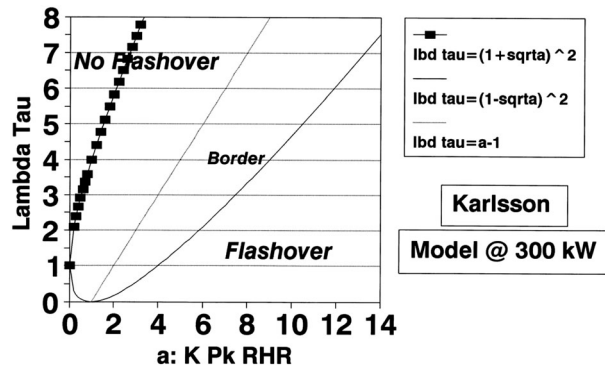
Figure 9. Safe zone predictions in wall linings based on Karlsson model and cone calorimeter data [28].

In conclusion, even from the limited amount of work discussed here, it is clear that the cone calorimeter can be used appropriately to assess fire performance of materials and products, and this will be performed in subsequent sections.

4. OTHER SMALL-SCALE HEAT RELEASE TESTS USEFUL AS PREDICTIVE TOOLS

The cone calorimeter (ASTM E1354 [11], ISO 5660 [36]) is a key tool for small-scale testing of materials, composites, and products to assess heat release rate. However, it is not the only such test, and two other key small-scale tests can be used to test materials for heat release: the Ohio State University (OSU) heat release rate calorimeter (Smith [37], ASTM E906 [38], FAA Aircraft Materials Fire Test Handbook Chapter 5 [39]) and the FM Fire Propagation Apparatus (Tewarson [40], ASTM E2058 [41], FM FPA). In this study, some OSU work will be discussed here but no specific FM FPA work.

In the past, a large number of fire tests or techniques have been used, and many are still being used, to measure various individual properties associated with the fire performance of materials (and sometimes products). The measurement of single properties is inconsistent with the concept of fire hazard, because fire hazard is associated with the combination of a multitude of fire properties, including the ignitability of a material, its flammability, the amount of heat released from it when it burns, the rate at which this heat is released, the rate at which the material is consumed, the smoke production tendency, and the intrinsic toxic potency of the smoke. In 1972, Edwin Smith published detailed information on one test method (OSU heat release rate apparatus) that is capable of

measuring combined properties including heat release [37]. Such combined properties are thus more directly associated with fire hazard than any individual fire property. Hirschler and Smith [42] correlated data from the OSU with data from a full-scale non-standard room–corner test (Table II), showing a reasonable degree of predictability from the test, in that materials showing high heat release in the OSU also show high heat release in the room and vice versa.

In much more extensive (and predictive) studies, the OSU was used by the Federal Aviation Administration (FAA) in order to correlate material (and composite) data with data from full aircraft burns [43]. The FAA established a four-part research program to define how heat release criteria would provide appropriate safety guidance. The concept was to see whether this could then be incorporated into regulations to ensure fire safety. Using time to flashover as the primary end-point, the FAA work established a full-scale aircraft post-crash scenario to evaluate and 'rank' the fire performance of the aircraft interior materials, while monitoring all major fire properties [44]. Then, the FAA evaluated and 'ranked' a group of five representative generic cabin interior wall panel constructions in the full-scale aircraft fire test scenario [45]. Subsequently, the FAA established a series of input conditions and pass/fail criteria using the OSU test to obtain results that could be used to 'rank' the five materials in the same order as they were ranked by the full-scale tests [46]. Finally, NIST and FM Global were commissioned to investigate whether the cone calorimeter (at NIST) and the FPA apparatus (at FM Global) would give reasonably correlated results: they gave the same type of rankings as the OSU, even if they gave different absolute numbers. The result of this work was the development of pass/fail criteria of $65\,kW/m^2$ peak heat release rate and $65\,kW\,min/m^2$ average total heat released after 2 min of test in a 5 min test in the OSU, at an incident heat flux of $35\,kW/m^2$. This reliance on heat release rate has proven to be extremely effective, and a July 2013 post-crash aircraft fire is an example of its effectiveness: an Asiana jet crashed in San Francisco airport with 307 people on board and no fire fatalities (although three passengers died of other injuries [47]).

5. NBS/NIST FULL-SCALE STUDIES ON FLAME RETARDED PRODUCTS

Much of the research on flame retarded materials has focused on individual materials or on products that contain them. The potential synergy between flame retarded materials in a room fire scenario is less well documented. In other words, the question is does individual product protection add up to a greater protection in a room containing several disparate product types? In an attempt to document

Table II. Comparison of heat release in OSU and room–corner test [42].

	Pk HRR OSU	THR OSU at 10 min	OSU heat flux	THR full
	kW/m^2	MJ/m^2	kW/m^2	MJ
Natural wood oak panel	74	24.8	30	90
Natural wood oak panel	121	30.2	41	90
FR ABS	112	13.6	30	70
FR ABS	264	29.9	41	70
Polycarbonate	211	31.2	30	134
Polycarbonate	434	102.2	41	134
FR Acrylic	37	9.2	30	37
FR Acrylic	52	17.9	41	37
Generic PVC	96	21.4	30	30
Generic PVC	109	24.8	45	30
Low smoke PVC	23	6.9	30	30
Low smoke PVC	70	29.3	45	30
CPVC	20	6.3	30	28
CPVC	20	6.3	41	28
Full-scale ignition source				*33*

Notes: Pk HRR OSU, peak heat release rate from Ohio State University (ASTM E906) heat release test; THR OSU, total heat released during Ohio State University heat release test; THR full, total heat released during full-scale room–corner test.

and understand this, NIST (then NBS) conducted a study in 1988 [48]. This seminal study went beyond just investigating the effects of flame retardants on improved fire safety for individual materials and products but looked at a full set of flame retarded materials, their use in products and a comparison with the corresponding non-flame-retarded materials.

The study involved five different product categories, which were assembled and tested in small-scale and in full-scale room fires. In one set of products, all five products were made with flame retarded materials, whereas in the other set, the same base polymers were used but without flame retardant additives. The products involved were (in the order in the report) the following: (1) television housings, (2) business machine housings, (3) upholstered chairs, (4) electric cable arrays, and (5) laminated electronic circuit boards. These products were studied thoroughly in full-scale fires, in bench-scale fire tests, and by computer modeling.

The objective of this study was to investigate the fire hazard of a wide array of flame retardant containing products relative to non-flame-retarded but otherwise substantially identical products. The question to be answered was whether the fire hazard is reduced. The flame retarded formulations were chosen, in accordance with the report, to represent ones that are (or were, at the time) commercially available and in common use, but which were anticipated to represent high quality performance. None of the systems was designed to provide exceptional fire performance.

In this publication, it was believed essential to retain, as much as possible, the language from the original NBS/NIST publication, from 1988, demonstrating that the systems were designed to provide adequate fire performance, within the state-of-art of the time. The executive summary states as follows: 'the two central issues to be explored were:

"(1) For today's most commonly used FR/polymer systems, is the overall fire hazard reduced, when compared to similar non-fire retarded (NFR) items?"
"(2) Since both the commercially popular FR chemicals and the base polymer formulations can be expected to change in the future, can appropriate bench-scale test methodologies be validated which would allow future testing to be quick and simple?"'

The executive summary continues with the following statement regarding approach. 'To answer these questions, a wide-ranging experimental program was formulated. Five representatives of commonly used plastic products were especially manufactured (using commercial formulations) for this program, each in an NFR and an FR version.' Note that the approach addressed 'commonly used plastic products' and 'commercial formulations' and that there was no intent to meet any specific regulatory requirement.

The formulations used were the following:

(a) TV cabinet housing: High impact polystyrene in both sets. The FR System was composed of 12% of a brominated material (decabromobiphenyl oxide) and 4% antimony oxide.
(b) Business machine housing: Polyphenylene oxide in both sets. The FR System was composed of triaryl phosphate ester for 1% P.
(c) Upholstered chair: Flexible polyurethane foam padding and the same nylon cover fabric ($250\,kg/m^2$) for both sets. The non-FR foam had a density of $25\,kg/m^3$, and the FR system contained an organic chlorinated phosphate, an organic brominated flame retardant, and 35% alumina trihydrate, for a content of 4.75% Br, 2.6% Cl, 0.32% P, and 10.0% Al and a density of $64\,kg/m^3$. The FR system was intended to perform better than foam intended for CA TB 117 use but was probably not as good as a BS 5852 crib # 5 foam.
(d) Cable array: Each electric cable contained five conductors (copper wires, 14 AWG, 1.63 mm diameter) with insulated wire outside diameter of 3.30 mm. The outside diameter of the jacketed cable was 12.7 mm. The same wire jacket was used in both sets, and it was a black chlorosulphonated polyethylene containing antimony oxide (12.2% Cl and 2% Sb). The insulation of the non-FR system was cross-linked ethylene vinyl acetate (EVA) copolymer with clay (18.9 phr), antioxidant (2 phr), processing aid (1 phr), and catalyst (1.5 phr). The FR system was cross-linked EVA copolymer with clay (28 phr), chlorinated cycloaliphatic flame retardant (38 phr), antimony oxide (18.9 phr), antioxidant (2 phr), processing aid (1 phr), and catalyst (1.5 phr). The FR system was probably intended to represent a vertical tray cable composition. It would not have complied with riser of plenum cable requirements.

(e) Laminated circuit board: This material was intended to represent glass/polyester electric circuit boards but contained no copper or electrical components. The board was 6.4 mm thick. The polymer in both systems was polyester resin. The non-FR system contained 38 wt% polyester, 44 wt% calcium carbonate, and 18 wt% fiberglass reinforcement. The FR system contained 39 wt% polyester, decabromobiphenyl oxide (10 wt%), antimony oxide (3 wt%), and alumina trihydrate (30 wt%) and 18 wt% fiberglass reinforcement. It was probably intended to represent a UL 94 V0 compound.

Tables III and IV contain the cone calorimeter data for the various products at two different incident heat fluxes. Clearly, flame retardants had a significant effect on heat release rate and effective heat of combustion. Furniture calorimeter tests (i.e., tests in which the product is placed on a load cell under a hood and the heat and smoke released are assessed) were conducted on all products. A natural gas burner with a nominal face of 180 mm × 150 mm and operating at 50 kW for 200 s was used for most tests, except for the cable products, in which case a line burner 0.36 m long with the same flow of natural gas was used. Table V shows the furniture calorimeter data. Once more, the improvement due to the flame retardants is very significant.

Table III. Cone calorimeter data of NBS/NIST products (30 kW/m^2 heat flux) [48].

Material	FR or NFR	Pk HRR (kW/m^2)	Effective heat combustion (MJ/kg)
TV cabinet	NFR	970	30
TV cabinet	FR	340	12
Bus. machine	NFR	650	30
Bus. machine	FR	280	21
Chair (fabric/foam)	NFR	470	27
Chair (fabric/foam)	FR	290	18
Chair (foam only)	NFR	540	27
Chair (foam only)	FR	180	15
Cable (jacket/insulation)	NFR	360	28
Cable (jacket/insulation)	FR	380	23
Cable (jacket)		270	23
Cable (jacket)		280	23
Cable (insulation)	NFR	740	39
Cable (insulation)	FR	260	23
Circuit board	NFR	250	21
Circuit board	FR	100	13

Notes: Pk HRR, peak heat release rate from cone calorimeter heat release test; NFR, non-flame retarded product; FR, flame retarded product.

Table IV. Cone calorimeter data of NBS/NIST products (100 kW/m^2 heat flux) [48].

Material	FR or NFR	Pk HRR (kW/m^2)	Effective heat combustion (MJ/kg)
TV cabinet	NFR	1400	29
TV cabinet	FR	480	10
Bus. machine	NFR	1100	29
Bus. machine	FR	570	20
Chair (fabric/foam)	NFR	1460	28
Chair (fabric/foam)	FR	760	18
Chair (foam only)	NFR	1580	29
Chair (foam only)	FR	310	14
Cable (jacket/insulation)	NFR	550	26
Cable (jacket/insulation)	FR	380	21
Cable (insulation)	NFR	1280	38
Cable (insulation)	FR	490	21
Circuit board	NFR	250	18
Circuit board	FR	147	14

Notes: Pk HRR, peak heat release rate from cone calorimeter heat release test; NFR, non-flame retarded product; FR, flame retarded product.

Table V. Furniture calorimeter data of NBS/NIST products [48].

Material	FR or NFR	Pk HRR (kW)	Effective heat combustion (MJ/kg)
TV cabinet	NFR	515	23
TV cabinet	FR	180	20
TV cabinet	FR	175	20
Bus. machine	NFR	560	24
Bus. machine	FR	380	28
Chair (fabric/foam)	NFR	1160	26
Chair (fabric/foam)	NFR	1205	27
Chair (fabric/foam)	FR	50	No data (too low)
Cable (vertical)	NFR	400	41
Cable (vertical)	FR	75	No data (too low)
Cable (jacket, vertical)		140	34
Cable (Z configuration)	NFR	245	35
Cable (Z configuration)	FR	130	34
Circuit board	NFR	205	18
Circuit board	FR	100	No data (too low)

Notes: Pk HRR, peak heat release rate from furniture calorimeter full-scale heat release test; NFR, non-flame retarded product; FR, flame retarded product.

In order to analyze the data for all products together, the full set of NFR products were set in an array as shown in Figure 10 and in a room–corridor arrangement as shown in Figure 11. The small-scale and furniture scale calorimeter data (Table V) predicted that the chair would ignite with the small 50 kW burner (on for 200 s) and then spread flame to get the other items ignited. When the same data were used for the FR products, the furniture calorimeter information showed that if the same array was used as used for the NFR products, only the TV cabinet and the chair would ignite, and the heat release/flame spread would originate virtually mainly from the burner and the TV and would give very low mass loss rate and would not contribute significantly to the fire buildup. Thus, it became clear to NBS/NIST that the array used for the NFR products would not be suitable to burn the FR products and that an auxiliary burner (120 kW, on for 2100 s, starting 300 s before the ignition of the 50 kW burner) would need to be used to avoid finding no flame propagation at all. Therefore, the arrangements shown in Figures 12 and 13 were used. The summary of the key data from the two sets of burns is shown in Table VI.

