Marcelo Hirschler

I am submitting comments expressing my concern about the proposed regulation and include several attachments.

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Comments on the draft rule regarding the use of organohalogen flame retardants

My name is Marcelo Hirschler and I have been an advocate for improved fire safety for many years, by working in the areas of codes and standards at various organizations (see attached recent Curriculum Vitae[1]).

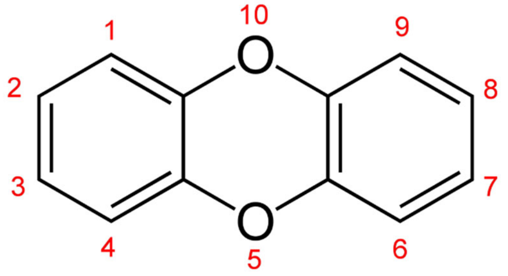
I am concerned about the proposed regulation, "Safer Products for Washington," that would prohibit the use of organohalogen flame retardants in a variety of applications. In particular, this relates to electric and electronic products with plastic external enclosures intended for indoor use. This category includes all types of appliances (large and small) and wires and cables.

My concern relates both to the extreme scope of the proposed regulation and to its implications.

Extreme scope of the proposed regulation: With regard to the extreme scope, let me clarify that I am fully cognizant that some organohalogen flame retardants that had been in use for many years have since been found to be of concern. Those flame retardants (specifically, for example pentabromodiphenyl ether [also known as pentabromodiphenyl oxide or pentaBDE, octabromodiphenyl ether [also known as octabromodiphenyl oxide or octaBDE, and decabromodiphenyl ether [also known as decabromodiphenyl oxide or decaBDE]) are no longer commercial products being manufactured in the US. In place of these materials a variety of alternative flame retardants have been developed by manufacturers and have undergone a plethora of tests to assess their potential toxicity and environmental effects and been found not to be of concern. Therefore, The approach of regulating organohalogen flame retardants as a class does not have the correct scientific basis. There is much scientific rigor if every individual flame retardant of concern is identified by its individual chemical structure (and/or its CAS registry number) instead of an inappropriate broad brush approach covering every single organohalogen flame retardant irrespective of whether it is or is not of concern, particularly since most of them have been identified, as a result of all the testing, as not being of concern.

Similar structure is not sufficient to classify generically: It has been shown repeatedly that the vast majority of the properties of a specific material can be very significantly different in terms of their properties from those of materials with very similar chemical composition. I will provide three examples.

<u>The first example</u> of this are the "polychlorinated dibenzodioxins", often simply known as "dioxins" or "PCDDs". In PCDDs, chlorine atoms are attached to a structure of two benzene rings joined by two oxygen bridges at any of 8 different places on the molecule, at positions 1–4 and 6–9, as shown below. They are named based on at which position the chlorine atom is attached.



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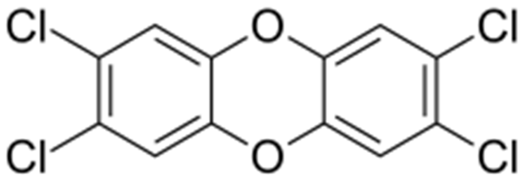
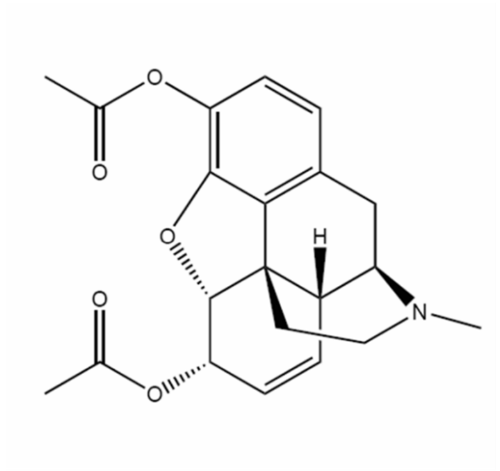
[1] Curriculum Vitae of Dr. Marcelo M. Hirschler, dated January 2023.

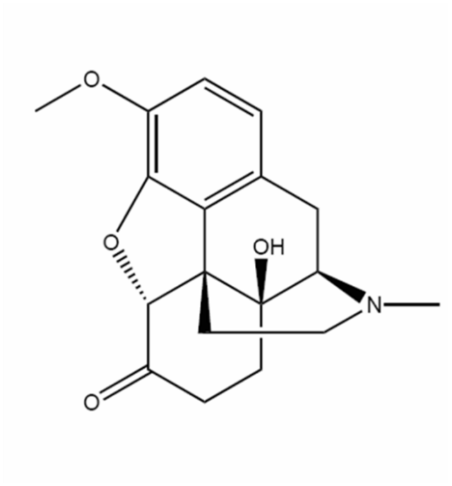
There are a total of 75 different PCDD congeners. The most widely known PCDD. the 2, 3,7, 8 tetrachlorodibenzodioxin, shown below, is often incorrectly labeled simply as “dioxin”:



The relative toxic equivalency factor of the vast majority of these PCDDs[2], when compared to the base one (2, 3, 7, 8 tetrachlorodibenzodioxin) is virtually negligible (meaning that they are virtually nontoxic), except for one that is about equally toxic (1,2,3,7,8-PeCDD), three that are 10 times less toxic, one that is 100 times less toxic and one that is 3,000 times less toxic. In spite of this scientific finding, all “dioxins” are treated as the same, when only a few of them are actually toxic. Obviously, I am not proposing that any PCDDs be allowed for use in any way. Moreover, I am not claiming that the proposed ban on the use of organohalogen flame retardants is in any way related to dioxins. However, the above is an example as to why it is important to identify materials specifically rather than dealing with them as a class.

The second example showing the fallacy of regulating all materials with similar chemical structure the same way can be found in the field of medicine. Let’s use the example of the opioids to illustrate this point. Below is shown the chemical structure of heroin (a dangerous illicit street drug; right) and of oxycodone (a prescription pain reliever medication; left). It is clear that these two drugs have very similar structures. However, one of them is dangerously toxic (and potentially lethal) while the other one is used as an effective painkiller.