With regard to smoke toxicity, the executive summary states 'The results showed that none of the test specimens produced smoke of extreme toxicity. The smoke from both the FR and NFR products
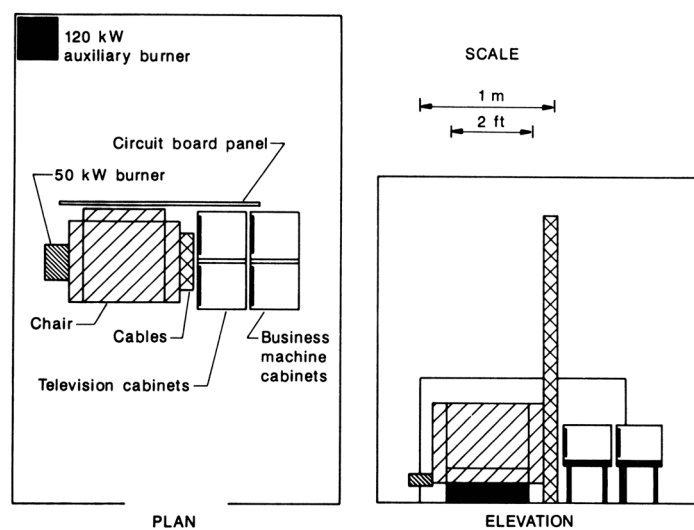
Figure 10. NBS/NIST layout of full-scale product burns for non-FR products [48].
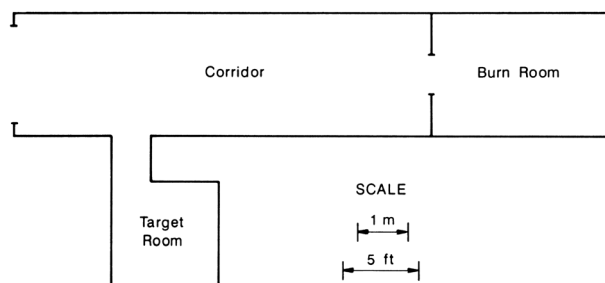
Figure 11. NBS/NIST room–corridor layout of full-scale product burns for non-FR products [48].
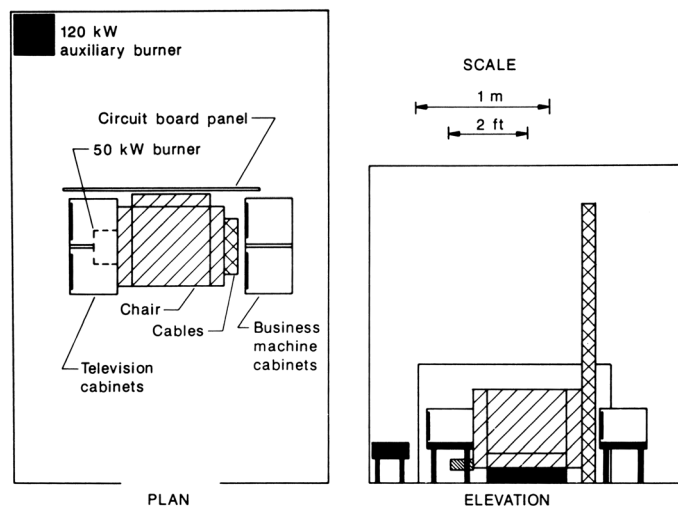
Figure 12. NBS/NIST layout of full-scale product burns for FR products [48].

was similar in potency and comparable to the potency of the smoke produced by materials commonly found in buildings.'

With regard to overall fire hazard, the executive summary states 'The impact of FR materials on the survivability of the building occupants was assessed in two ways: (1) Comparing the time to untenability in the burn room; this is applicable to the occupants of the burn room. (2) Comparing the total production of heat, toxic gases, and smoke from the fire; this is applicable to occupants of the building remote from the room of fire origin.' It continues 'For the FR tests, the average available escape time was more than 15-fold greater than for the occupants of the NFR room. With regard to the production of combustion products,

- "The amount of material consumed in the fire for the FR tests was less than half the amount lost in the NFR tests."
- "The FR tests indicated an amount of heat released from the fire which was ¼ that released by the NFR tests."
- "The total quantities of toxic gases produced in the room fire tests, expressed in 'CO equivalents,' were ⅓ for the FR products, compared to the NFR ones."
- "The production of smoke was not significantly different between the room fire tests using NFR products and those with FR products."

"Thus, in these tests, the fire retardant additives did decrease the overall hazard of their host products."'

In summary, the study showed that the proper selection of flame retardants can improve fire and life safety by significantly lowering heat release, toxic product release, and mass loss, while dramatically
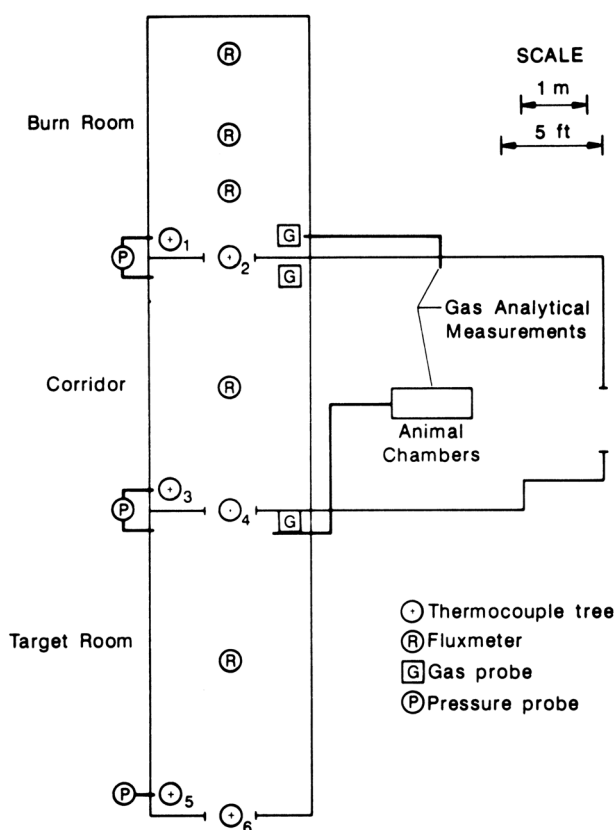
Figure 13. NBS/NIST room–corridor layout of full-scale product burns for FR products [48].

Table VI. Summary of full-scale results in NBS/NIST Tests [48].

	NFR array	FR array	Comparison
Available escape time	113 s	1789 s	15.8 fold longer time to escape from FR
Total heat released	750 MJ	200 MJ	3.5–4.0 fold heat released by NFR
Smoke released	(Overall)		No significant difference between systems
Toxic gas production	(As CO equivalent)		3 fold less toxicity from FR
Mass loss	(Based on initial mass)		Less than half the amount lost from FR
Auxiliary burner	Did not affect NFR Products		No Burning of FR Products Without It
Predicted heat release	1640 kW	345 kW	4–5 fold higher heat release rate for NFR

Notes: NFR array, array of non-flame retarded products; FR array, array of flame retarded products.

increasing time available for escape or rescue. In summary, the FR products are associated with a much lower fire hazard. Moreover, the ignition sources needed to cause FR products to burn are much larger than those for non-flame retarded products, if the products have been properly flame retarded. The authors noted that it is possible to develop flame retarded products that are not effective in lowering fire hazard because they are either ineffective systems or are being added at insufficient levels.

An interesting subsequent analysis of the NBS/NIST test data [49] found that the flame retardants added (many of which were brominated materials) did not just have an 'overall positive effect' from the point of view of fire hazard (over the non-flame-retarded products), something which has been demonstrated statistically, but that there is no evidence that the flame retardants adversely affected *any aspect* of fire hazard.

The NBS/NIST work was also analyzed soon after its completion by two of the authors [2] for the identification of the most important physical variable in the tests, which is a predictor of the resulting fire hazard. They found that a key conclusion of the work was that the heat release rate was that

variable and that it was much more predictive than time to ignition and toxicity of the difference in hazard. This brings this present work full circle, to the analysis shown at the beginning of the paper.

6. EFFECTS ON SMOKE RELEASE

This subject will be addressed very briefly. A study was made looking at five series of studies of room–corner tests in which heat and smoke release was assessed [8]. The analysis of these five series of full-scale room–corner tests in which heat and smoke release was measured showed that, in most cases, when heat release is low (as represented in Table VII by the 'materials with adequate heat and low smoke'), the material or product will generate low heat and low smoke. On the opposite end of the scale, there are materials reaching early flashover, and they will often release very high smoke. In between, those two cases can be found some 10% of materials or products that release adequate (or low) heat but high smoke. This is the basis for data analyses that developed properties known as 'smoke parameter' or 'smoke factor' that combine heat release rate data and smoke obscuration data so as to give a better understanding of the type of smoke obscuration to be expected in real fires or in large-scale tests as opposed to the (often misleading) data obtained from small-scale tests. The consequence of this is that smoke release needs to be considered to identify those few cases where high smoke is associated with low heat. In general, however, as flame retardants tend to lower heat release (as shown earlier), they will either have minimal effect on full-scale smoke release or decrease such smoke release. This is important for the present analysis to highlight the positive effect of flame retardants.

7. MAJOR CONE CALORIMETER STUDIES OF INDIVIDUAL AND GROUPS OF FLAME RETARDED MATERIALS

In one study, 35 materials were investigated with the cone calorimeter at three incident heat fluxes (20, 40, and 70 kW/m^2) [4]. In that study, several of the materials tested represented flame retarded and non-flame-retarded versions of the same polymers for similar types of applications. In some cases, there is more than one flame retarded version. Table VIII shows the peak heat release rate of a flame retarded and a non-flame-retarded version and the ratio between the two. In each case, the peak heat release rate is significantly decreased by the flame retardant system, in some cases by an order of magnitude. Some information on the materials tested is shown in the notes to the table. Table IX shows some other materials (for which less detailed information is available) [50, 51], tested either in the cone calorimeter or in the OSU calorimeter (ASTM E906 [38]). Some additional materials, also tested in the cone calorimeter, were also added [52]. The conclusions are similar to those for the results in Table VIII. Another comprehensive study looked at a large number of different polymers and at the effects of flame retardants on all of them [53]; there is too much information in the study to summarize it here, other than to indicate that flame retardants lowered heat release for all polymers studied.

When investigating flexible polyurethane foam, which is widely used for upholstered furniture, one study [5] looked at the effects of incorporating flame retardants into polyurethane foam on the cone calorimeter, and some results are shown in Table X. The effectiveness (to some extent) of adding flame retardants to achieve compliance with the traditional open flame test in CA TB 117 [22] is

Table VII. Full-scale room–corner tests measuring heat and smoke [8].

Room–corner test series	Materials reaching early flashover	Materials with adequate heat and low smoke	Materials with adequate heat and high smoke	Number of materials tested
SwRI	1	8	1	10
EUREFIC	14	12	2	28
SBI	12	15	3	30
Coast Guard	3	5	1	9
BFGoodrich	1	5	1	7
Overall	31	45	8	84

Table VIII. Effect of flame retardants on cone calorimeter peak heat release rate [4].

Material	Heat flux	Pk HRR non-FR	Pk HRR FR	Ratio of HRR
	kW/m^2	kW/m^2	kW/m^2	
ABS (+ FR1)	20	614	224	2.7
ABS (+ FR1)	40	944	402	2.3
ABS (+ FR1)	70	1311	409	3.2
ABS (+ FR2)	20	614	224	2.7
ABS (+ FR2)	40	944	291	3.2
ABS (+ FR2)	70	1311	419	3.1
PE	20	913	88	10.3
PE	40	1408	192	7.3
PE	70	2735	268	10.2
PVC rigid	20	102	25	4
PVC rigid	40	183	84	2.2
PVC rigid	70	190	93	2.1
PVC wire and cable	20	116	9	12.8
PVC wire and cable	40	167	64	2.6
PVC wire and cable	70	232	100	2.3
PVC wire and cable # 2	20	116	72	1.6
PVC wire and cable # 2	40	167	92	1.8
PVC wire and cable # 2	70	232	134	1.7
Polystyrene	20	723	277	2.6
Polystyrene	40	1101	334	3.3
Polystyrene	70	1555	445	3.5

Notes: ABS non-FR, Cycolac CTB acrylonitrile butadiene styrene terpolymer (Borg Warner); ABS/FR1, Cycolac KJT acrylonitrile butadiene styrene terpolymer flame retarded with bromine compounds (Borg Warner); ABS/FR2, polymeric system containing ABS and some PVC as additive; LDPE, polyethylene (Marlex HXM 50100), LDPE/FR Black non-halogen flame retarded, irradiation cross-linkable, polyethylene copolymer cable jacket compound (DEQD-1388, Union Carbide); PVC rigid, poly(vinyl chloride) rigid weatherable extrusion compound with minimal additives (BFGoodrich); PVC rigid FR, chlorinated PVC sheet compound (BFGoodrich); PVC wire and cable, flexible wire and cable PVC compound (non-flame retarded) (BFGoodrich); PVC wire and cable/FR 1, flexible vinyl thermoplastic elastomer alloy wire and cable jacket experimental compound, example of a family of VTE alloys (BFGoodrich); PVC wire and cable/FR 2, flexible wire and cable poly(vinyl chloride) compound (containing flame retardants) (BFGoodrich); Polystyrene crystal, Huntsman 333 (Huntsman); FR, flame retarded polystyrene crystal, Huntsman 351 (Huntsman); Pk HRR non-FR, peak heat release rate in cone calorimeter test for non-flame retarded materials; Pk HRR FR, peak heat release rate in cone calorimeter test for flame retarded materials; ratio of HRR, ratio between Pk HRR non-FR and Pk HRR FR.

weak but clear. However, much better improvements can be found with additional levels of flame retardants. The importance of choosing the right level of flame retardant additives is exemplified by a recent unpublished cone calorimetric study of two foams [54] with a small amount of flame retardant added, in order to comply with the widely criticized FMVSS 302 [55] test used for foams (and other plastics) inside automobiles. The study showed that the foams treated purely to meet FMVSS 302 and the untreated foams exhibited virtually no difference in heat release (Figure 14). The effect of adding enough flame retardants to polyurethane foam simply to meet CA TB 117 has some effect, albeit not very large, on heat release. However, results from a US National Institute of Justice (NIJ) research study on estimations of the burning rates of upholstered furniture [56] show something that had not been identified earlier. When polyurethane foam is treated with flame retardants to achieve CA TB 117 level and the foam is used in conjunction with a flame retarded fabric (the study used a cotton fabric that met the requirements of NFPA 701 [57]), the effect on heat release is very significant, while it is much less significant when used with a very flammable fabric (compare Figures 15 and 16, both showing cone calorimeter data) [58]. The same work also expanded the work by conducting full-scale tests. Figure 17 shows the effect of using CA TB 117 foam as compared to non-FR foam with an FR cotton fabric on a one seat sofa ignited in the seat by the ASTM E1537 square burner [59]. The figure shows that the system with the flame retarded foam and the flame retarded fabric has such a significant effect on heat release that there is virtually no fire from the sofa after ignition. For comparison, Figure 18 shows that, if neither the foam nor the

Table IX. Effect of flame retardants on cone calorimeter or Ohio State University calorimeter peak heat release rate [50–52].

Material	Heat flux	Pk HRR non-FR	Pk HRR FR	Ratio of HRR
	kW/m^2	kW/m^2	kW/m^2	
EVA (cross-linked)	30	463	110	4.2
EVA (thermoplastic)	30	574	83	6.9
HDPE	30	1803	114	15.8
HDPE # 2	50	1167	476	2.5
Polypropylene	30	1555	174	8.9
PVC rigid # 2	30	98	42	2.3
PVC rigid # 3	30	118	56	2.1
Plywood	25	114	43	2.7
Plywood	50	150	75	2.0
Particle board *	25	151	66	2.3
Particle board B (+ FR1)	25	160	70	2.3
Particle board B (+FR1)	50	227	141	1.6
Particle board B (+FR2)	50	227	52	4.4
Polyethylene wire and cable (+ Cl FR1)	50	800	165	4.8
Polyethylene wire and cable (+ Cl FR2)	50	800	517	1.5
Polyethylene wire and cable (+ mineral FR3)	50	800	126	6.3
Polyethylene wire and cable (+ ATH FR4)	50	800	271	3.0
Polyethylene wire and cable (+ ATH FR5)	50	800	179	4.5
Lumber (+ FR to FSI < 25)	75	226	83	2.7

All tests in cone calorimeter except for those marked with an asterisk (*) for particle board. The tests on polyethylene wire and cable compounds originate from reference [47], lumber and FR lumber from reference [49], and all others from reference [46].
Notes: Pk HRR non-FR, peak heat release rate in cone calorimeter test for non-flame retarded materials; Pk HRR FR, peak heat release rate in cone calorimeter test for flame retarded materials; ratio of HRR, ratio between Pk HRR non-FR and Pk HRR FR.

Table X. Cone calorimeter study of various polyurethane foams [5].

Type of foam	Incident heat flux	Peak heat release rate	Effective heat of combustion
Units	kW/m^2	kW/m^2	MJ/kg
Non-FR foam	25	420	25.6
CA TB 117 foam	25	350	22.7
Non-FR foam	35	910	23.1
CMHR foam	35	110	10.8

Notes: Non-FR foam, polyurethane foam without added flame retardants; CA TB 117 foam, polyurethane foam with added flame retardants to achieve compliance with CA TB 117 test; CMHR foam, polyurethane foam with added flame retardants to achieve compliance with an improved (unnamed) fire test.

fabric is flame retarded, the sofa releases abundant heat and results in a significant fire and flashover, while a sofa with non-FR cotton and CA TB 117 foam gave off much less (but still too much) heat. Note that this particular study was performed using two seat sofas in a very large room. The effect on heat release of adding flame retardants to the foam is clearly noticeable but is less pronounced than it is in the presence of a flame retarded fabric.

Another study investigated polyurethane foam in the cone calorimeter (at an incident heat flux of 25 kW/m^2) and in the British Standard BS 5852 [60], using various wood cribs, ranging from # 4 (smallest, 8.5 g), through # 5 (17.0 g) up to # 7 (largest, 126 g) [61]. It showed that well flame retarded polyurethane foam (using, in this case, melamine flame retardants) could resist very severe ignition sources and, even if ignited, would generate low heat release and perform very well in mock-up furniture tests. The study used two foams (one without flame retardants and one that met BS 5852 crib # 5). Some cone calorimeter results, together with the pass/fail results according to BS
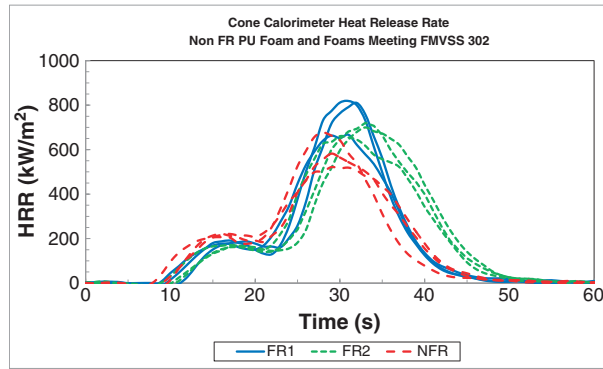
Figure 14. Alexander Morgan cone calorimeter: polyurethane foam treated for FMVSS 302 [54].
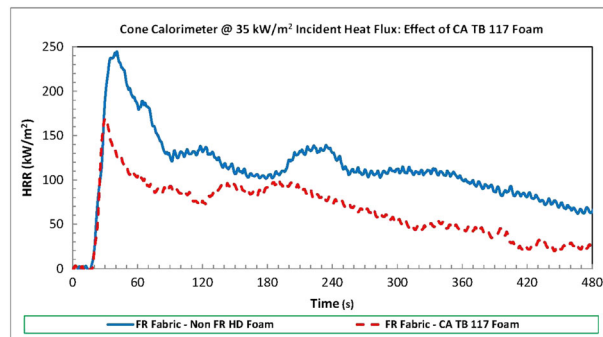
Figure 15. NIJ cone calorimeter comparison of polyurethane foam treated for CA TB 117 and non-FR with an FR cotton fabric treated for NFPA 701 [56,58].
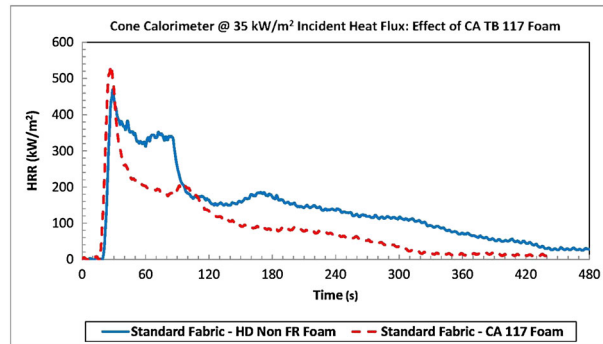
Figure 16. NIJ cone calorimeter comparison of polyurethane foam treated for CA TB 117 and non-FR with a non-FR cotton fabric [56,58].

5852, are shown in Table XI. It was of interest that one of the fabrics (polyolefin) was so poor that it would fail the BS 5852 test with both foams while one of the fabrics was so good that even the non-flame-retarded foam passed the BS 5852 test with the largest wood crib.

One type of materials needs to be considered separately: those are foam plastic insulation materials. It is often difficult to conduct a proper fire test with these materials, especially those that are melting materials, such as polystyrene foam. In the USA, these materials are usually assessed for code use by means of the Steiner tunnel (ASTM E84 [62]), while in the EU, they are being assessed primarily by means of the Euroclass testing system, via the SBI test (EN 13823 [35]) or by the
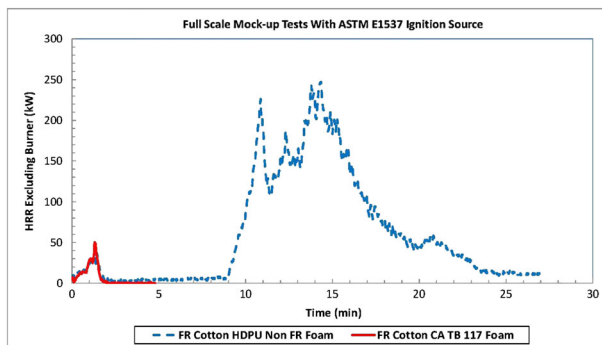
Figure 17. NIJ full-scale (ASTM E1537, one seat sofa) comparison of polyurethane foam treated for CA TB 117 and non-FR with an FR cotton fabric treated for NFPA 701 [56,58].
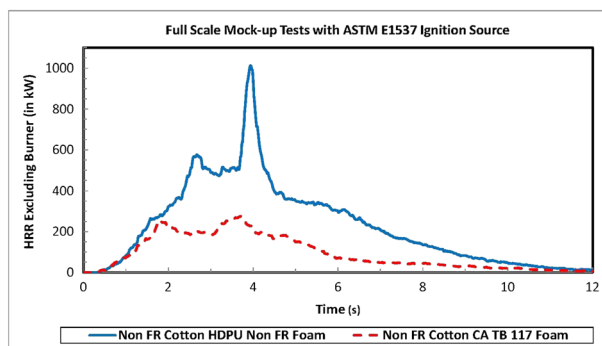
Figure 18. NIJ full-scale (ASTM E1537, two seat sofa) comparison of polyurethane foam treated for CA TB 117 and non-FR with non-FR cotton fabric [56,58].

Table XI. Cone calorimeter study of two polyurethane foams with and without fabrics [58].

Type of system	Time to ignition	Pk HRR	Eff. Ht. Comb	BS 5852/crib #
	s	kW/m^2	MJ/kg	
Non-FR foam	3	533	29	Fail/4
Melamine foam	7007	97	6	Pass/7
Polyolefin/non-FR foam	15	613	35	Fail/4
Polyolefin/mel foam	22	450	31	Fail/4
Nylon/non-FR foam	515	341	20	Fail/4
Nylon/mel foam	3349	313	23	Pass/5
Canvas/non-FR foam	134	355	12	
Canvas/mel foam	159	187	19	
Flex vinyl/non-FR foam	548	142	8	Pass/7
Flex vinyl/mel foam	10,000	117	3	Pass/7

Notes: Non-FR Foam, polyurethane foam without added flame retardants; melamine foam (mel foam), polyurethane foam with added melamine flame retardants to achieve compliance with an improved (unnamed) fire test; Pk HRR, peak heat release rate in cone calorimeter test; Eff. Ht. Comb., effective heat of combustion in cone calorimeter test.

ignition test (ISO 11925-1 [63]). With both systems, the flame retarded polystyrene foam significantly outperforms the foam that is not flame retarded. In the ASTM E84 test, flame retarded foam typically exhibits a flame spread index (FSI) in the range of 20–70 and a smoke developed index (SDI) of less than 450 (code requirements are for an FSI less of than 75 and an SDI of less than 450). On the other

hand, if the foam is not flame retarded, it inevitably fails the requirements. In the EU, flame retarded extruded or expanded polystyrene will normally result in a Euroclass ranging from B (rarely) to E (depending on the level of flame retardants added), while a non-flame-retarded foam will almost always result in a fail (i.e., Euroclass F) [64].

A comprehensive study of the flammability characteristics of foam plastics at NIST [65] was designed to try to obtain a test method for foam plastics that is a suitable alternative to the Steiner Tunnel Test as a measure of flammability for foamed plastic. The work investigated test apparatuses such as the cone calorimeter and the lateral ignition and flame spread test apparatus (LIFT, ASTM E1321, [66]), and the authors were attempting to more completely characterize foamed plastic flammability. Key flammability properties were obtained from these apparatuses to describe ignitability, flame spread rate, heat release rate, and smoke obscuration. An extensive data set of these flammability properties for 10 selected foamed plastics was generated. The tested materials included melting foams (polystyrene foams) and charring foams (polyurethanes, polyisocyanurate, and phenolic foams). The problems due to the effects of melting and dripping were limited by testing the materials in the horizontal orientation. In addition, an integrated approach to material flammability characterization was presented that uses these parameters to predict fire growth potential. The results were somewhat disappointing in that no test apparatus was identified that would assess the materials appropriately. The authors developed variations of both the cone calorimeter and the LIFT, but they were still unsatisfactory, and they recommended that modeling work be used. However, this does not affect the conclusions from the actual tests conducted, namely, that flame retarded foam plastics outperform non-flame-retarded ones.

Important work on television sets, which are emblematic of other appliances, was primarily conducted by Jürgen Troitzsch [67, 68], who was able to show that non-flame-retarded television sets, such as those commonly used in Europe, can quickly take a room to flashover. The main full-scale fire test was carried out with a TV set purchased in Germany, with a 20×20 mm hole cut in the lateral right front side of the back plate adjacent to the housing, where flame originating from a solid fuel pellet (0.15 g, 40–55 W, 5–10 mm flame) was applied. After ignition, the solid fuel pellet flame impinged on the back plate on top of it and later on the edge of the housing, simulating an external and internal low intensity ignition source. After just 24 s following pellet ignition, the TV back plate began to burn, and after 4.5 min, a pre-flashover situation developed in the room, with full flashover at 7 min, when all the furniture started burning, with big flames and high temperatures. The fire safety requirements for the cabinet of that TV set were no more than the horizontal (HB) version of the UL 94 test [69]. In contrast, TV sets purchased in the USA and in Japan, where the cabinets had to be flame retarded in order to meet the vertical requirements of the UL 94 test (Class UL 94 V2, V1, V0, or 5 V), either did not ignite or extinguished quickly when exposed to ignition sources as high as 200 mL of isopropanol or cloth soaked in isopropanol (representing up to 40 kW insults).

A separate study by Margaret Simonson on TV sets showed the vital benefit (for fire safety and environmental issues) found in life cycle analyses of flame retarded products versus non-flame-retarded products conducted at SP in Sweden [70]. Similar studies followed later also on upholstered furniture [71] and on cables [72], also at SP.

8. DISCUSSION AND CONCLUSIONS

A recent study found, based on much of the same data reviewed here, that the addition of flame retardants improves fire safety in a variety of ways but with particular emphasis on the fact that it increases time available for escape and rescue [73]. A 1999 publication [45] looked specifically at the NBS/NIST work discussed in depth in the first part of this study and concluded that the addition of flame retardants had a positive effect on not just the overall time available for escape but also on the smoke toxicity of the fire atmospheres. The author stated 'there is no evidence that [the flame retardants] adversely affect any aspect of fire hazard. Because they reduce ignitability they reduce flame spread, because they reduce flame spread they reduce the fire's burning rate; because they reduce the burning rate they reduce the quantity of smoke the fire produces.'

Another study investigated the safety, health, and environmental aspects of flame retardants [74] and concluded that 'this survey shows that the appropriate use of flame retardants, as a class, effectively provides improved fire safety via lowering the probability of ignition, the heat released and the amounts of smoke, combustion products and dangerous environmental toxicants. In consequence the use of flame retardants increases the available time for escape from a fire.' Much of the work in this specific study was based on earlier work [75] that received insufficient analysis.

In this work, the investigation of the importance of heat release rate in fire hazard, the investigation of the use of small-scale heat release tests for predictions of real-scale heat release information, and the in-depth analysis of the NBS/NIST work are all based on the best fire safety science.

In summary, this work demonstrates the following:

(1) Heat release (and particularly heat release rate) is the most important property associated with fire hazard and fire safety.
(2) The NBS/NIST work of 1988 demonstrated that flame retardants (as used in five products) decreased heat release and significantly increased time available for escape and rescue from a fire and fire safety.
(3) Cone calorimeter (and OSU calorimeter) data on small-scale samples can be used to measure heat release rate and to predict the results of fires in full scale with many materials and products.
(4) Flame retardants, when added as appropriately researched systems, will decrease heat release rate by well beyond statistical deviations for the polymeric materials studied, which represent most of those where fire safety is a potential concern.

In conclusion, this work demonstrates that the correct use of flame retardants (by using efficient systems, designed for the substrate, at sufficient levels) will decrease heat release rate and thus have a very positive effect on fire safety.

ACKNOWLEDGEMENT

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Flame retardants and heat release: review of data on individual polymers

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SUMMARY

This work is the second of two parts that considered the following issue: do flame retardants affect heat release of polymers? The reason for investigating the issue is because it is important to assess whether the addition of flame retardants positively decreases fire hazard. This part of the work considered the two following issues. (1) Analysis of the individual polymeric materials that need to be studied. (2) Analysis of the data found on heat release (particularly peak heat release rate), ignitability (if available), and other thermal properties (as available) of polymers in small-scale test data in recent years. The effects are being presented in terms of the percentage of improvement. The work demonstrated that, almost without exception, when adequately compounded systems were developed, the peak heat release rate of the flame retarded system was lower than that of the non-flame retarded system. The overall conclusion of the two-part study was that flame retardants does indeed improve fire safety (when used appropriately) and that a key reason for the beneficial effect of flame retardants is that they decrease heat release. Copyright © 2014 John Wiley & Sons, Ltd.

1. INTRODUCTION

The first part of this two-part study [1] investigated the effects of flame retardants on heat release of products and of groups of polymers. It concluded that the correct use of flame retardants (by using efficient systems, designed for the substrate, at sufficient levels) will decrease heat release rate and thus have a very positive effect on fire safety.

Until relatively recently, heat release rate measurements were seen by some people as just another piece of data to gather. In fact, the importance of heat release as a fundamental fire safety property is still not a full part of the public understanding of fire safety. However, fire scientists have now concluded that heat release is much more than a set of data. It has been shown by multiple analyses of fire hazard that heat release rate is the most important fire property and that the peak heat release rate (Pk HRR) is the numerical indicator of the intensity of a fire [2–8]. One key study has demonstrated that heat release rate is much more critical than either ignitability or smoke toxicity in affecting the probability of survival in a fire [2].

Fire safety can be improved in one of two ways, or via a combination of both, as shown later. This work will address exclusively passive fire protection.

- Passive fire protection. This means using materials and products with superior fire performance so as to either minimize the probability of ignition or, if ignition does occur, minimize the damaging effects of the resulting fire.

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- Active fire protection. This means relying on fire detection and suppression systems (such as smoke alarms and sprinklers). Fire detection systems alert the occupants (and/or first responders, such as fire fighters) while fire suppression systems extinguish the fire.