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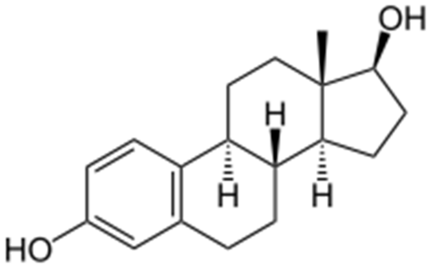
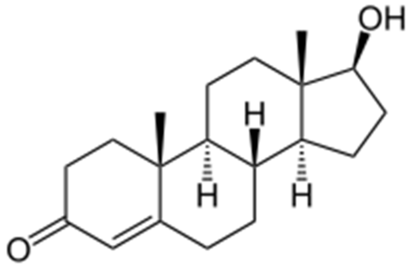
[2] “The 2005 World Health Organization Re-evaluation of Human and Mammalian Toxic Equivalency Factors for Dioxins and Dioxin-like Compounds”, by Martin van den Berg, Linda S. Birnbaum, Michael Denison, Mike De Vito, William Farland, Mark Feeley, Heidelore Fiedler, Helen Hakansson, Annika Hanberg, Laurie Haws, Martin Rose, Stephen Safe, Dieter Schrenk, Chiharu Tohyama, Angelika Tritscher, Jouko Tuomisto, Mats Tysklind, Nigel Walker, and Richard E. Peterson, published in Toxicological Science 2006 Oct; 93(2): 223–241.

The third example is of two substances with very similar chemical structure but very different function. In this example there is the case of estradiol (which is a female sex hormone, on the left) and testosterone (which is a male sex hormone, on the right). They have a similar structure but very different activity.





Not all organohalogen flame retardants are similar: Many of the newer organohalogen flame retardants are polymeric (and not monomeric) flame retardants, with very high molecular weight, meaning that the probability of their volatilization to become airborne and cause respiratory effects is very low. Many other newer organohalogen flame retardants are reactive, and not additive, meaning that they are incorporated into the substrate (the plastic material) by covalently reacting with the plastic (or polymeric) material when the plastic material is being created. The finished material thus contains a built-in flame retardant that cannot easily migrate out (volatilize, or bloom to the surface) like the less strongly bound additive flame retardants. It is essential that any regulation of flame retardant use must take into account the difference between polymeric, oligomeric, and monomeric flame retardants and between additive and reactive flame retardants. It is also essential that the opportunity for innovation must be provided, which is not available when a full class of materials (including some that have not yet been developed) is being banned, thereby declaring as unsafe potential materials that do not yet exist.

Also, a standard has relatively recently been approved by ASTM, as ASTM D8280-20a (Standard Test Method for Determination of the Blooming of Brominated Flame Retardants onto the Surface of Plastic Materials by Ion Chromatography), which allows the quantitative determination of the bromine originating from any flame retardant that has bloomed onto the surface of the plastic after aging under specified conditions. With this test, based on the known structure of the flame retardant used, the amount of the flame retardant that bloomed can also be calculated. More importantly, the test can be used as a pass/fail assessment to determine whether or not the flame retardant actually escapes onto the surface of the material into which it has been incorporated. The use of this technique as a regulatory tool would allow brominated flame retardants that "pass" the test to be used instead of just all brominated flame retardants being lumped together .

The proposed regulation has the potential to lower fire safety.

Flame retardants improve fire safety and halogenated flame retardants are very efficient

The proposed regulation implies that any flame retardant can simply be substituted for an alternate one. There is abundant evidence that this is not a valid assumption. In particular, this will be, at least partially, of the mechanism of action of the flame retardants in question. It has been shown that brominated flame retardants (for example) act primarily in the gas phase while many phosphorus-containing flame retardants act primarily in the condensed phase (I attach a study of mine from back in 1982[3], with information that was "recent" at the time). Therefore, it is clear that replacing a brominated flame retardant by a phosphorus-containing one will not be a simple one-to-one replacement.

A few years ago (initially in 2005, and updated in 2015), for example, the US Environmental Protection Agency[4] conducted a study looking at replacing a halogenated flame retardant (pentabromodiphenyl ether) that was found to be undesirable and had been used to protect flexible polyurethane foam. As stated earlier, the US manufacture of pentabromodiphenyl ether has long since been discontinued. However, the reason the study is important to note is that it found that there were no easy replacements that were equally efficient in providing the needed fire performance.

Another example of the fact that direct replacement is often not possible to achieve with the same result is the case of plenum cables. In the US all electrical and optical fiber cables intended for use in plenums (which are the spaces above the dropped ceiling where the air distribution system is located, meaning heating and air conditioning) are required by the National Electrical Code and all building codes to meet a very severe flammability requirement. In spite of over 30 years of research and development it has been found that only systems that does contain halogenated materials are capable of achieving the required fire performance, in terms of flame spread and smoke release. The result of that is that, if halogenated materials were not allowed in plenum cables, a complete type of product would have to be discontinued. I understand that electrical and optical fiber cables are (fortunately) not covered by the proposed regulation.

I attach three documents that I authored demonstrating the improvements in fire safety as a result of the use of flame retardants. They are a short 2016 report on the benefits of flame retardants[5], and two studies on the effects of flame retardants on heat release, published in Fire and Materials (a scientific journal)[6][7]. The studies on the effects of flame retardants on heat release are particularly important because it has been shown that heat release rate is the most critical parameter associated with fire safety[8]. Consequently, eliminating the use of flame retardants will lead to a significant lowering of fire safety.

Studies by the Swedish scientist Dr. Margaret Simonson on life cycle analyses (LCA) on TV sets[9], cables[10], and upholstered furniture[11] showed that flame retardants do not pose environmental damage by virtue of effectively improving fire performance and releasing much fewer polynuclear aromatic

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[3] "Recent developments in flame-retardant mechanisms", M.M. Hirschler, in "Developments in Polymer Stabilisation, Vol. 5", Ed. G. Scott, pp. 107-52, Applied Science Publ., London, 1982.

[4] https://www.epa.gov/saferchoice/flame-retardants-used-flexible-polyurethane-foam

[5] "Benefits of Flame Retardants", by Marcelo Hirschler (unpublished report, January 2016).

[6] "Flame Retardants and Heat Release: Review of Traditional Studies on Products and on Groups of Polymers", M.M. Hirschler, Fire and Materials (Article published online, Fire and Materials, 03/11/2014, DOI: 10.1002/fam.2243), 2014 [39, 207-231, 2015].

[7] "Flame Retardants and Heat Release: Review of Data on Individual Polymers", M.M. Hirschler, Fire and Materials (Article published online, Fire and Materials, 03/11/2014, DOI: 10.1002/fam.2242), 2014 [39, 232-258, 2015].