Flame retardants are materials that can be incorporated into combustible materials to improve their fire performance. It has been shown in many studies that flame retardants can be effective in having effects such as making materials or products less easily ignitable and/or reducing flame spread and they are extensively used to help materials and/or products meet certain fire test requirements. In view of the fact that there is no fire if ignition does not occur, a delay in ignition will improve fire safety. However, fire hazard assumes that ignition has occurred, so it is important to study the effects of flame retardants on fire hazard, with an emphasis on the key property of heat release, as explained later.

Fire risk is the combination of fire hazard and of the probability of fire occurring. Fire hazard is defined as 'the potential for harm associated with fire'. Fire risk is defined as 'an estimation of expected fire loss that combines the potential for harm in various fire scenarios that can occur with the probabilities of occurrence of those scenarios'. It is essential to understand that it is possible to have high fire hazard but low fire risk because the probability of such a fire is low.

Most, if not all, solid combustible materials (plastics, wood, textiles, rubbers, and so on) are polymeric (meaning that they have a complex chemical structure, with repeating units). Many polymeric materials, whether natural or synthetic, have poor fire performance in the absence of added flame retardants. That is particularly important for those polymers that are in widest use, such as polyolefins (polyethylene or polypropylene (PP)), polyurethane, polystyrene, polyethylene terephthalate (PET), nylon, or cotton. When a polymer is used in applications where fire safety is an important consideration, the lack of intrinsic fire safety must be addressed for ensuring passive fire protection. The following are examples of different approaches:

- adding flame retardants (i.e., using additive flame retardants),
- creating new polymers with better fire performance though syntheses of variations of the polymer (i.e., using reactive flame retardants),
- blending or otherwise compounding it with other polymers with better fire performance (i.e., creating blends or mixtures), and
- encapsulating the polymer or separating it from the potential exposure to the heat insult.

This study will look primarily at the first aspect, namely, additive flame retardants and fire hazard. Typical applications where fire safety can be critical are upholstered furniture, mattresses, wire and cable, interior finish, insulation, appliance, and computer housings, among others.

2. KEY POLYMERS OR MATERIALS TO INVESTIGATE

The world of natural and synthetic polymers is enormous, and it is literally impossible to study every polymer that is commercially available or that may become commercially available in the near future. Therefore, it is important to prioritize the polymers that are of major importance and that need to be investigated. Several criteria were considered in order to come to a determination of a list. First, it is essential to consider all synthetic polymers that are of major use worldwide (or at least in the developed world) and that decision can be made based on the amount of material sold. Another important criterion is that polymers that are important in critical applications where fire safety is a major concern need to be investigated. A third criterion used was to choose natural materials that have the potential to be flame retarded and that are used in key applications where fire safety matters and where synthetic polymers are possible alternatives. A fourth criterion was not to choose polymers that rarely require additional flame retardance, primarily because of their inherent excellent fire performance or because they are used in applications where fire safety is rarely a major concern.

Statistics from the American Chemistry Council (among others) show that the synthetic polymer with the highest production volume is polyethylene (including high density polyethylene, low density polyethylene (LDPE), linear LDPE, and various blends). In terms of volume, polyethylene is followed by PP, poly(vinyl chloride) (PVC), and polystyrene. The major markets for these polymers

are building and construction, transportation, electrical and electronics, furniture and furnishings, appliances, and packaging. According to the American Chemistry Council, sales of thermoplastics in the USA in 2012 is distributed in the following markets: packaging (34%), consumer and institutional (20%), building and construction (16%), transportation (4%), furniture and furnishings (2%), electrical and electronic (2%), and industrial and machinery (1%), with the remainder all others or export. In all of these areas (with the possible exception of packaging), multiple applications exist where fire safety needs to be considered.

In the area of building and construction, fire safety is an important consideration particularly for interior finish, insulation, roofing, siding, and exterior veneers. Polymers of interest here include polyolefins, polystyrene, rigid PVC, wood, cellulose, and rigid polyurethane. In the area of transportation, many polymers are used, including primarily the following (as analyzed, for highway vehicles, for a recent NFPA document (NFPA 556)): polyurethanes, PP, PVC, polyethylene, nylons/polyamides, ABS, and engineering thermoplastics. In the area of furniture and furnishings, fire safety is essential, especially for upholstered furniture and mattresses, because that is the area where the highest heat content in buildings is found. Polymers of interest here include flexible polyurethanes and materials used for fabrics, such as cotton, polyester, nylon, wool and silk, and wood. Protective clothing is an area where fire safety is a consideration, and the typical materials used are aromatic polyamides and cellulosics. In the area of electrical and electronics, the key areas are wire and cable, connectors, and circuit/wiring boards. Polymers of interest here include flexible PVC, polyolefins (including polyethylene and ethylene vinyl acetate (EVA)), thermoplastic polyurethanes, epoxies, and fluoropolymers. In the area of appliances, there are two types of products with fire safety considerations: housings for appliances and electronic/computer equipment and the interior circuitry for such products. Polymers of interest here include various engineering thermoplastics, such as styrenics (including ABS and high impact polystyrene or HIPS), polycarbonate (PC), polyesters (including PET and polybutylene terephthalate, PBT), poly ether ether ketone and similar polymers, polyamides/nylons, polyphenylene oxide based blends, and rigid PVC. In the area of packaging, there are relatively low fire safety concerns. A few of the polymeric materials mentioned earlier need not be investigated further in this work because they are rarely treated with flame retardants, because of their intrinsically excellent fire performance.

The resulting list of materials is not necessarily comprehensive but will cover a very significant range. With these criteria, the following list was created (in alphabetical order):

- ABS and/or other styrenics, including HIPS,
- cellulose or cotton fabrics,
- engineering thermoplastics (including PC),
- epoxy resins,
- EVA and/or other polyolefin blends and/or copolymers,
- flexible PVC,
- LDPE,
- nylon and/or other polyamides,
- polyesters (including also PET fabrics),
- polycarbonate,
- polypropylene,
- polystyrene,
- polyurethane (foam and thermoplastic polyurethane),
- rigid PVC, and
- wood (different species, if possible).

With the criteria earlier, the following short list was created of materials that need not be investigated (in alphabetical order).

- aromatic polyamides {very high thermal stability; often used without additives for protective clothing or barriers},
- fluoropolymers (including polytetrafluoroethylene and others) {superior fire performance; normally used as is for electrical and piping applications},

- poly ether ether ketone and similar polymers {superior fire performance; normally used as is for engineered plastics applications},
- silk {sufficient fire performance for high-end textile applications}, and
- wool {sufficient fire performance for certain textile applications}.

The major polymeric system that was considered for analysis and was not investigated (because no data have been published) is cellulose loose fill insulation, a material that is extensively used and almost always used in flame retarded form, but which does not seem to have been tested for heat release rate, either before or after the addition of flame retardants.

3. HEAT RELEASE EFFECTS OF FLAME RETARDANTS ON INDIVIDUAL POLYMERS

The cone calorimeter is a specialized piece of fire test equipment that is used to assess heat release data, as well as ignitability, mass loss, and smoke released by burning materials. There have been a large number of studies that have demonstrated that the cone calorimeter (ASTM E1354 [9]) can be successfully used for many products to predict full-scale (or at least relatively large scale) fire performance of the corresponding products. The most widely studied products are wires and cables, upholstered furniture, mattresses, wall linings, and aircraft panels. The cone calorimeter is the primary fire testing technique used in the studies reviewed here.

Another heat release technique was developed by Richard Lyon, at the Federal Aviation Administration (FAA) in 2004, namely, the pyrolysis–combustion flow calorimeter (PCFC) or micro calorimeter [10]. This new fire test instrument was later standardized as ASTM D7309 [11], and it quickly and easily measures the combustibility or pyrolysis (aerobic or anaerobic) of materials, such as plastics, wood, or textiles, with samples that are only a few milligrams and results that are obtained in minutes. Its output includes the heat release capacity, a fundamental material property that can be correlated with the heat release rate. Lyon and co-workers have developed correlations with other standard heat release instrument fire test data (including the cone calorimeter). Lyon and collaborators have published extensively using this technique and showed its effectiveness in classifying polymeric materials on the basis of their heat release capacity. These publications also include results using flame retarded materials. However, the direct comparisons of results of flame retarded materials with their non-flame retarded alternates are easier understood using the cone calorimeter, and that is the focus that will be used in this work.

The effects of the flame retardant additives on each of the individual properties studied are being presented in a variety of tables and calculated as a percentage improvement.

3.1. Polyolefins

Polyolefins are among the highest heat release polymers and are also among the most widely used materials for a variety of applications. The first part of this study [1] includes tables that contain data on the heat release of a variety of polyolefin systems [4,12–14] and demonstrates the effectiveness of flame retardants in decreasing heat release for such polymers. An NBS/NIST study [14] discussed in detail in the first part of this work also included a cable coating compound that is composed of polyolefins. Some other recent work on polyolefins follows. Tables I and II include work on the effectiveness of inorganic and phosphorus-based flame retardants on EVA and on a PP copolymer, tested in the cone calorimeter at an initial test heat flux of $40\,kW/m^2$ [15]. The three flame retardant additives used were aluminum trihydrate (ATH), magnesium hydroxide (MDH), and Fyrol P26 (a proprietary commercial additive with 36% phosphorus). It is notable that there is a significant improvement in heat release rate, particularly Pk HRR, for both polymers but a much lower effect on time to ignition (TTI) or on the ratio of the two properties (FPI or fire performance index). The percentage improvement in Pk HRR in the EVA systems investigated is in the 76-88% range, and in the PP systems, it ranged from 60 to 79%.

A different study on EVA cable jacket compounds (containing calcium carbonate) uses several mineral fillers, namely, ATH, MDH, huntite (HU), and hydromagnesite (HM) plus combinations of these additives [16] (Table III). The numbers in the table following the HU and HM designations

Table I. Effectiveness of inorganic and phosphorus-containing flame retardants on heat and ignitability properties of EVA [15].

EVA	TTI	Pk HRR	FPI	Avg HRR	THR
	s	kW/m^2	(m^{2}skW^{-1})	kW/m^2	MJ/m^2
40 kW/m^2					
Untreated	25	1905	0.01	645	88
Plus 60% ATH	28	460	0.06	244	64
Improvement %	12	76	364	62	27
Plus 57% ATH 3% Fyrol	35	221	0.16	147	63
Improvement %	40	88	1107	77	28
Plus 60% MDH	44	381	0.12	286	68
Improvement %	76	80	780	56	23
Plus 57% MDH 3% Fyrol	38	311	0.12	183	63
Improvement %	52	84	831	72	28

Notes: TTI, time to ignition in cone calorimeter test; Pk HRR, peak heat release rate in cone calorimeter test; Avg HRR, average heat release rate during test in cone calorimeter test; THR, total heat released in cone calorimeter test; FPI, fire performance index (ratio of time to ignition and peak heat release rate, in cone calorimeter test); ATH, aluminum trihydrate; MDH: magnesium hydroxide; Fyrol, Fyrol P26, a proprietary commercial phosphorus-containing flame retardant with 36% phosphorus; improvement %, percentage improvement in relevant property based on the untreated material.

Table II. Effectiveness of inorganic and phosphorus-containing flame retardants on heat and ignitability properties of PP [15].

PP copolymer at 40 kW/m^2	TTI	Pk HRR	FPI	Avg HRR	THR
	s	kW/m^2	m^{2}skW^{-1}	kW/m^2	MJ/m^2
Untreated	19	2540	0.01	805	105
Plus 30% MDH	21	1010	0.02	550	91
Improvement %	11	60	178	32	13
Plus 25% MDH 5% Fyrol	12	545	0.02	355	84
Improvement %	-37	79	194	56	20

Notes: TTI, time to ignition in cone calorimeter test; Pk HRR, peak heat release rate in cone calorimeter test; Avg HRR, average heat release rate during test in cone calorimeter test; THR, total heat released in cone calorimeter test; FPI, fire performance index (ratio of time to ignition and peak heat release rate, in cone calorimeter test); MDH, magnesium hydroxide; Fyrol, Fyrol P26, a proprietary commercial phosphorus-containing flame retardant with 36% phosphorus; improvement %, percentage improvement in relevant property based on the untreated material.

indicate the amount of each flame retardant added. The fire test is the cone calorimeter at initial test heat fluxes of 30, 50, and 70 kW/m^2. The range of improvements in Pk HRR is in the range of 17–46%.

Some effects of adding clays and ammonium phosphate on HDPE are shown in Table IV [17]. The testing was conducted in the cone calorimeter at an initial test heat flux of 35 kW/m^2. The three additives used were clay (sodium montmorillonite), ammonium phosphate monobasic (MB), and sodium montmorillonite modified with ammonium phosphate monobasic (M1). It is notable that there is a significant improvement in heat release rate, particularly Pk HRR but a much lower effect on TTI or on the ratio of the two properties (FPI). This is a consequence of the polymer being investigated and of the type of flame retardant additive used, which affects primarily heat release rate. The percentage improvement in Pk HRR in the systems investigated ranged from 21% to 47%.

Table V shows the effects on another two wire and cable polyolefin systems, LDPE, and ethyl butyl acetate (EBA) using inorganic additives and silicone coupling agents [18]. The mix of additives used was a masterbatch containing 30% calcium carbonate and 12.5% silicone. The test method is the cone calorimeter at an initial test heat flux of 35 kW/m^2. There are improvements in both heat release and ignitability, with the Pk HRR being improved 77% in LDPE and 50–75% in EBA.

Table III. Effectiveness of inorganic flame retardants on heat and ignitability properties of an EVA cable jacket compound [16].

EVA cable jacket compound	TTI s	Pk HRR kW/m²	FPI m²skW⁻¹	Avg HRR kW/m²
30 kW/m²				
Untreated (plus calcium carbonate)	210	186	1.13	107
Plus ATH	226	117	1.93	81
Improvement %	8	37	71	24
Plus Hydromagnesite	302	117	2.58	83
Improvement %	44	37	129	22
Plus HU24HM67	249	139	1.79	73
Improvement %	19	25	59	32
Plus HU43HM50	219	130	1.68	68
Improvement %	4	30	49	36
Plus HU77HM18	227	135	1.68	64
Improvement %	8	27	49	40
Plus HU95HM5	236	154	1.53	52
Improvement %	12	17	36	51
50 kW/m²				
Untreated (plus calcium carbonate)	83	257	0.32	107
Plus ATH	98	169	0.58	84
Improvement %	18	34	80	21
Plus MDH	125	163	0.77	88
Improvement %	51	37	137	18
Plus Hydromagnesite	101	168	0.60	89
Improvement %	22	35	86	17
Plus HU24HM67	93	162	0.57	74
Improvement %	12	37	78	31
Plus HU41HM57	88	168	0.52	71
Improvement %	6	35	62	34
Plus HU43HM50	81	154	0.53	56
Improvement %	−2	40	63	48
Plus HU77HM18	90	138	0.65	41
Improvement %	8	46	102	62
Plus HU95HM5	78	174	0.45	57
Improvement %	−6	32	39	47
70 kW/m²				
Untreated (plus calcium carbonate)	43	251	0.17	187
Plus ATH	54	208	0.26	102
Improvement %	26	17	52	45
Plus Hydromagnesite	48	197	0.24	106
Improvement %	12	22	42	43
Plus HU24HM67	44	190	0.23	90
Improvement %	2	24	35	52
Plus HU43HM50	40	191	0.21	84
Improvement %	−7	24	22	55
Plus HU77HM18	40	189	0.21	85
Improvement %	−7	25	24	55
Plus HU95HM5	43	202	0.21	103
Improvement %	0	20	24	45

Notes: TTI, time to ignition in cone calorimeter test; Pk HRR, peak heat release rate in cone calorimeter test; Avg HRR, average heat release rate during test in cone calorimeter test; FPI, fire performance index (ratio of time to ignition and peak heat release rate, in cone calorimeter test); ATH, aluminum trihydrate; HU, huntite; HM, hydromagnesite, numbers indicate amounts of HU and of HM; improvement %, percentage improvement in relevant property based on the untreated material.