[8] " Heat Release Rate: The Single Most Important Variable in Fire Hazard", V. Babrauskas and R.D. Peacock, Fire Safety J. 18, 255-272 (1992).

[9] "Fire-LCA Model: TV Case Study", SP Report 2000:13, Simonson, M., Blomqvist, P., Boldizar, A., Möller, K., Rosell, L., Tullin, C., Stripple, H. and Sundqvist, J.O., , Swedish National Testing and Research Institute, Fire Technology (2000).

[10] "Fire-LCA Model: Cables Case Study" SP Report 2001:22, Simonson, M., Andersson, P., Rosell L., Emanuelsson, V. and Stripple H., Swedish National Testing and Research Institute, Fire Technology (2001).

[11] "Fire Safety of Upholstered Furniture - LCA Analysis" SP Report 2003:22, Andersson, P., Simonson, M. and Stripple H., Swedish National Testing and Research Institute, Fire Technology (2003).

hydrocarbons (PAH). Data from these studies demonstrated that PAH emissions from the improved fire performance materials (such as TVs or upholstered furniture) were only some 3% of those from the products with low fire performance. Thus, the studies showed that a reduction in the number of fires because of the use of products containing materials with improved fire performance was associated with significant benefit to the environment as well as saving lives from fires. In fact, the studies also identified the fact that the reduction in problematic emissions of combustion products when using flame retardants also led to a significant decrease in the overall toxicity of the products emitted.

Another study of particular interest was conducted at the National Bureau of Standards (now called the National Institute of Standards and technology, NIST) published in 1988, where they compared the effect on a variety of fire safety parameters of fire retarded and non-fire retarded products[12]. The products involved were the following: a TV cabinet, a business machine housing, an upholstered chair, an electric cable, and an electric circuit board. Studies involved small-scale tests and room-scale tests. The conclusions were overwhelming: the fire retarded products were much safer. From the other studies mentioned above it was to be expected that the heat released by the fire retarded products was much lower than that released by the non-fire retarded ones. Of special interest, however, were the facts that the time available for escape was so much longer when the products were fire retarded (in fact 15 times longer times available for escape for the fire retarded products) as was the toxicity of the atmosphere containing the combustion products (3 times lower toxicity for the fire retarded products).

It is useful also to compare the amount of flame retardant that needs to be added to a plastic to achieve an acceptable level of fire performance. For example, inorganic halogen-free flame retardants such as alumina trihydrate needs to be used at additive levels as high as 70% for a variety of different polymeric materials while brominated flame retardants can generate similar fire performance at additive (or reactive) levels that are on the order of 10% only.

Summary

- The proposed ban on using any halogenated fire retardants without specifying the actual material involved is technically incorrect since it does not distinguish (a) between materials that should not be used and those that are safe for use, (b) between monomeric and polymeric flame retardants and (c) between additive and reactive flame retardants.
- The proposed ban on using halogenated flame retardants has the potential for making it not possible to achieve certain levels of fire performance that may not be obtainable with other flame retardants.
- The proposed ban on using halogenated flame retardants may lead to a lowering of fire safety without any associated advantage in terms of other environmental or toxicity issues.

Marcelo M. Hirschler

Marcelo M. Hirschler – January 30, 2023

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[12] "Fire Hazard Comparison of Fire-Retarded and Non-Fire-Retarded Products (NBS Special Publication SP 749)", Babrauskas, V., Harris, R. H., Jr., Gann, R. G., Levin, B. C., Lee, B. T., Peacock, R. D., Paabo, M., Twilley, W., Yoklavich, M. F., and Clark, H. M., National Bureau of Standards, Gaithersburg, MD (1988).

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MARCELO M. HIRSCHLER, Lic., Ph.D.

CURRICULUM VITAE

EDUCATION

University:	University of Buenos Aires 1966-70 Licentiate in Chemistry - Major: Physical Chemistry
Post-graduate:	University of Buenos Aires 1971-75 Doctor in Chemistry - Major: Polymer Physical Chemistry

EMPLOYMENT HISTORY

- September 1995 -
  Fire Science Consultant/President
  GBH International, Mill Valley, California
- March 1995 - September 1995
  Fire Science Consultant
  GBH International, Rocky River, Ohio
- March 1991 - February 1995
  Fire Science Consultant
  Safety Engineering Laboratories, Inc., Rocky River, Ohio
- December 1986 - February 1991
  R & D Manager - Fire Sciences
  BFGoodrich Co. - Geon Vinyl Division, Avon Lake, Ohio
- June 1986 - December 1986
  Sr. R & D Associate - Flammability
  BFGoodrich Co. - Geon Vinyl Division, Avon Lake, Ohio
- August 1984 - June 1986
  R & D Associate - Flammability
  BFGoodrich Co. - Chemical Group, Avon Lake, Ohio
- October 1977 - July 1984
  Temporary Lecturer (Physical Chemistry)
  Department of Chemistry - The City University, London, England
- October 1975 - October 1977
  Post Doctoral Research Fellow
  School of Molecular Sciences - University of Sussex, Brighton, England

- June 1975 - October 1975
  Researcher - Physical Chemistry of Carbons
  R & D Department - ALUAR Aluminio Argentino, Buenos Aires, Argentina
- March 1971 - June 1975
  Post-graduate Research Assistant, Department of Physical Chemistry
  School of Pharmacy and Biochemistry - University of Buenos Aires
  Buenos Aires, Argentina
- March 1970 - December 1971
  Undergraduate Teaching Assistant, Department of Physical Chemistry
  School of Exact and Natural Sciences - University of Buenos Aires
  Buenos Aires, Argentina

SOME AWARDS

- Interflam Trophy (UK): 1988
- ASTM E-5 Certificate of Appreciation: 1989
- Wire Association International: Best Electrical Paper 1989
- ASTM Society Frank W. Reinhardt Award for Fire Terminology: 1990
- ASTM E-5 Award of Recognition: 1995
- ASTM E-5 Award of Recognition: 1998
- Canadian Standards Association: Award of Merit: 1999
- ASTM D-9 Award of Appreciation: 2001
- ASTM E-5 Wayne Ellis Award from Society Chairman: June 2002
- ASTM E-5 Award of Appreciation: 2005
- ASTM E-5 Award of Special Recognition: 2006
- ASTM D-20 Award of Appreciation: 2006
- ASTM E-5 Award of Appreciation: 2007
- ASTM E-5 Certificate of Appreciation: 2008
- ASTM E-5 Award of Recognition: 2009
- NFPA Committee Service Award: 2011
- ASTM D-20 Award of Recognition: 2012
- ASTM E-5 Award of Recognition: 2012
- NFPA Certificate of Appreciation: 2013
- ASTM E-5 Award of Recognition: 2013
- ASTM E-5 Special Recognition Award: 2015
- ASTM E-5 Award of Recognition: 2015
- ASTM Society: Award of Merit: 2017
- ASTM D-20: Outstanding Achievement Award: 2017
- ASTM E-5 Award of Recognition: 2019

LANGUAGES

English, German, Spanish, French

MEMBERSHIP PROFESSIONAL SOCIETIES

- American Society for Testing and Materials (ASTM): (See below for committee details)
- Canadian Standards Association (CSA)
- Combustion Institute (Western States Section)
- Institute of Electrical and Electronics Engineers (IEEE)
- International Association for Fire Safety Science
- International Association of Plumbing and Mechanical Officials (IAPMO)
- International Code Council (ICC)
- International Heat Release Association (IHRA)
- National Fire Protection Association (NFPA) (Various Sections and committees)

ACTIVITIES

Marcelo Hirschler Provides Technical Expertise in Fire Safety Including:

- **Product Liability Expert Witness**
- **Codes and Standards**
- **Fire Safety Research and Testing Projects**

WORK ACCOMPLISHED

- **Consultancy**

Product Liability: Expert Witness on Fire Safety Subjects

- Fire safety of mattresses
- Fire safety of upholstered furniture
- Flammability of textiles, including apparel and protective clothing
- Fire safety in transportation, including especially automobiles and trains
- Fire properties and fire testing of plastics
- Fire properties and fire testing of cables
- Smoke toxicity
- Smoke corrosivity
- Fire hazard
- Codes and standards

Fire Research (Public Activities)

- Manager Program for Interlaboratory Precision of Intermediate Scale Calorimeter Test Method (ASTM E1623) (1997-1998)
- Technical Coordinator, Fire Protection Research Foundation (NFPA, FPRF) Research Advisory Council on Transportation Vehicles (2002-06)
- Member of NIBS Smotox Steering Committee (1987-91)
- Member of NFPRF Risk Assessment Advisory Committee (1987-91)

- Session chairman at many fire conferences, including: Fire and Materials, Materials for Increased Fire Safety at Int. Conf. Fire Safety (Dr. C.J. Hilado), BCC Flame Retardancy, Int. Association Fire Safety Science, Combustion Institute, American Chemical Society Fire & Polymers, Fire Retardant Chemicals Association.

Editorial

- Associate Editor, Fire and Materials Journal (1991-)
- Editor: Flame Retardancy News (2005)
- Editor: Fire Safety & Technology Bulletin (2006 -)
- Member Editorial Board Journal Fire Sciences, Fire Safety Journal, Fire & Flammability Bulletin (1995 to 2003), Journal of Testing and Evaluation

California State Fire Marshal Advisory Committees:

- Member California State Fire Marshal Flame Retardant Advisory Committee (2013-5)
- Member California State Fire Marshal Working Group on Implementation of Assembly Bill 127 regarding flammability testing for insulation (2014-2015)
- Member California State Fire Marshal Working Group on Wildland Urban Interface Code (2016 through 2020, ongoing)

Codes and standards:

- **International Code Council**

- Member International Building Code Fire Safety Code Committee (2006-7, 2008-9 and 2010-11)
- Proponent of code changes for IBC, IEBC, IFC, IMC, IPC, IRC, IWUIC, IgCC, at various code development cycles

- **ASTM Committee Memberships**

C16: Thermal Insulation
D07: Wood
D09: Electrical and Electronic Insulating Materials
D11: Rubber and Rubber-like Materials
D13: Textiles
D20: Plastics
E05: Fire
E34: Occupational Health and Safety
F07: Aerospace and Aircraft
F08: Sports Equipment, Playing Surfaces, and Facilities
F15: Consumer Products
F23: Personal Protective Clothing and Equipment
F24: Amusement Rides and Devices
F25: Ships and Marine Technology
F33: Detention and Correctional Facilities
F44: General Aviation Aircraft

- **ASTM E05 (Fire Standards):**

* Chairman ASTM E-5.91 and First Vice-Chairman Committee E05: Subcommittee on Fire and Planning and Review (2014 -19)
* Chairman ASTM E-5.15: Subcommittee on Fire and Interior Furnishings and Contents (1990-95)
* Chairman ASTM E-5.17: Subcommittee on Fire and Transportation (2010-15): developed ASTM E2574, new standard fire test for school bus seating
* Chairman ASTM E-5.21: Subcommittee on Smoke and Combustion Products (2004-9)
* Chairman ASTM E-5.31: Subcommittee on Fire Terminology and Editorial (2000-5)
* Recording Secretary ASTM E05: Committee on Fire Standards (2000-5)
* Member-at-large of executive subcommittee of ASTM E05 (2006 - 07)
* Membership Secretary ASTM E05 (2008-13)
* Recording Secretary ASTM E-5.15: Subcommittee on Fire and Interior Furnishings and Contents (1988-90 and 1996-2015)
* Recording Secretary ASTM E-5.91: Subcommittee on Planning and Review of Fire Standards (1990-1999 and 2000-14)
* Recording Secretary ASTM E-5.17: Subcommittee on Fire and Transportation (2003-2009)
* Recording Secretary ASTM E-5.21: Subcommittee on Smoke and Combustion Products (2010-17)
* Chairman ASTM E-5.22.02: Task Group on ASTM E84 Steiner Tunnel Mounting Methods (2002-). Developed several tunnel testing mounting practices - including ASTM E2231, ASTM E2404, ASTM E2573, ASTM E2579 and ASTM E2599
* Chairman ASTM E-5.13.1: Task Group on ASTM E603, Standard Guide for Room Fire Experiments (1992-2009).
* Chairman ASTM E-5.13.8: Task Group on New Practice for Large Scale Heat Release Tests (1997-2009). Developed practice ASTM E2067 and test method ASTM E2257
* Chairman ASTM E-5.15.3: Task Group on Fire Hazard Assessment of Floor Coverings (1987-92)
* Chairman ASTM E-5.15.8: Task Group on Full Scale Fire Testing of Upholstered Furniture (1989-). Developed full scale fire test methods: ASTM E1537, ASTM E1590 and ASTM E1822
* Chairman ASTM E-5.15.12: Task Group on Vandalized Mattresses for Correctional Institutions (1991-93).
* Chairman ASTM E-5.15.13: Task Group on Fire Hazard Assessment of Upholstered Furniture (1994-2009). Developed ASTM E2280, Standard guide on fire hazard assessment for health care occupancies
* Chairman ASTM E-5.17.94: Task Group on Fire Hazard Assessment of Rail Transportation Vehicles (1991-). Developed ASTM E2061, new guide on fire hazard assessment of passenger rail vehicles
* Chairman ASTM E-5.21.13: Task Group on Smoke Toxicity for Flashover Fires (1993-)
* Chairman ASTM E-5.21.33: Task Group on ASTM E906 (Ohio State University Rate of Heat Release Apparatus) (1994-2004).
* Chairman ASTM E-5.21.34: Task Group on Intermediate Scale Calorimeter (1997-2004). Managed interlaboratory round robin for ASTM E1623 and updated standard