NFPA 556 [19] is a guide on hazard assessment of passenger road vehicles, and it contains heat and ignitability parameters from cone calorimeter tests for a set of 9 PP materials that have been flame retarded (Table VI). It does not contain the data for the corresponding non-flame retarded PP, but data from Hirschler [4] show that Pk HRR for non-flame retarded PP was measured at 1170 kW/m²

Table IV. Effectiveness of clay and phosphate-treated clay flame retardants on heat and ignitability properties of HDPE [17].

HDPE at 35 kW/m²	TTI	Pk HRR	FPI	Avg HRR	THR
	s	kW/m²	m²skW⁻¹	kW/m²	MJ/m²
Untreated	91	1744	0.05	502	174
Plus 5% clay	67	1218	0.06	550	171
Improvement %	−26	30	5	−10	2
Plus 7.5% clay	71	927	0.08	478	142
Improvement %	−22	47	47	5	18
Plus 10% clay	52	1006	0.05	483	165
Improvement %	−43	42	−1	4	5
Plus 5% M1	83	1288	0.06	456	143
Improvement %	−9	26	24	9	18
Plus 7.5% M1	88	1147	0.08	441	142
Improvement %	−3	34	47	12	18
Plus 10% M1	63	946	0.07	414	147
Improvement %	−31	46	28	18	16
Plus 5% MB + 5% M1	48	1361	0.04	510	165
Improvement %	−47	22	−32	−2	5
Plus 10% MB + 2.5% M1	53	1051	0.05	479	135
Improvement %	−42	40	−3	5	22
Plus 7.5% MB + 5% M1	43	1194	0.04	653	166
Improvement %	−53	32	−31	−30	5
Plus 10% MB + 5% M1	41	1372	0.03	506	159
Improvement %	−55	21	−43	−1	9
Plus 5% MB + 10% M1	42	1309	0.03	460	156
Improvement %	−54	25	−39	8	10

Notes: TTI, time to ignition in cone calorimeter test; Pk HRR, peak heat release rate in cone calorimeter test; Avg HRR, average heat release rate during test in cone calorimeter test; THR, total heat released in cone calorimeter test; FPI, fire performance index (ratio of time to ignition and peak heat release rate, in cone calorimeter test); clay, sodium montmorillonite; MB, ammonium phosphate monobasic; M1, and sodium montmorillonite modified with ammonium phosphate monobasic; improvement %, percentage improvement in relevant property based on the untreated material.

Table V. Effectiveness of calcium and silicon mixed flame retardants on heat and ignitability properties of polyolefin wire and cable compounds [18].

	TTI	Pk HRR	FPI	Eff. Heat Comb.
	s	kW/m²	m²skW⁻¹	MJ/kg
LDPE alone	76	1420	0.05	41.0
LDPE and Ca Si mix	95	320	0.30	26.0
Improvement %	25	77	455	37
Ethyl butyl acetate	77	1304	0.06	40.9
EBA and silicone alone	84	1044	0.08	33.4
Improvement %	9	20	36	18
EBA and calcium carbonate only	102	658	0.16	26.3
Improvement %	32	50	163	36
EBA and Ca Si mix	148	326	0.45	24.1
Improvement %	92	75	669	41

Notes: TTI, time to ignition in cone calorimeter test; Pk HRR, peak heat release rate in cone calorimeter test; Eff. Heat Comb., effective heat of combustion in cone calorimeter test; FPI, fire performance index (ratio of time to ignition and peak heat release rate, in cone calorimeter test); EBA, ethyl butyl acetate; improvement %, percentage improvement in relevant property based on the untreated material.

at an incident heat flux of 20 and 1509 kW/m² at an incident heat flux of 40 kW/m². Similar information can be found in a table in part 1 of this study [1]. These data again show the positive effect of flame retardants on the heat release of this polyolefin.

Table VI. Cone calorimeter data for nine flame retarded polypropylene materials at heat flux indicated (in kW/m2) [19].

	TTI	Pk HRR	FPI	Avg HRR 3	Eff. Heat Comb
	s	kW/m2	$m^2 skW^{-1}$	kW/m^2	MJ/kg
At 20 kW/m2					
# 1	382	236	1.62	183	23.6
# 2	325	168	1.93	136	29.8
# 3	377	207	1.82	173	24.4
# 4	384	195	1.97	157	25.3
# 5	396	301	1.32	199	24.3
# 6	387	215	1.80	131	25.9
# 7	402	228	1.76	185	27.1
# 8	377	207	1.82	173	26.8
# 9	386	202	1.91	173	27.8
At 40 kW/m2					
# 1	80	243	0.33	170	23.9
# 2	63	206	0.31	144	28.6
# 3	62	209	0.30	167	25.2
# 4	72	206	0.35	144	25.4
# 5	74	231	0.32	160	25.2
# 6	70	193	0.36	155	26.1
# 7	75	193	0.39	138	25.9
# 8	71	188	0.38	139	25.8
# 9	67	172	0.39	127	25.7

Notes: TTI, time to ignition in cone calorimeter test; Pk HRR, peak heat release rate in cone calorimeter test; Avg HRR 3, average heat release rate during the 3 min following ignition in cone calorimeter test; Eff. Heat Comb, effective heat of combustion in cone calorimeter test.

Another study looked at the effects of adding, to polyethylene and to PP, 3% of an organically modified clay (a proprietary commercial additive called Cloisite 30B) and 3% of various brominated materials, creating halogen-containing polymer nanocomposites [20]. The four brominated additives are butyric acid pentabromobenzyl ester (FR1), pentabromobenzyl ester polyacrylate (FR2), methacrylate acid pentabromobenzyl ester (FR3), and acrylic acid pentabromobenzyl ester (FR4). The results are shown in Table VII. There is clearly a good reduction in Pk HRR, but the TTI and the total heat released remain virtually unchanged, within statistical significance. The fact that the TTI is lowered means, the nanocomposites are usually easier to ignite than the virgin polymer and the fact that the THR is unchanged means that the nanocomposite essentially burns up completely.

Having introduced the concept of using nanocomposites as flame retardant additives, it is worth mentioning here that such materials have been used in numerous studies with a variety of polymers (very often polyolefins and styrenics) and they show huge decreases in heat release rate (particularly Pk HRR), but these decreases are often accompanied by the same type of effect discussed earlier: no effect (or detrimental effect) on TTI and no effect on total heat released. Moreover, the Pk HRR of the flame retarded system is often still quite high. In a study by Kashiwagi *et al*. [21], the Pk HRR of a PP system decreased from over 3000 kW/m^2 to values ranging from 600 to 800 kW/m^2. The extensive amount of scientific literature on these systems will not be reviewed here because it would go beyond the scope of the present work. However, interested readers should consult work included in a Wilkie and Morgan book on flame retardants [22], including studies by Jiang [23], Lopez-Cuesta [24], Marosi [25], and Delichatsios [26], as well as a Wilkie and Morgan book entitled 'Flame Retardant Polymer Nanocomposites' [27] and additional work by Beyer [28], Gilman [29], and Schartel [30]. Typically, nanocomposites are parts of complex multi-component systems.

A pair of interesting NIST studies [31, 32] looked at the fire testing of materials intended for use in electronic equipment, in small scale and in full scale. The small-scale work [31] showed that the heat released by the type of PP chosen for the cone calorimeter tests is very high and that not all flame retardant systems can be effective in reducing the heat release rate to manageable levels. However, the addition of a 'non-halogen' flame retardant system resulted in a PP material with a Pk HRR of

Table VII. Effectiveness of halogen-containing nanocomposites as flame retardants on heat and ignitability properties of some polyolefins [20].

Cone calorimeter at 35 kW/m^2	TTI	Pk HRR	FPI	THR
	s	kW/m^2	m^{2}skW^{-1}	MJ/m^2
Polyethylene				
Untreated	73	1949	0.04	100
Plus FR4	75	1577	0.05	92
Improvement %	3	19	27	8
Plus FR2	64	1817	0.04	95
Improvement %	−12	7	−6	5
Plus FR1	75	1190	0.06	88
Improvement %	3	39	68	12
Plus FR3	67	1762	0.04	97
Improvement %	−8	10	2	3
Polypropylene				
Untreated	50	1642	0.03	60
Plus FR4	44	1656	0.03	72
Improvement %	−12	−1	−13	−20
Plus FR1	48	1281	0.04	73
Improvement %	−4	22	23	−22
Plus FR3	46	957	0.05	74
Improvement %	−8	42	58	−23
Plus FR2	67	1762	0.04	97
Improvement %	−6	54	103	−2

Notes: TTI, time to ignition in cone calorimeter test; Pk HRR, peak heat release rate in cone calorimeter test; THR, total heat released during test in cone calorimeter test; FPI, fire performance index (ratio of time to ignition and peak heat release rate, in cone calorimeter test); FR1, butyric acid pentabromobenzyl ester; FR2, pentabromobenzyl ester polyacrylate; FR3, methacrylate acid pentabromobenzyl ester; FR4, acrylic acid pentabromobenzyl ester; improvement %, percentage improvement in relevant property based on the untreated material.

some 450 kW/m^2, compared to a corresponding value of more than 2000 kW/m^2 for the (untested) non-flame retarded PP material. No tabular data are presented because no direct comparison can be referenced. In later sections of this work, some of the data on other polymeric systems from the studies will be presented.

3.2. Styrenics

Polystyrene and ABS are widely used thermoplastic engineering polymers, which are also poor fire performers in the absence of flame retardants. The NBS/NIST data [14] show that the heat release rate of the TV cabinet material (made out of polystyrene) is improved by flame retardants, and a table in part 1 of this study includes data that shows how the heat release rate of ABS and of polystyrene are also very positively affected by flame retardants [1]. The following data comes from more recent studies on specific polymers: three studies on polystyrene and one on ABS.

The same work that studied the effects of adding, to polyolefins, 3% of an organically modified clay (Cloisite 30B) and 3% of various brominated materials, creating halogen-containing polymer nanocomposites, also studied the effects on polystyrene [20]. In this case, an added flame retardant was also used, namely, antimony trioxide (ATO). Conclusions are similar to those for the polyolefins, and the data are shown in Table VIII.

Table IX shows that brominated additives are effective at decreasing heat release and ignitability of HIPS [33], particularly in the presence of antimony oxide as a synergist. The tests were conducted in a cone calorimeter at an incident heat flux of 40 kW/m^2. The combined systems have particularly strong effects on the FPI. One study investigated the effects of synthetic micas (or synthetic clays) and of natural clays (sodium montmorillonite and treated versions of sodium montmorillonite) on polystyrene and on a combination of polystyrene and a polystyrene co-maleic anhydride. The results are shown later in Tables X–XII [34]. A recent study looked at layered double hydroxides as flame retardants for polystyrene (Table XIII) [35].

Table VIII. Effectiveness of halogen-containing nanocomposites and antimony oxide as flame retardants on heat and ignitability properties of polystyrene materials [20].

Cone calorimeter at 35 kW/m²	TTI	Pk HRR	FPI	THR
	s	kW/m²	(m²skW⁻¹)	MJ/m²
Polystyrene				
Untreated	59	1242	0.05	100
Plus FR1	43	1065	0.04	77
Improvement %	−27	14	−15	23
Plus FR1 + ATO	41	590	0.07	50
Improvement %	−31	52	46	50
Plus FR2	33	707	0.05	62
Improvement %	−44	43	−2	38
Plus FR2 + ATO	42	541	0.08	45
Improvement %	−29	56	63	55
Plus FR3	34	967	0.04	71
Improvement %	−42	22	−26	29
Plus FR3 + ATO	43	813	0.05	51
Improvement %	−27	35	11	49
Plus FR4	34	813	0.04	75
Improvement %	−42	35	−12	25
Plus FR4 + ATO	44	875	0.05	61
Improvement %	−25	30	6	39

Notes: TTI, time to ignition in cone calorimeter test; Pk HRR, peak heat release rate in cone calorimeter test; THR, total heat released during test in cone calorimeter test; FPI, fire performance index (ratio of time to ignition and peak heat release rate, in cone calorimeter test); FR1, butyric acid pentabromobenzyl ester; FR2, pentabromobenzyl ester polyacrylate; FR3, methacrylate acid pentabromobenzyl ester; FR4, acrylic acid pentabromobenzyl ester; ATO, antimony oxide; improvement %, percentage improvement in relevant property based on the untreated material.

Table IX. Effectiveness of brominated additives (with and without antimony oxide) as flame retardants on heat and ignitability properties of high impact polystyrene [33].

Cone at 40 kW/m²	TTI	Pk HRR	Av HRR 3 min	Eff. Ht Comb	FPI
	s	kW/m²	kW/m²	MJ/kg	m²skW⁻¹
HIPS	60	968	621	30.7	0.06
HIPS + SbO	62	910	580	28.6	0.07
HIPS + Deca	55	708	470	17.0	0.08
HIPS + Deca + SbO	72	360	255	10.1	0.20
HIPS + DBE	54	782	487	18.6	0.07
HIPS + DBE + SBO	78	393	302	10.8	0.20
HIPS + BT93	54	768	509	19.6	0.07
HIPS + BT93 + SbO	88	423	293	12.2	0.21
HIPS + HBCD	72	885	710	23.2	0.08
HIPS + HBCD + SbO	80	766	423	13.2	0.10
Improvement % SbO	3	6	7	7	10
Improvement % Deca	−8	27	24	45	25
Improvement % Deca + SbO	20	63	59	67	223
Improvement % DBE	−10	19	22	39	11
Improvement % DBE + SbO	30	59	51	65	220
Improvement % BT93	−10	21	18	36	13
Improvement % BT93 + SbO	47	56	53	60	236
Improvement % HBCD	20	9	−14	24	31
Improvement % HBCD + SbO	33	21	32	57	68

Notes: Brominated additives at 12%; antimony oxide at 4%; Sb, antimony oxide; Deca, decabromodiphenyl oxide; DBE, decabromodiphenyl ethane; BT93, ethylenebis(tetrabromophthalimide); HBCDE, hexabromocyclododecane; TTI, time to ignition in cone calorimeter test; Pk HRR, peak heat release rate in cone calorimeter test; Avg HRR 3 min, average heat release rate during the 3 min following ignition in cone calorimeter test; Eff. Ht Comb, effective heat of combustion in cone calorimeter test; FPI, fire performance index (ratio of time to ignition and peak heat release rate, in cone calorimeter test).

Table X. Effectiveness of synthetic micas as flame retardants on heat and ignitability properties of polystyrene materials [34].

Cone at 50 kW/m^2	TTI	Pk HRR	FPI	Ht Comb	THR
Synthetic Micas	s	kW/m^2	m^{2}skW^{-1}	MJ/kg	MJ/m^2
Polystyrene	65	1294	0.05	30.6	111
PS + 1 (18.6 wt% Mica O)	51	513	0.10	27.9	94
PS + 2 (9.3 wt% Mica O)	49	428	0.11	27.1	98
PS + 3 (1.9 wt% Mica O)	63	911	0.07	29.4	111
PS + 4 (10 wt% Mica N)	41	995	0.04	30.8	113
PS + 5 (5 wt% Mica N)	43	1146	0.04	31.7	117
PS + 6 (1 wt% Mica N)	52	1201	0.04	31.9	117
Mica O: dimethyl, di(hydrogenated tallow) ammonium treated sodium fluorinated synthetic mica					
Mica N: sodium fluorinated synthetic mica					
Improvement % 1	−22	60	98	9	15
Improvement % 2	−25	67	128	11	12
Improvement % 3	−3	30	38	4	0
Improvement % 4	−37	23	−18	−1	−2
Improvement % 5	−34	11	−25	−4	−5
Improvement % 6	−20	7	−14	−4	−5

Notes: TTI, time to ignition in cone calorimeter test; Pk HRR, peak heat release rate in cone calorimeter test; THR, total heat released during test in cone calorimeter test; Ht Comb, effective heat of combustion in cone calorimeter test; FPI, fire performance index (ratio of time to ignition and peak heat release rate, in cone calorimeter test); improvement %, percentage improvement in relevant property based on the untreated material.