- Chairman ASTM E-5.21.35: Task Group on Rate of Heat Release Apparatus by Thermopile Method (1995-). Developed new test method ASTM E2102
- Chairman ASTM E-5.21.3: Task Group on ISO (5659-2) Smoke Chamber (1995-2004) and NBS Smoke Chamber. Developed new test method ASTM E1995
- Chairman ASTM E-5.21.60: Task Group on cone calorimeter (ASTM E 1354) (2009-)
- Chairman ASTM E-5.21.80: Large scale heat release (2009-)
- Chairman ASTM E-5.23.1: Task Group on Non-Combustibility (2008 -12) (merged into ASTM E-5.23.2)
- Chairman ASTM E-5.23.2: Task Group on Alternate Method of Non-Combustibility (2007 -): Developed Test Method ASTM E2652
- Chairman ASTM E-5.31/91 Task Group on Uncertainty (2002-)
- Chairman ASTM E-5.31 Task Group on Terminology (2014-)
- Chairman ASTM E-5.31 Task Group on Services/Functions Standards (2014-)
- Chairman ASTM E-5.32.2: Task Group on 1990 Symposium on Fire Hazard and Fire Risk Assessment (1988-1992). Editor of ASTM STP 1150 (Fire Hazard & Fire Risk Assessment)
- Chairman ASTM E-5.35.2: Task Group on Examples of Fire Hazard Assessment Standards (1989-91)

- **NFPA**

- Chairman NFPA Technical Committee on Hazard and Risk of Contents and Furnishings (2001-2013). Developed new NFPA 556, Guide on Vehicle Fire Safety, & NFPA 557, Standard on Fire Loads
- Chairman NFPA Technical Advisory Committee on Glossary of Terminology (2007-15)
- Member NFPA Life Safety Technical Committee on Furnishings and Contents (1991-)
- Member NFPA Building Code Technical Committee on Structures, Construction, and Materials (2014 -)
- Member NFPA Technical Committee on Hazard and Risk of Contents and Furnishings (1991-)
- Member NFPA National Electrical Code CMP 15: National Electrical Code Panel on Places of Assembly (1993-2001)
- Member NFPA Technical Committee on Fire Tests: (1996-)
- Member NFPA Technical Committee on Merchant Vessels: (1998-)
- Member (Alternate, for Society of the Plastics Industry) of NFPA Technical Committee on Fixed Guideway Transit Systems [Trains]: (2001)
- Member (for North American Flame Retardant Alliance/Plenum Cable Association) of NFPA Technical Committee on Air Conditioning [NFPA 90A-B]: (2002-)
- Member (for North American Flame Retardant Alliance) of NFPA Technical Committee on Fixed Guideway Transit Systems [Trains] [NFPA 130]: (2019-)

- **ASTM D09 (Electrical Insulation Materials)**

* Chairman ASTM D09: (2017-)
* Chairman ASTM D-9.94: Subcommittee on Editorial (2008-)
* Chairman ASTM D-9.21: Subcommittee on Fire Performance Standards (2010-6)
* Chairman ASTM D-9.17: Subcommittee on Fire and Thermal Properties (2016 -)
* Secretary ASTM D09: (2016-2017)
* Secretary ASTM D-9.94: Subcommittee on Terminology and Editorial for Electrical Insulation Materials (1994-2008)
* Chairman ASTM D-9.21.3: Task Group on Smoke Obscuration on Burning of Electrical Cables (1987-2016). Developed ASTM D5424
* Chairman ASTM D-9.21.7: Task Group on Rate of Heat Release from Electrical Cables (1992-2016). Developed ASTM D5537 and ASTM D6113
* Chairman ASTM D-9.21.1: Task Group on Fire Hazard Assessment of Electrotechnical Products (1995-2016). Developed Guide ASTM D5425
* Chairman ASTM D-9.97-1: Task Group on March1999 "90th Anniversary Symposium on Electrical Insulating Materials: International Issues" (1997-1999). Editor of ASTM STP 1376 (1999)
* Chairman ASTM D-9.97 Task Group on ASTM D9 Symposium on Electrical Materials and Fire October 2004.

- **ASTM D20 (Plastics)**

* Chairman ASTM D20-20: Subcommittee on Plastic Lumber (2009-) [Originally subcommittee on Plastic Products]
* Vice-chairman ASTM D20.20.03: Section on Plastics and Combustibility (2013-2017)
* Chairman Task Group on ASTM D4968 (Practice for Review of Test Methods and Specifications for Plastics (2015-)
* Chairman ASTM D20-92: Subcommittee on Terminology (2022 -)

- **ASTM F33 (Detention and Correctional Occupancies)**

* Chairman ASTM F33.05 Task Group on Furnishings within Detention Occupancies (1997-). Developed test methods ASTM F1534 and F1550 and guide ASTM F1870.

- **ASTM F15, ASTM F08 and other ASTM committees:**

* Chairman ASTM F15.15: Subcommittee on Wall Coverings (Responsible for a standard specification and a standard classification for wall coverings)
* Task group chair and member various task groups.

- **CSA (Canadian Standards Association)**

* Chairman Task Group on Circuit Integrity for CSA C22.2 No. 0.3 (1997-2000)
* Member Committee CSA C22.2 No. 0.3 Wiring Test Methods (1992 -2010)
* Member Committee CSA C22.2 No. 239 Control & Instrumentation Cables (1995 -2010)

- **IEEE (Institution of Electrical and Electronic Engineers)**

* Member IEEE Technical Committee on Electrical Installations in Ships (IEEE 45) (1999-2007)
* Member IEEE Technical Committee on Shipboard Wire and Cable (IEEE 1580) (2000-07)
* Member IEEE Technical Committee on Environmental Assessment of Computer Products, Imaging Equipment and Television (IEEE 1680) (2010-2018)

- **ISO (International Organization for Standardization)**

* Convenor ISO TC 61 SC4 WG8 (Plastics – Burning Behavior - Ignitability and fire growth tests) (2013 -)
* Convenor ISO TC 92 WG8 (Fire Safety – Fire terms and definitions) (2013 -)
* Member ISO TC61 SC4 (Plastics Burning Behavior)
* Member ISO TC61 SC4 WG2 (Smoke and corrosivity) (2017 -)
* Member ISO TC61 SC4 WG9 (Other Products) (2017 -)
* Member ISO TC61 SC4 WG11 (PVC Products) (2015 -2019)
* Member ISO TC92 SC1 (Building Products - Reaction to fire)
* Member ISO TC92 SC3 (Building Products – Toxicity)

- **IEC (International Electrotechnical Commission)**

* Member US TAG IEC TC89 (Cables and Fire)

Fire Safety Industrial Consultant (Public Information)

- Consultant to the Vinyl Institute on fire and PVC (1991-)
- Consultant to the Fire Retardant Chemicals Association/American Fire Safety Council/North American Flame Retardants Alliance on codes and standards (1997 -)
- Consultant to the National Cotton Council on code issues (2003 -05)
- Expert on various fire issues, for a variety of industrial clients

EMPLOYMENT RESPONSIBILITIES IN PREVIOUS WORK

■ BFGoodrich - Geon Vinyl Division (Fire Sciences Manager)

- Head of BFGoodrich fire testing laboratory: routine small-scale tests.
- Head of BFGoodrich fire research: smoke toxicity and fire hazard assessment; combustion and thermal analysis of poly(vinyl chloride) and other polymers; generation, transport and decay of hydrogen chloride; smoke corrosivity; analytical techniques for measuring combustion products. Provided a presence at national and international fire conferences, for participation and presentation of scientific work. Carried out full scale fire demonstrations, for research and public relations purposes. Supported line groups in the development of new commercial compounds.
- Technical consultant for BFGoodrich on litigation and other external affairs regarding fire and combustion toxicity
- Standards activities representing BFGoodrich: e.g. ASTM, NFPA, Canadian Standards Association.
- Vinyl industry spokesperson
- Chairman Technical Fire Sciences Subcommittee, Coordinating Committee for Fire Safety, Society of the Plastics Industry. Main spokesperson on fire activities for the plastics industry. Liaison with Center for Fire Research (National Bureau of Standards), NFPA, NIBS, etc.
- Technical Monitor SPI Carbon Monoxide and Fire Fatalities Project, etc. (1987-91)
- Chairman Combustibility Subcommittee, Vinyl Institute Technical Committee.
  Technical monitor of projects at Center for Fire Research (NBS), Southwest Research Institute
- Chairman ASTM E-5.15: Subcommittee on Fire and Interior Furnishings and Contents
- Secretary ASTM E-5.91: Subcommittee on Planning and Review of Fire Standards
- Chairman ASTM E-5.15.3: Task Group on Fire Hazard Assessment of Floor Coverings
- Chairman ASTM E-5.15.8: Task Group on Full Scale Fire Testing of Upholstered Furniture
- Chairman ASTM E-5.31.3: Task Group on Smoke Toxicity Definitions
- Chairman ASTM E-5.32.2: Task Group on 1990 Symposium on Fire Hazard and Fire Risk Assessment
- Chairman ASTM E-5.35.2: Task Group on Examples of Fire Hazard Assessment Standards
- Chairman ASTM D-9.21.3: Task Group on Smoke Obscuration on Burning of Electrical Cables
- Member of NIBS Smotox Steering Committee (1987-91)
- Member of NFPRF Risk Assessment Advisory Committee (1987-91)
- Session chairman on Materials for Increased Fire Safety at Int. Conf. Fire Safety (Dr. C.J. Hilado) (1987-91)
- Session chairman at Combustion Institute Eastern Section meetings
- Session Chairman at Fire Retardant Chem. Association meetings
- Member of ASTM Task Groups E-5.21.70 and D-9.21-4 (smoke corrosivity test development), ASTM E-5.21.02 and E-5.21.03 (smoke obscuration test development), and E5-21.11 (quick toxic fire hazard assessment)

■ **BFGoodrich - Chemical Group & Geon Vinyl Division**

- As subsequent job, at a lower level of responsibility.

■ **Department of Chemistry - The City University**

- Supervision of post-graduate and undergraduate research students
- Research in combustion and air pollution: medium and high molecular weight hydrocarbons, liquid fuels (gasoline, diesel efficiency and effects of additives), polymers (thermal decomposition, flammability and flame retardance: efficiency and mechanism), cellulosic materials (cellulose, cotton, cigarette paper: mechanisms and means of decreasing emissions), emission processes of gaseous pollutants, etc.
- Consultant to the "Unit for Oxidation and Combustion Technology": Ministry of Defense and industrial contract research organization.
- Consultant to the OECD (Organization for Economic Cooperation and Development; Paris, France): industrial and automotive pollution issues.

■ **School of Molecular Sciences - University of Sussex**

- Research in physical organic chemistry: syntheses and kinetics of radioactive decay by protiodetritiation of polycyclic aromatic hydrocarbons.

■ **R & D Department - ALUAR Aluminio Argentino**

- Planning for setting up a laboratory and literature search

■ **Department of Physical Chemistry - School of Pharmacy and Biochemistry - University of Buenos Aires**

- Research into polymerization mechanisms, leading to Ph.D.

PUBLICATIONS

Books:

1) “The Combustion of Organic Polymers”, C.F. Cullis and M.M. Hirschler, Oxford University Press, Oxford, UK, 1981.

2) “Oxidation of Organic Compounds. Solvent Effects in Radical Reactions”, N.M. Emanuel', G.E. Zaikov and Z.K. Maizus, translators: A.K. Henn and I.G. Evans, translation editor: M.M. Hirschler, Pergamon Press, Oxford, UK, 1984.