Table XI. Effectiveness of sodium montmorillonites as flame retardants on heat and ignitability properties of polystyrene materials [34].

Cone at 50 kW/m^2	TTI	Pk HRR	FPI	Ht Comb	THR
Sodium montmorillonite	s	kW/m^2	(m^{2}skW^{-1})	MJ/kg	MJ/m^2
Polystyrene	65	1294	0.05	30.6	111
PS + 1 (16.2 wt% MMT O)	52	446	0.12	26.9	97
PS + 2 (8.1 wt% MMT O)	58	555	0.10	26.6	98
PS + 3 (1.6 wt% MMT O)	66	1080	0.06	29.9	111
PS + 4 (10 wt% MMT N)	40	792	0.05	29.2	106
PS + 5 (5 wt% MMT N)	41	993	0.04	29.5	111
PS + 6 (1 wt% MMT N)	57	1106	0.05	29.8	110
MMT O: dimethyl, di(hydrogenated tallow) ammonium treated montmorillonite (Cloisite 15A)					
MMT N: sodium montmorillonite (Cloisite Na+)					
Improvement % 1	−20	66	132	12	13
Improvement % 2	−11	57	108	13	12
Improvement % 3	2	17	22	2	0
Improvement % 4	−38	39	1	5	5
Improvement % 5	−37	23	−18	4	0
Improvement % 6	−12	15	3	3	1

Notes: TTI, time to ignition in cone calorimeter test; Pk HRR, peak heat release rate in cone calorimeter test; THR, total heat released during test in cone calorimeter test; Ht Comb, effective heat of combustion in cone calorimeter test; FPI, fire performance index (ratio of time to ignition and peak heat release rate, in cone calorimeter test); improvement %, percentage improvement in relevant property based on the untreated material.

A different recent study, using a mass loss cone (ASTM E2102 [36]), looked at ABS and a combination of three flame retardants: ethane-1,2-bis pentabromophenyl, antimony oxide, and zinc borate. The effects are very significant, as shown in Table XIV [37].

The NIST work discussed earlier, on materials for electronic equipment, [31] included comparisons for HIPS, and the data are being analyzed in Table XV. The flame retardants used are identified simply as brominated and non-halogen. In both cases, improvements can be found on Pk HRR (31–57%) as well as in the other key parameters (TTI, effective heat of combustion, and total heat released).

Table XII. Effectiveness of phosphonium synthetic micas as flame retardants on heat and ignitability properties of polystyrene and associated materials [34].

Cone at 50 kW/m^2	TTI	Pk HRR	FPI	Ht Comb	THR
Phosphonium treated synthetic micas	s	kW/m^2	(m^{2}skW^{-1})	MJ/kg	MJ/m^2
Polystyrene	65	1294	0.05	30.6	30.6
PS + 1 (styrene/maleic anhydride)	64	1280	0.05	30.8	30.8
PS + 2 (PS + 1 + 8.3 wt% Mica P)	65	557	0.12	26.5	26.5
PS + 3 (8.3 wt% Mica P)	64	586	0.11	26.6	26.6
Mica P: triphenyl, n-hexadecyl phosphonium treated sodium fluorinated synthetic mica					
System 1: addition of styrene/maleic anhydride					
Improvement % 1	−2	1	0	−1	−1
Improvement % 2	0	57	132	13	13
Improvement % 3	−2	55	117	13	13

Notes: TTI, time to ignition in cone calorimeter test; Pk HRR, peak heat release rate in cone calorimeter test; THR, total heat released during test in cone calorimeter test; Ht Comb, effective heat of combustion in cone calorimeter test; FPI, fire performance index (ratio of time to ignition and peak heat release rate, in cone calorimeter test); improvement %, percentage improvement in relevant property based on the untreated material.

Table XIII. Effectiveness of layered double hydroxides as flame retardants on heat and ignitability properties of polystyrene [35].

	TTI	Pk HRR	FPI	THR
Cone at 35 kW/m^2	s	kW/m^2	(m^{2}skW^{-1})	MJ/m^2
Polystyrene	88	813	0.11	138
PS + 5 wt% LDH-DBP	72	616	0.12	133
Improvement %	−18	24	8	4
PS + 5 wt%5 LDH-SMM 30 min DBP	65	517	0.13	133
Improvement %	−26	36	16	4
PS + 5 wt% LDH-SMM 60 min DBP	66	621	0.11	131
Improvement %	−25	24	−2	5
PS + 5 wt% LDH syntal DBP	59	627	0.09	129
Improvement %	−33	23	−13	7
PS + 10 wt% LDH-DBP	74	444	0.17	127
Improvement %	−16	45	54	8
PS + 15 wt% LDH-DBP	95	402	0.24	125
Improvement %	8	51	118	9

Notes: DBP, 3,4-dihydroxybenzophenone; LDH, layered double hydroxides; SMM, surface modification; LDH syntal, commercial material; TTI, time to ignition in cone calorimeter test; Pk HRR, peak heat release rate in cone calorimeter test; THR, total heat released during test in cone calorimeter test; Ht Comb, effective heat of combustion in cone calorimeter test; FPI, fire performance index (ratio of time to ignition and peak heat release rate, in cone calorimeter test); improvement %, percentage improvement in relevant property based on the untreated material.

Recent cone calorimeter work compared the fire performance of a commercial non-flame retarded expanded polystyrene (EPS) foam with a commercial flame retarded EPS foam [38]. The work both conducted its own cone calorimeter work, at an incident heat flux of 35 kW/m^2, and compared work performed earlier [39, 40] with other foamed EPS systems, at incident heat fluxes ranging from 30 to 50 kW/m^2. The results (Table XVI) show that a certain level of improvement was obtained on the Pk HRR and on the TTI for all systems.

3.3. Engineering thermoplastics

Engineering thermoplastics are widely used for a large number of applications, even if they are not as high volume as polyolefins or styrenics. The NBS/NIST study [14] included two products that fall under this category: the business machine housing (a polyphenylene oxide) and the laminated circuit board (a polyester). Some other recent work on engineering thermoplastics follows. A study on PC

Table XIV. Mass loss cone study of the effectiveness of various flame retardants on heat and ignitability properties of ABS [37].

Mass loss cone at 35 kW/m^2	TTI	Pk HRR	FPI	THR
	s	kW/m^2	(m^{2}skW^{-1})	MJ/m^2
Untreated ABS	83	900	0.09	134
Plus FR1	64	239	0.27	44
Plus FR2	67	257	0.26	40
Plus FR3	65	203	0.32	31
Plus FR4	60	265	0.23	35
Plus FR5	72	360	0.20	57
Plus FR6	64	336	0.19	92
Improvement % FR1	−23	73	190	67
Improvement % FR2	−19	71	183	70
Improvement % FR3	−22	77	247	77
Improvement % FR4	−28	71	146	74
Improvement % FR5	−13	60	117	57
Improvement % FR6	−23	63	107	31

Notes: FR1, EBP + 6 phr antimony oxide; FR2, EBP + 4.5 phr antimony oxide + 1.5 phr zinc borate; FR3, EBP + 3 phr antimony oxide + 3 phr zinc borate; FR4, EBP + 1.5 phr antimony oxide + 4.5 phr zinc borate; FR5, EBP + 6 phr zinc borate; FR6, zinc borate only; EBP, ethane-1,2-bis pentabromophenyl; TTI, time to ignition in mass loss cone (ASTM E2102) test; Pk HRR, peak heat release rate in mass loss cone test with thermopile column; THR, total heat released during test in mass loss cone test; FPI, fire performance index (ratio of time to ignition and peak heat release rate, in mass loss cone test); improvement %, percentage improvement in relevant property based on the untreated material.

Table XV. Effectiveness of flame retardant systems on heat and ignitability properties of polystyrene (HIPS) [31].

Cone at 50 kW/m^2	TTI	Pk HRR	FPI	THR	Ht Comb
	s	kW/m^2		MJ/m^2	MJ/kg
HIPS	30	723	0.04	59.5	33.9
HIPS + brominated FR	33	318	0.10	23.8	12.3
HIPS + brominated FR	41	502	0.08	33.8	16.4
HIPS + non-halogen FR	34	313	0.11	42.2	22.3
Improvement % brominated FR (1)	10	56	150	60	64
Improvement % brominated FR (2)	37	31	97	43	52
Improvement % non-halogen FR	13	57	162	29	34

Notes: TTI, time to ignition in cone calorimeter test; Pk HRR, peak heat release rate in cone calorimeter test; THR, total heat released during test in cone calorimeter test; Ht Comb, effective heat of combustion in cone calorimeter test; FPI, fire performance index (ratio of time to ignition and peak heat release rate, in cone calorimeter test); improvement %, percentage improvement in relevant property based on the untreated material.

was recently conducted in the cone calorimeter at an incident heat flux of 50 kW/m^2, using intumescent flame retardants containing nitrogen and phosphorus (Table XVII) [41]. The next table (Table XVIII) shows the effect (based on mass loss cone data) of a variety of flame retardants on a polyamide 6 (nylon) [42]. One study on a plastic PET is shown in Table XIX [43]. The same work also addresses PET fabrics and that will be shown in the section on fibers. An engineering thermoplastic often used in wire and cable applications is thermoplastic polyurethane and a recent study will be shown here, although this could also have been added to a section on polyurethanes. The study used the cone calorimeter at an incident heat flux of 50 kW/m^2, and the results are shown in Table XX [44].

The NIST work discussed earlier, on materials for electronic equipment [31], included comparisons for PC and PC/ABS blends, and the data is being analyzed in Table XXI. The flame retardants used are identified simply as brominated, phosphorus containing, and non-halogen. In the case of PC alone, the brominated flame retarded materials have very significant improvements in Pk HRR (57–68%), but the effects on other key parameters (TTI, effective heat of combustion, and total heat released) are negligible or even detrimental. The non-halogen system used has little effect. In the case of PC/

Table XVI. Effectiveness of flame retardant systems on heat and ignitability properties of foamed expanded polystyrene (EPS) [38].

Foamed EPS at 35 kW/m^2	TTI	Pk HRR	FPI
	s	kW/m^2	MJ/m^2
EPS	77.7	310.5	0.25
EPS Plus Commercial FR	81	230.6	0.35
Improvement % FR	4	26	40
Foamed EPS at 30 kW/m^2	TTI	Pk HRR	FPI
	s	kW/m^2	MJ/m^2
EPS	73	299	0.24
EPS Plus Commercial FR	77	238	0.32
Improvement % FR	5	20	33
Foamed EPS at 40 kW/m^2	TTI	Pk HRR	FPI
	s	kW/m^2	MJ/m^2
EPS	28	394	0.07
EPS Plus Commercial FR	40	321	0.12
Improvement % FR	43	19	75
Foamed EPS 50 kW/m^2	TTI	Pk HRR	FPI
	s	kW/m^2	MJ/m^2
EPS	18	407	0.04
EPS Plus Commercial FR	24	379	0.06
Improvement % FR	33	7	43

Notes: Data at 35 kW/m^2 were determined by the authors [38], while data at 30, 40, and 50 kW/m^2 were obtained by comparison of published data from other authors [39, 40]. TTI, time to ignition in cone calorimeter test; Pk HRR, peak heat release rate in cone calorimeter test; FPI, fire performance index (ratio of time to ignition and peak heat release rate, in cone calorimeter test); improvement %, percentage improvement in relevant property based on the untreated material.

Table XVII. Effectiveness of intumescent flame retardants on heat and ignitability properties of a polycarbonate material [41].

Polycarbonate	TTI	Pk HRR	FPI	THR
Cone at 50 kW/m^2	s	kW/m^2	(m^{2}skW^{-1})	MJ/m^2
Untreated polycarbonate	58	357	0.16	80
Plus FR1	52	219	0.24	69
Plus FR2	54	192	0.28	52
FR1: intumescent FR with P and N BASPB: bis-aminobenzyl spirocylic pentaerythritol bisphosphonate				
FR2: intumescent FR with P and N ABDPP: arylene-N,N0-bis(2,2-dimethyl-1,3-propanediol phosphoramidate)				
Improvement % FR1	−10	39	46	14
Improvement % FR2	−7	46	73	35

Notes: TTI, time to ignition in cone calorimeter test; Pk HRR, peak heat release rate in cone calorimeter test; THR, total heat released during test in cone calorimeter test; Ht Comb, effective heat of combustion in cone calorimeter test; FPI, fire performance index (ratio of time to ignition and peak heat release rate, in cone calorimeter test); improvement %, percentage improvement in relevant property based on the untreated material.

ABS, very significant improvements were found in all the key fire properties, including 85% improvement in FPI.

3.4. Poly(vinyl chloride)

Poly(vinyl chloride) can be used as a rigid material (for pipes, conduits, siding, and profiles) or as a flexible material (typically for wire and cable, wall coverings, or floor coverings). The most common need for improved fire performance is in the area of flexible PVC because rigid PVC already has good fire performance. Numerous tables in part 1 of this study [1] include several examples of the positive effects of flame retardants on heat release of both rigid and flexible PVC. Some newer examples (three for wire and cable compounds, one for wall coverings, and one for

Table XVIII. Mass loss cone study of the effectiveness of various flame retardants on heat release of a polyamide 6 [42].

Nylon polyamide 6	Pk HRR	Avg HRR	THR
Mass loss cone at 35 kW/m^2	kW/m^2	kW/m^2	MJ/m^2
PA6	975	375	163
PA6 + OP2	695	300	158
PA6 + OP3	480	235	136
PA6 + OP4	335	190	122
PA6 + OP5	755	345	160
PA6 + OP6	720	325	149
PA6 + OP7	575	315	143
PA6 + OP8	380	186	135
PA6 + OP9	535	288	141
Improvement % OP2	29	20	3
Improvement % OP3	51	37	17
Improvement % OP4	66	49	25
Improvement % OP5	23	8	2
Improvement % OP6	26	13	9
Improvement % OP7	41	16	12
Improvement % OP8	61	50	17
Improvement % OP9	45	23	13

Notes: OP2, 15% organic phosphinate; OP3, 14% OP 1% Zn borate; OP3, 12% OP 3% Zn borate; OP5, 14% OP 1% borophosphate; OP6, 12% OP 3% borophosphate; OP7, 14% OP 1% organo clay; OP8, 13% OP 1% zinc borate 1% organo clay; OP9, 13% OP 1% borophosphate 1% organo clay; Pk HRR, peak heat release rate in mass loss cone test with thermopile column (ASTM E2102); THR, total heat released during test in mass loss cone test; Avg HRR, average heat release rate during mass loss cone test; improvement %, percentage improvement in relevant property based on the untreated material.

Table XIX. Effectiveness of expanded graphite flame retardants on heat and ignitability properties of a PET material [41].