3) “Fire hazard and fire risk assessment”, ASTM STP 1150, Amer. Soc. Testing and Materials, Philadelphia, PA, US, Editor: M.M. Hirschler, (1992).

228) “Carbon monoxide and human lethality: Fire and non fire studies”, Editor in Chief: M.M. Hirschler, Associate Editors: S.M. Debanne, J.B. Larsen and G.L. Nelson, Elsevier, New York, US, 1993.

274) “Fire Calorimetry”, Editors: M.M. Hirschler and R.E. Lyon, DOT/FAA/CT-95-46, NTIS, Alexandria, VA, US, 1995.

345) “Electrical Insulating Materials - International Issues”, ASTM STP 1376, Amer. Soc. Testing and Materials, West Conshohocken, PA, US, Editor: M.M. Hirschler (2000).

453) “Practical Guide to Smoke and Combustion Products from Burning Polymers – Generation, Assessment and Control”, M.M. Hirschler, S. Levchik and E.D. Weil, Smithers Rapra Technical Publications, Shawbury, UK, 2011.

Other Scientific Publications and Presentations:

1974

4) "Free radical polymerization of methyl methacrylate in the presence of benzoquinone and triethyl aluminium", J. Grotewold and M.M. Hirschler, Int. Symp. On Macromolecules, Rio de Janeiro, Brazil, July 26-31, 1974.

5) "Formation of a methyl methacrylate oligomer by combining triethyl aluminium and azobisisobutyronitrile", J. Grotewold and M.M. Hirschler, Kinetics and Photochemistry Symposium, Rio Cuarto (Argentina), August 6-10, 1974.

1975

6) "Mechanism of polymerization of methyl methacrylate in the presence of triethyl aluminium together with a typical free radical inhibitor or an initiator", Doctoral Dissertation, University of Buenos Aires.

7) "Report on carbons, carbonization, additives (oxidative and reductive) and polycyclic aromatic hydrocarbons", M.M. Hirschler, Internal Publication, ALUAR Aluminio Argentino, 1975.

1977

8) "Stoichiometric formation of methyl methacrylate oligomer by triethyl aluminium in the presence of azobisisobutyronitrile", J. Grotewold and M.M. Hirschler, J. Polymer Sci., A-1 (Polymer Chemistry), 15, 383-91 (1977).

9) "Triethyl aluminium as a concentration-dependent coinitiator and chain-transfer agent of free radical polymerization of methyl methacrylate in the presence of benzoquinone", J. Grotewold and M.M. Hirschler, J. Polymer Sci., A-1 (Polymer Chemistry), 15, 393-404 (1977).

10) "Electrophilic aromatic substitution. Part 18. Protiodetritiation of anthracene, coronene and triphenylene in anhydrous trifluoroacetic acid", H.V. Ansell, M.M. Hirschler and R. Taylor, J. Chem. Soc., Perkin II, 353-5 (1977).

1978

11) "The formation and destruction of pentenes during the combustion of pentane", C.F. Cullis and M.M. Hirschler, Proc. Royal Soc. (London) A 364, 75-88 (1978).

12) "Isotopic tracer studies of the further reactions of pentenes in the combustion of pentane", C.F. Cullis and M.M. Hirschler, Proc. Royal Soc. (London) A 364, 309-29 (1978).

1979

13) "Sulphur emissions into the atmosphere", C.F. Cullis and M.M. Hirschler, Int. Symp. On Sulphur Emissions and the Environment, London (U.K.), May 8-10, Soc. Chem. Industry, pp. 1-23 (1979).

1980

14) "Atmospheric cycles of some common elements: II. Man's activities", C.F. Cullis and M.M. Hirschler, Educ. Chem. 17, 40-3 (1980).

15) "Sulphur emissions, the environment and chemical industry", M.M. Hirschler, Introductory Lecture, Int. Symp. On Sulphur Emissions and the Environment, London (U.K.), May 8-10, 1979, Soc. Chem. Industry, pp. 445-55 (Discussion Volume) (1980).

16) "Atmospheric sulphur: natural and man-made sources", C.F. Cullis and M.M. Hirschler, Atmos. Environ., 14, 1263-78 (1980).

17) "Ignition of Kynar oxygen valve material", M.M. Hirschler, Report for Health and Safety Executive, U.K., Contract No. 1186-46.04, November 1980.

18) "The effect of atropisomerism upon electrophilic aromatic reactivity: detritiation of hexa- and tetra-o-phenylene", M.M. Hirschler and R. Taylor, J. Chem. Soc., Chem. Comm., 967-9 (1980).

1981

19) "Man's emission of carbon dioxide into the atmosphere", M.M. Hirschler, Atmos. Environ., 15, 719-27 (1981).

20) "Smoking and air pollution", C.F. Cullis and M.M. Hirschler, Seventh Int. Clean Air Conf., Clean Air Soc. Australia and New Zealand, Adelaide (Australia), August 21-27, pp. 115-29 (1981).

21) "Biogenic sulphur emissions", M.M. Hirschler, Atmos. Environ. 15, 1336 (1981).

22) "The oxidative thermal stability of plastic propellants", A.W. Benbow and M.M. Hirschler, Report for Procurement Executive, Propellants, Explosives and Rockets Motor Establishment, Ministry of Defence, U.K., Contract No. D/RM 1/11/240, February 1981.

23) "The combined action of aluminium oxides and halogen compounds as flame retardants", F.K. Antia, C.F. Cullis and M.M. Hirschler, Europ. Polymer J., 17, 451-5, (1981).

24) "The inhibition of polymer combustion by metal oxides", F.K. Antia, C.F. Cullis and M.M. Hirschler, First Specialists' Mtg Combustion Institute, Bordeaux (France), July 20-25, pp. 602-7 (1981).

25) "Experimental techniques for the combustion of fuels of low volatility and high reactivity", C.F. Cullis, M.M. Hirschler and R.L. Rogers, 18th. Symp. (Int.) on Combustion, pp. 1575-82, The Combustion Institute, Pittsburgh, 1981.

26) "The oxidation of decane in the gaseous and liquid phases", C.F. Cullis, M.M. Hirschler and R.L. Rogers, Proc. Royal Soc. (London), A <u>375</u>, 543-63 (1981).