	TTI	Pk HRR	FPI
PET plastic cone at 35 kW/m^2	s	kW/m^2	(m^{2}skW^{-1})
Untreated PET plastic	209	523	0.40
Plus exp. graphite (EG)	189	303	0.62
Plus Nano1	187	349	0.54
Plus Nano 2	174	440	0.40
Plus Nano 3	220	438	0.50
Plus EG + Nano1	179	231	0.77
Plus EG + Nano2	210	304	0.69
Plus EG + Nano 3	222	347	0.64
Improvement % EG	−10	42	56
Improvement % Nano1	−11	33	34
Improvement % Nano2	−17	16	−1
Improvement % Nano3	5	16	26
Improvement % EG Nano1	−14	56	94
Improvement % EG Nano2	0	42	73
Improvement % EG Nano3	6	34	60

Notes: TTI, time to ignition in cone calorimeter test; Pk HRR, peak heat release rate in cone calorimeter test; FPI, fire performance index (ratio of time to ignition and peak heat release rate, in cone calorimeter test); improvement %, percentage improvement in relevant property based on the untreated material.

conduits and window profiles) are also shown. In the case of rigid PVC, the effects of flame retardants on heat release tend to be low because the primary reason these materials are being added is smoke release or other issues.

Table XXII shows heat release testing results for rigid PVC materials at incident heat fluxes of 30 and 50 kW/m^2 [45] in the Ohio State University calorimeter (OSU, ASTM E906 [46]). Tables XXIII

Table XX. Effectiveness of nanocomposites as flame retardants on heat and ignitability properties of a thermoplastic polyurethane (TPU) [44].

TPU	TTI	Pk HRR	FPI	Avg HRR 3 min	Ht Comb
Cone at 50 kW/m^2	s	kW/m^2	(m^{2}skW^{-1})	kW/m^2	MJ/kg
Untreated TPU	28	1031	0.03	515	27
TPU + 5% Cloisite 30B	27	518	0.05	376	28
TPU + 5% Multiwalled carbon nanotubes (MWNT)	21	571	0.04	492	28
TPU + 5% Carbon nanofibers	21	808	0.03	361	27
Improvement %, Cloisite 30B	−4	50	92	27	−4
Improvement %, carbon nanotubes	−25	45	35	4	−4
Improvement %, carbon nanofibers	−25	22	−4	30	0

Notes: Cloisite 30B, montmorillonite (MMT) surface treated with methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium; TTI, time to ignition in cone calorimeter test; Pk HRR, peak heat release rate in cone calorimeter test; Avg HRR 3 min, average heat release rate during 3 min following ignition in cone calorimeter test; Ht Comb, effective heat of combustion in cone calorimeter test; FPI, fire performance index (ratio of time to ignition and peak heat release rate, in cone calorimeter test); improvement %, percentage improvement in relevant property based on the untreated material.

Table XXI. Effectiveness of flame retardant systems on heat and ignitability properties of polycarbonate and polycarbonate/ABS blends [31].

	TTI	Pk HRR	FPI	THR	Ht Comb
Cone at 50 kW/m^2	s	kW/m^2		MJ/m^2	MJ/kg
PC	77	885	0.09	37.5	24.0
PC + brominated FR	51	378	0.13	25.2	22.3
PC + brominated FR	41	280	0.15	45.9	21.2
PC + non-halogen FR	46	829	0.06	38.8	23.6
Improvement % brominated FR (1)	−34	57	55	33	7
Improvement % brominated FR (2)	−47	68	68	−22	12
Improvement % non-halogen FR	−40	6	−36	−3	2
Cone at 50 kW/m^2	TTI	Pk HRR	FPI	THR	Ht Comb
	s	kW/m^2		MJ/m^2	MJ/kg
PC/ABS	34	543	0.06	44.4	29.7
PC/ABS + Phosphorus FR	45	388	0.12	35	20.6
Improvement % Phosphorus FR	32	29	85	21	31

Notes: TTI, time to ignition in cone calorimeter test; Pk HRR, peak heat release rate in cone calorimeter test; THR, total heat released during test in cone calorimeter test; Ht Comb, effective heat of combustion in cone calorimeter test; FPI, fire performance index (ratio of time to ignition and peak heat release rate, in cone calorimeter test); improvement %, percentage improvement in relevant property based on the untreated material.

and XXIV show results of wire and cable compounds tested in the cone calorimeter [47, 48]. Significant improvements in heat release are evident. Work conducted in the cone calorimeter to look at the effects of various additives, with particular emphasis on a phosphate plasticizer as a flame retardant additive which also replaces traditional phthalate plasticizers, in wall coverings and in plenum cables is shown in Tables XXV and XXVI [49].

3.5. Polyurethane foams

Polyurethane foams have been discussed extensively earlier, including in the NBS/NIST work. However, it is worth noting that the improvement keeps being found, even in recent work, both on flexible foams (Table XXVII) [50] and on rigid foams (Tables XXVIII [50] and XXIX [16]). Moreover, a recent analysis has looked at flexible polyurethane foam used in upholstered furniture [51] and found the significant positive contributions to heat release made by flame retardants, provided they are added at a sufficiently high level to be effective (i.e., beyond just the level needed to comply with the discredited automotive test FMVSS 302 [52]).

Table XXII. Effectiveness of molybdenum smoke suppressants as flame retardants on heat release of rigid PVC materials [45].

OSU calorimeter	Pk HRR at 30 kW/m^2	Pk HRR at 50 kW/m^2
PVC for conduits	60	76
PVC + AOM 0.5 phr	64	60
PVC + AOM 1 phr	62	63
PVC + AOM 2.5 phr	50	53
PVC + AOM 5 phr	47	54
Improvement % AOM 0.5 phr	−7	21
Improvement % AOM 1 phr	−3	17
Improvement % AOM 2.5 phr	17	30
Improvement % AOM 5 phr	22	29
PVC for window profile	70	
PVC + AOM 1.3 phr	58	
PVC + AOM 2.5 phr	60	
PVC + AOM 5 phr	57	
PVC + Mo tri 1.3 phr	58	
PVC + Mo tri 2.5 phr	57	
Improvement % AOM 1.3 phr	17	
Improvement % AOM 2.5 phr	14	
Improvement % AOM 5 phr	19	
Improvement % Mo Tri 1.3 phr	17	
Improvement % Mo Tri 2.5 phr	19	

Notes: AOM, ammonium molybdate; Mo Tri, molybdenum trioxide; Pk HRR, peak heat release rate from Ohio State University (ASTM E906) heat release test at relevant heat flux; improvement %, percentage improvement in relevant property based on the untreated material.

Table XXIII. Effectiveness of flame retardants on heat and ignitability properties of PVC with phosphorus-containing plasticizers [47].

Cone at 50 kW/m^2 With P plasticizers	TTI s	Pk HRR kW/m^2	FPI (m^{2}skW^{-1})
PVC for cables	29	190	0.15
PVC + system 1	23	115	0.20
PVC + system 2	28	123	0.23
PVC + system 3	25	141	0.18
PVC + system 4	30	118	0.25
PVC + system 5	25	121	0.21
PVC + system 6	26	121	0.21
Improvement % 1	−21	39	31
Improvement % 2	−3	35	49
Improvement % 3	−14	26	16
Improvement % 4	3	38	67
Improvement % 5	−14	36	35
Improvement % 6	−10	36	41

Notes: TTI, time to ignition in cone calorimeter test; Pk HRR, peak heat release rate in cone calorimeter test; FPI, fire performance index (ratio of time to ignition and peak heat release rate, in cone calorimeter test); improvement %, percentage improvement in relevant property based on the untreated material.

3.6. Epoxy resins

Epoxy resins are used extensively in two primary applications: printed wiring or circuit boards and adhesives. Table XXX presents some recent data [53]. The improvement in Pk HRR from the addition of the flame retardants (in that particular system) exceeds 80%.

Table XXIV. Effectiveness of tin-based flame retardants on heat and ignitability properties of PVC with phosphorus-containing plasticizers [48].

PVC for cables with P plasticizers	TTI	Pk HRR	FPI
Cone at 50 kW/m^2	s	kW/m^2	(m^{2}skW^{-1})
PVC control	22	260	0.08
PVC + ATH	45	163	0.28
PVC + ATH + LDH	52	72	0.72
PVC + ATH + Sn LDH1	46	74	0.62
PVC + ATH + Sn LDH2	48	73	0.66
PVC + ATH + Sn LDH3	56	59	0.95
Improvement % ATH	105	37	226
Improvement % ATH + LDH	136	72	754
Improvement % ATH Sn LDH1	109	72	635
Improvement % ATH Sn LDH2	118	72	677
Improvement % ATH Sn LDH3	155	77	1022

Notes: Plasticizer, 8-Methylnonyl diphenyl phosphate; LDH, layered double hydroxide with Mg + Al nitrates; LDH Sn, LDH + Sn, various ratios; ATH, alumina trihydrate; TTI, time to ignition in cone calorimeter test; Pk HRR, peak heat release rate in cone calorimeter test; FPI, fire performance index (ratio of time to ignition and peak heat release rate, in cone calorimeter test); improvement %, percentage improvement in relevant property based on the untreated material.

Table XXV. Effectiveness of flame retardants on heat release of PVC wall coverings using phosphorus-containing plasticizers [49].

Cone at 50 kW/m^2	Pk HRR	Improvement	Avg HRR	Ht Comb
PVC wall coverings	kW/m^2	%	kW/m^2	MJ/kg
PVC + 40 DOP + 20 Ca (control)	228	0	146	16.9
Additive system 1	167	27	116	14.0
Additive system 2	191	16	127	11.2
Additive system 3	203	11	132	13.0
Additive system 4	135	41	104	10.8
Additive system 5	90	61	83	11.9
Additive system 6	91	60	89	11.3
Additive system 7	102	55	84	9.8
Additive system 8	94	59	79	10.7
Additive system 9	102	55	83	11.7
Additive system 10	99	57	81	9.9
Additive system 11	99	57	82	10.1
Additive system 12	107	53	85	9.3
Additive system 13	109	52	90	9.6
Additive system 14	95	58	77	8.5
Additive system 15	91	60	73	8.3
Additive system 16	81	64	69	8.8
Additive system 17	159	30	102	10.5
Additive system 18	165	28	101	13.0
Additive system 19	105	54	80	10.6
Additive system 20	83	64	63	11.0
Additive system 21	98	57	67	10.4

Notes: DOP, dioctyl phthalate plasticizer; Ca, calcium carbonate; TTI, time to ignition in cone calorimeter test; Pk HRR, peak heat release rate in cone calorimeter test; Avg HRR, average heat release rate during test in cone calorimeter test; Ht Comb, effective heat of combustion in cone calorimeter test; FPI, fire performance index (ratio of time to ignition and peak heat release rate, in cone calorimeter test); improvement %, percentage improvement in Pk HRR based on the untreated material.

Table XXVI. Effectiveness of flame retardants on heat release of PVC plenum cable compounds using phosphorus-containing plasticizers [49].

Cone at 40 kW/m^2	Pk HRR	Improvement	Avg HRR	Ht Comb
PVC cables (for plenum)	kW/m^2	%	kW/m^2	MJ/kg
PVC Non FR + DOP (control)	283	0	170	15.7
Additive system 1	161	43	47	12.9
Additive system 2	132	53	76	11.5
Additive system 3	134	53	64	12.0
Additive system 4	158	44	83	10.7
Additive system 5	128	55	80	10.8
Additive system 6	127	55	94	11.4
Additive system 7	117	59	76	11.4

Notes: Pk HRR, peak heat release rate in cone calorimeter test; Avg HRR, average heat release rate during test in cone calorimeter test; Ht Comb, effective heat of combustion in cone calorimeter test; improvement %, percentage improvement in Pk HRR based on the untreated material.

Table XXVII. Effectiveness of flame retardants on heat release of a flexible polyurethane foam [50].

Cone at 25 kW/m^2	TTI	Pk HRR	Improvement	FPI	Avg HRR	THR
Flexible PU foam	s	(kW/m^2)	%	m^{2}skW^{-1}	kW/m^2	MJ/ m^2
Control	15.6	412	0	0.04	225	57.4
Additive system 1	13.7	249	40	0.06	126	54.2
With Zn stearate	372	340	17	1.09	174	64.4
With Mg stearate	39.1	444	8	0.09	194	70.8
With ATH	16.0	401	3	0.04	218	60.1
With Fyrol RDP	22.6	429	4	0.05	210	56.7
With Fyrol FR2	18.4	326	21	0.06	163	48.2
With Cl P ester	28.4	315	24	0.09	144	19.9
With alkyl aryl phosphate	26.1	274	33	0.10	154	49.2

Notes: TTI, time to ignition in cone calorimeter test; Pk HRR, peak heat release rate in cone calorimeter test; Avg HRR, average heat release rate during test in cone calorimeter test; THR, total heat released during test in cone calorimeter test; FPI, fire performance index (ratio of time to ignition and peak heat release rate, in cone calorimeter test); improvement %, percentage improvement in Pk HRR based on the untreated material.

Table XXVIII. Effectiveness of flame retardants on heat release of a rigid polyurethane foam [50].

Cone at 25 kW/m^2	TTI	Pk HRR	Improvement	FPI
Rigid PU foam	s	kW/m^2	%	m^{2}skW^{-1}
Control	26	890	0	0.03
With alkyl aryl phosphate	41	548	38	0.07
With Fyrol RDP	65	910	2	0.07
With Fyrol RDP + Zn stearate	33	720	19	0.05
With Zn stannate and Zn stearate	9	485	46	0.02
With Zinc stannate	31	424	52	0.07
With Zn hydroxystannate	36	471	47	0.08

Notes: TTI, time to ignition in cone calorimeter test; Pk HRR, peak heat release rate in cone calorimeter test; FPI, fire performance index (ratio of time to ignition and peak heat release rate, in cone calorimeter test); improvement %, percentage improvement in Pk HRR based on the untreated material.

Table XXIX. Effectiveness of flame retardants on heat release of a polyisocyanurate foam [16].

Cone at 40 kW/m^2	TTI	Pk HRR	FPI	Av HRR	THR
Polyisocyanurate foam	s	kW/m^2	m^{2}skW^{-1}	kW/m^2	MJ/m^2
Untreated	4.3	161	0.03	69	11
Plus TCPP	4.6	87	0.05	19	5
Improvement %	7	46	98	72	55

Notes: TTI, time to ignition in cone calorimeter test; Pk HRR, peak heat release rate in cone calorimeter test; Avg HRR, average heat release rate during test in cone calorimeter test; THR, total heat released during test in cone calorimeter test; FPI, fire performance index (ratio of time to ignition and peak heat release rate, in cone calorimeter test); improvement %, percentage improvement in relevant property based on the untreated material; TCPP, tris (1-chloro-2-propyl) phosphate.

Table XXX. Effectiveness of flame retardants on heat release of an epoxy resin [53].

	TTI	Pk HRR	FPI	THR	Avg HRR	Eff. Ht Combust
Cone at 50 kW/m^2	s	kW/m^2	m^{2}skW^{-1}	MJ/m^2	kW/m^2	MJ/kg
Epoxy	62	1192	0.05	184	350	26.8
Epoxy + APP	41	200	0.21	104	107	23.8
Epoxy + Mod APP	47	184	0.26	98	77	20.5
Improvement % APP	−34	83	294	43	69	11
Improvement % ModAPP	−24	85	391	47	78	24

Notes: APP, ammonium polyphosphate; ModAPP, APP modified with silane; TTI, time to ignition in cone calorimeter test; Pk HRR, peak heat release rate in cone calorimeter test; Avg HRR, average heat release rate during test in cone calorimeter test; THR, total heat released during test in cone calorimeter test; Eff. Ht Combust, effective heat of combustion during cone calorimeter test; FPI, fire performance index (ratio of time to ignition and peak heat release rate, in cone calorimeter test); improvement %, percentage improvement in relevant property based on the untreated material.

Table XXXI. Effectiveness of expanded graphite flame retardants on heat and ignitability properties of a PET fiber material [43].

PET fibers	TTI	Pk HRR	FPI
Cone at 35 kW/m^2	s	kW/m^2	m^{2}skW^{-1}
Untreated PET fibers	128	510	0.25
Plus exp. graphite (EG)	102	92	1.11
Plus Nano1	128	213	0.60
Plus EG + Nano1	106	272	0.39
Improvement % EG	−20	82	342
Improvement % Nano1	0	58	139
Improvement % EG Nano1	−17	47	55

Notes: TTI, time to ignition in cone calorimeter test; Pk HRR, peak heat release rate in cone calorimeter test; FPI, fire performance index (ratio of time to ignition and peak heat release rate, in cone calorimeter test); improvement %, percentage improvement in relevant property based on the untreated material.

3.7. Textiles

Four examples are being presented associated with textiles: one work on PET polyester fibers (Table XXXI) [43], three types of work on cotton fibers (Tables XXXII–XXXIV [54–56]), and one study on a glass-reinforced polyester composite, with and without a barrier (Table XXXV) [57]. In all cases, the cone calorimeter was used for the studies and showed significant improvements in Pk

Table XXXII. Effectiveness of a flame retardant additive on heat release of cotton fabric and fiber [54].

Cotton	Cotton fabric		Cotton fiber	
	Pk HRR	THR	Pk HRR	THR
Cone at 50 kW/m^2	kW/m^2	MJ/m^2	kW/m^2	MJ/m^2
Untreated cotton	220	2.7	145	2.4
Cotton + FR 50 g/L	180	2.5	115	2.2
Cotton + FR 100 g/L	170	2.3	105	1.7
Cotton + FR 150 g/L	160	2.0	100	1.6
Cotton + FR 200 g/L	155	2.0	90	1.4
Cotton + FR 250 g/L	150	2.0	75	1.3
Cotton + FR 300 g/L	135	1.9	70	1.3
Improvement % 50	18	7	21	8
Improvement % 100	23	15	28	29
Improvement % 150	27	26	31	33
Improvement % 200	30	26	38	42
Improvement % 250	32	26	48	46
Improvement % 300	39	30	52	46

Notes: Pk HRR, peak heat release rate in cone calorimeter test; THR, total heat released during test in cone calorimeter test; improvement %, percentage improvement in relevant property based on the untreated material.

Table XXXIII. Effectiveness of flame retardants on heat and ignitability properties of cotton in normal and enriched atmospheres [55].

Cotton fabric	TTI	Pk HRR	FPI	Eff. Ht Combust	Avg HRR
Cone at 25 kW/m^2	s	kW/m^2	m^{2}skW^{-1}	MJ/kg	kW/m^2
Atmosphere: air					
Untreated cotton	22	340	0.06	12	200
Cotton + N FR	34	120	0.28	7	60
Improvement % N FR	55	65	338	42	70
Atmosphere: 30% oxygen					
Untreated cotton	21	360	0.06	13.0	230
Cotton + N FR	34	170	0.20	7.0	70
Cotton + M FR	39	110	0.35	3.5	30
Improvement % N FR	62	53	243	46	70
Improvement % M FR	86	69	508	73	87

Notes: TTI, time to ignition in cone calorimeter test; Pk HRR, peak heat release rate in cone calorimeter test; Avg HRR, average heat release rate during test in cone calorimeter test; THR, total heat released during test in cone calorimeter test; Eff. Ht Combust, effective heat of combustion during cone calorimeter test; FPI, fire performance index (ratio of time to ignition and peak heat release rate, in cone calorimeter test); improvement %, percentage improvement in relevant property based on the untreated material.

HRR. The PET fabric study (Table XXXI) involved additives (based primarily on expanded graphite and nanocomposites) that were similar to those used in the PET plastic study presented earlier [44]; the Pk HRR improvements exceeded 45% in all cases studied. The same team that did the PET studies also investigated cotton fabrics (Table XXXII); in this case, the additives were able to decrease Pk HRRs by 18–39% (unfortunately, the flame retardant additives are identified only by a trade name). Two other teams did cotton heat release additive studies on cotton fabrics relatively recently. In one case, the Pk HRR decreased significantly when burnt both in air (65%) and in a 30% oxygen atmosphere (53 and 69%); the additives were described by commercial trade names only (Table XXXIII [55]). The other cotton study (from the US Forest Products Lab) looked at the effect of adding diammonium phosphate (SRRC2) or a mixture of diammonium phosphate and dimethyloldihydroxyethyleneurea (SRRC1) to cotton fabrics; they found improvements of 43–65% depending on the heat flux (Table XXXIV).

Table XXXIV. Effectiveness of flame retardants on heat and ignitability properties of cotton [56].

Cone testing of cotton	TTI	Pk HRR	FPI	Eff. Ht Combust
	s	kW/m^2	m^{2}skW^{-1}	MJ/kg
20 kW/m^2				
Untreated	14	137	0.10	15.9
Cotton + SRRC 1	23	57	0.40	10.4
Cotton + SRRC 2	28	48	0.58	8.2
Improvement % SRRC1	64	58	295	35
Improvement % SRRC2	100	65	471	48
30 kW/m^2				
Untreated	9	152	0.06	16.5
Cotton + SRRC 1	10	86	0.12	13.2
Cotton + SRRC 2	12	86	0.14	10.9
Improvement % SRRC1	11	43	96	20
Improvement % SRRC2	33	43	136	34
50 kW/m^2				
Untreated	5	196	0.03	17.7
Cotton + SRRC 1	8	102	0.08	13.5
Cotton + SRRC 2	12	83	0.14	11.6
Improvement % SRRC1	60	48	207	24
Improvement % SRRC2	140	58	467	34

Notes: SRRC 1 Mix, with N and P; SRRC 2 Mix, with P; TTI, time to ignition in cone calorimeter test; Pk HRR, peak heat release rate in cone calorimeter test; Eff. Ht Combust, effective heat of combustion during cone calorimeter test; FPI, fire performance index (ratio of time to ignition and peak heat release rate, in cone calorimeter test); improvement %, percentage improvement in relevant property based on the untreated material.

Table XXXV. Effectiveness of flame retardants on heat and ignitability properties of GRP composites [57].

GRP composites	TTI	Pk HRR	Eff. Ht Comb	THR
Cone at 50 kW/m^2	s	kW/m^2	MJ/kg	MJ/m^2
Polyester + glass				
GRP	29	343	25.0	52
GRP + MP	28	262	19.0	36
GRP + APP	23	268	23.0	37
GRP + MPP	24	303	22.0	41
GRP + ATH	30	243	23.0	45
GRP + FR	29	176	12.0	28
Improvement % MP	−3	24	24	31
Improvement % APP	−21	22	8	29
Improvement % MPP	−17	12	12	21
Improvement % ATH	3	29	8	13
Improvement % FR	0	49	52	46
GRP composites/barrier				
Polyester + glass				
GRP	229	220	20.0	45
GRP + MP	200	196	20.0	38
GRP + APP	230	175	21.0	49
GRP + MPP	213	210	19.0	46
GRP + ATH	251	196	19.0	42
GRP + FR	204	148	17.0	37
Improvement % MP	590	43	20	27
Improvement % APP	693	49	16	6
Improvement % MPP	634	39	24	12
Improvement % ATH	766	43	24	19
Improvement % FR	603	57	32	29

Notes: MP, melamine phosphate; APP, ammonium polyphosphate; MPP, melamine pyrophosphate; FR, halogenated phosphate ester; ATH, alumina trihydrate; TTI, time to ignition in cone calorimeter test; Pk HRR, peak heat release rate in cone calorimeter test; THR, total heat released during test in cone calorimeter test; Eff. Ht Combust, effective heat of combustion during cone calorimeter test; improvement %, percentage improvement in relevant property based on the untreated material.

The data from study on GRP and barriers can be found in Table XXXV [57]. The composite was studied as is or with a thin silicate insulative fabric. The flame retardant additives used were melamine phosphate (MP), melamine pyrophosphate (MPP), ammonium polyphosphate (APP), a halogenated phosphate ester (FR), and ATH. The improvements in Pk HRR were particularly impressive with the insulative fabric, but even without it, improvement of 49% was found, for example, with the halogenated phosphate ester.

3.8. Wood

The last series of examples being presented involve various wood products. Note that it has already been discussed, in the first paper of this project [1], earlier that fire-retardant treated wood, a product that is regulated via a flame spread test and not a heat release test, exhibits reduced heat release in comparison with wood that is untreated. In all cases, flame retardants improve heat release. Two of the studies involved cone calorimeter testing (Tables XXXVI and XXXVII [58, 59] and one involves mass loss cone testing Table XXXVIII [60]). In one case, the information presented includes also the Euroclass achieved by the different wood specimens, showing that lower heat release also has regulatory implications, in the European Union in this case, but this effect is also valid in US codes (with different classifications).

Table XXXVI. Effectiveness of flame retardants on heat release of some particleboards [58].

Wood Materials	TTI	Pk HRR	Avg HRR 3 min
Cone at 50 kW/m^2	s	kW/m^2	kW/m^2
Untreated low density particleboards			
1	45	225	176
2	39	212	161
3	32	227	158
4	36	202	156
5	34	227	160
6	41	256	185
7	47	213	160
8	25	238	140
9	33	261	169
Average of above	37	229	163
FRT low density particleboards			
1	55	118	66
2	54	151	92
3	47	183	107
Average of above	52	151	88
Improvement % due to FR	41	34	46
Untreated medium density particleboards			
1	35	248	160
2	38	264	168
3	31	254	157
4	32	290	168
Average of above	34	264	163
FRT medium density particleboards			
1	641	117	84
2	942	68	94
3	29	175	102
4	38	166	109
5	828	81	93
Average of above	496	121	96
Improvement % due to FR	1358	54	41

Notes: TTI, time to ignition in cone calorimeter test; Pk HRR, peak heat release rate in cone calorimeter test; Avg HRR 3 min, average heat release rate during 3 min following ignition in cone calorimeter test; improvement % due to FR, percentage improvement in relevant property based on the untreated material; average of above, average values of the individual cone calorimeter tests above this row.

Table XXXVII. Effectiveness of flame retardants on heat release of two different species of wood [59].

Cone at 50 kW/m^2	TTI s	Pk HRR kW/m^2	FPI m^{2}s kW^{-1}	Euroclass
Wood (larch)				
Untreated	17	171	0.10	C
Plus FRT treatment 1	38	136	0.28	C
Plus FRT treatment 2	26	76	0.34	B
Improvement % FRT treatment 1	124	20	181	
Improvement % FRT treatment 2	53	56	244	
Wood (thermowood pine)				
Untreated	14	165	0.08	C
Plus FR treatment 3	108	56	1.93	B
Plus FR treatment 4	31	84	0.37	B
Plus FR treatment 5	125	51	2.45	B
Improvement % FRT treatment 3	535	67	1840	
Improvement % FRT treatment 4	82	51	271	
Improvement % FRT treatment 5	635	70	2365	

Notes: TTI, time to ignition in cone calorimeter test; Pk HRR, peak heat release rate in cone calorimeter test; FPI, fire performance index (ratio of time to ignition and peak heat release rate, in cone calorimeter test); Euroclass, classification in the European Union classification system for construction materials; improvement %, percentage improvement in relevant property based on the untreated material.

Table XXXVIII. Mass loss cone study of the effectiveness of various flame retardant systems on heat and ignitability properties of pine wood [60].

Wood (pine)	TTI	Pk HRR	FPI
Mass loss cone at 35 kW/m^2	s	kW/m^2	m^{2}skW^{-1}
Untreated	98	182	0.54
Plus FR1	115	139	0.83
Plus FR2	101	121	0.83
Plus FR3	127	144	0.88
Plus FR4	81	103	0.79
Plus FR5	120	107	1.12
Plus FR6	70	107	0.65
Plus FR7	68	137	0.50
Plus FR8	55	97	0.57
Plus FR9	72	78	0.92
Improvement % FR1	17	24	54
Improvement % FR2	3	34	55
Improvement % FR3	30	21	64
Improvement % FR4	−17	43	46
Improvement % FR5	22	41	108
Improvement % FR6	−29	41	21
Improvement % FR7	−31	25	−8
Improvement % FR8	−44	47	5
Improvement % FR9	−27	57	71

Notes: FR1, Cu based wood preservative Cu: 0.11% w/w; FR2, tribromoneopentyl alcohol 1.1–0.81% Br; FR3, phosphoric acid 3-(diphenoxy-phosphoryloxy)-phenyl ester diphenyl ester 5.5–0.58% P; FR4, chlorinated paraffin with 65% Cl content 22.7–14.8% Cl; FR5, tetrabromobisphenol A bis (2,3-dibromopropyl ether) 1.9–0.65% aliphatic Br and 0.65% aromatic Br; FR6, Cu preservative + FR2; FR7, Cu preservative + FR3; FR8, Cu preservative + FR4; FR9, Cu preservative + FR5; TTI, time to ignition in cone calorimeter test; Pk HRR, peak heat release rate in cone calorimeter test; FPI, fire performance index (ratio of time to ignition and peak heat release rate, in cone calorimeter test); improvement %, percentage improvement in relevant property based on the untreated material.

4. DISCUSSION AND CONCLUSIONS

It is worth mentioning that a few other publications have investigated different aspects of the effects of flame retardants on fire safety. In one study [61], it was found that the addition of flame retardants improves fire safety in a variety of ways but with particular emphasis on the fact that it increases time available for escape and rescue. In a 1999 study [62], the seminal NBS/NIST work [14] was analyzed. The author concluded that the addition of flame retardants did not just have a positive effect on the overall time available for escape (a key fire hazard issue) but that it also positively affected the smoke toxicity of the fire atmospheres. The author stated 'there is no evidence that [the flame retardants] adversely affect any aspect of fire hazard. Because they reduce ignitability they reduce flame spread, because they reduce flame spread they reduce the fire's burning rate; because they reduce the burning rate they reduce the quantity of smoke the fire produces.' Another study that investigated the safety, health, and environmental aspects of flame retardants [63] concluded that 'this survey shows that the appropriate use of flame retardants, as a class, effectively provides improved fire safety via lowering the probability of ignition, the heat released and the amounts of smoke, combustion products and dangerous environmental toxicants. In consequence the use of flame retardants increases the available time for escape from a fire.' Much of the work in that specific study was based on earlier work that had received insufficient analysis.

The first part of this work, which included an in-depth analysis of the seminal NBS/NIST work [14] as well as a consideration of the importance of heat release rate in fire hazard and the usefulness of cone calorimeter data to predict real scale heat release information, was based on the best fire safety science. The initial work concluded that the NBS/NIST work of 1988 demonstrated that flame retardants (as used in five products) decreased heat release and significantly increased time available for escape and rescue from a fire and fire safety. It also showed that cone calorimeter (and OSU calorimeter) data on small-scale samples can be used to measure heat release rate and to predict the results of fires in full scale with many materials and products.

The studies reviewed in the present portion of the work were those conducted primarily in the initial 21st century years. The choice of studies was based on the availability of the data, and some of the studies are of uneven quality. However, the breadth of the work covered and the similarity of the interpretation that can be obtained from the studies indicate that the conclusions that can be drawn are fully appropriate.

In summary, this work demonstrates that flame retardants, when added as appropriately researched with the correct systems and in the proper amounts, will decrease the heat release rate for virtually all polymeric materials. Thus, the correct use of flame retardants will decrease heat release rate and lower fire hazard and, thus, have a very positive effect on fire safety.

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