1) "The Combustion of Organic Polymers", C.F. Cullis and M.M. Hirschler, Oxford University Press, Oxford, 1981.

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27) "The cool-flame combustion of decane", C.F. Cullis, M.M. Hirschler and R.L. Rogers, Proc. Royal Soc. (London), A <u>382</u>, 429-40 (1982).

28) "Recent developments in flame-retardant mechanisms", M.M. Hirschler, in "Developments in Polymer Stabilisation, Vol. 5", Ed. G. Scott, pp. 107-52, Applied Science Publ., London, 1982.

29) "Binary mixtures of metal compounds as flame retardants for organic polymers", F.K. Antia, C.F. Cullis and M.M. Hirschler, Europ. Polymer J., <u>18</u>, 95-107 (1982).

30) "Comprehensive study of the effect of composition on the flame-retardant activity of antimony oxide and halogenated hydrocarbons in thermoplastic polymers", F.K. Antia, P.J. Baldry and M.M. Hirschler, Europ. Polymer J., <u>18</u>, 167-74 (1982).

31) "Effect of oxygen on the thermal decomposition of poly(vinylidene fluoride)", M.M. Hirschler, Europ. Polymer J. <u>18</u>, 463-7, (1982).

32) "Relation between the thermal behaviour and flame-retardant effectiveness of metal oxides in halogen-containing thermoplastics", M.M. Hirschler, Sixth European Conf. on Flammability and Fire Retardants, Alena Enterprises of Canada, June 24-25, Nice (France), 1982.

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34) "The role of specific elements in flame-retardant mechanisms", M.M. Hirschler, Polymer Flammability: Mechanistic and Practical Aspects, P.D.D.G. Conf., Macro Group U.K. (Royal Soc. Chemistry), September 2-3, Cambridge (U.K.), 1983 (Industrial Chemistry Bulletin, <u>2</u>, 52 (1983)).

35) "The pyrolysis of cellulose under conditions of rapid heating", C.F. Cullis, M.M. Hirschler, R.P. Townsend and V. Visanuvimol, Combust. Flame <u>49</u>, 235-48 (1983).

36) "The combustion of cellulose under conditions of rapid heating", C.F. Cullis, M.M. Hirschler, R.P. Townsend and V. Visanuvimol, Combust. Flame <u>49</u>, 249-54 (1983).

37) "Flame retardance and smoke suppression by tin (IV) oxide phases and decabromobiphenyl", J.D. Donaldson, J. Donbavand and M.M. Hirschler, Europ. Polymer J. <u>19</u>, 33-41 (1983).

38) "Thermal analysis and flammability of polymers: Effect of halogen-metal additive systems", M.M. Hirschler, Europ. Polymer J. <u>19</u>, 121-9 (1983).

39) "The effect of combinations of aluminium (III) oxides and decabromobiphenyl on the flammability of and smoke production from acrylonitrile-butadiene-styrene terpolymer", M.M. Hirschler and O. Tsika, Europ. Polymer J., <u>19</u>, 375-80 (1983).

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41) "The significance of thermoanalytical measurements in the assessment of polymer flammability", C.F. Cullis and M.M. Hirschler, Polymer, 24, 834-40 (1983).

42) "The influence of metal chelates on the oxidative degradation of polypropylene", C.F. Cullis and M.M. Hirschler, in Proc. Fifth Ann. Int. Conf. Advances in the Stabilisation and Controlled Degradation of Polymers, Zurich (Switzerland), June 1-3, pp. 195-207 (1983).

43) "Metal oxides as flame retardants-smoke suppressants: recent developments", M.M. Hirschler, Seventh Europ. Conf. on Flammability and Fire Retardants, Alena Enterprises of Canada, London (U.K.), June 9-10, 1983.

44) "A novel dilution tunnel-flame burner system for studying the effects of automotive diesel fuels on air quality", C.F. Cullis, M.M. Hirschler and M.A.M. Stroud, Sixth World Congress on Air Quality, Paris (France), May 16-20, Int. Union Air Pollution Prevention Assocns, Vol. 4, pp. 265-72 (1983).

45) "Effects of organic sulphur compounds on the ignition of unleaded and leaded hydrocarbon fuels", C.F. Cullis, M.M. Hirschler and G.O.G. Okorodudu, 19th. Symp. (Int.) on Combustion, pp. 1475-86, The Combustion Institute, Pittsburgh, 1983.

46) "The effects on alkane combustion of added sulphur compounds", C.F. Cullis, M.M. Hirschler, G.O.G. Okorodudu and H.A.G. Okuns, Combust. Flame 54, 209-24 (1983).

1984

47) "Char formation from polyolefins: correlations with low-temperature oxygen uptake and with flammability in the presence of metal-halogen systems", C.F. Cullis and M.M. Hirschler, Europ. Polymer J. 20, 53-60 (1984).

48) "Reduction of smoke formation from and of flammability of thermoplastic polymers by metal oxides", M.M. Hirschler, Polymer 25, 405-11 (1984).

49) "Degradation of polystyrene in the presence of magnesium compounds", M.M. Hirschler and T.R. Thevaranjan, Pre-prints, Polymer Div., Amer. Chem. Soc., 189th. Ann. Mtg, pp 91-2 (1984).

50) "Effect of dispersing and binding agents on the flammability of, and smoke production from, thermoplastic polymers", J.D. Donaldson, J. Donbavand and M.M. Hirschler, Europ. Polymer J., 20, 323-7 (1984).

51) "The flame retardance of a natural polymer by a sulphur-aluminium-bromine system", C.F. Cullis, M.M. Hirschler and M.A.A.M. Khattab, Europ. Polymer J. 20, 559-62 (1984).

52) "The flame-retardant and smoke-suppressant activity of molybdenum (VI) oxide and other metal oxides", C.F. Cullis, M.M. Hirschler and T.R. Thevaranjan, Eighth Europ. Conf. on Flammability and Fire Retardants, Alena Enterprises of Canada, Amsterdam (Holland), June 8-9, 1984.

53) "Combustion of cigarette paper under conditions similar to those during smoking", C.F. Cullis, D. Goring and M.M. Hirschler, Cellucon '84 (Macro Group U.K.), Wrexham (Wales), Chapter 35, pp. 401-10, July 16-20, Ellis Horwood, Chichester, 1984.

54) "Heat transfer from fires", M.M. Hirschler, Report for BFGoodrich Chemical Co., July 1984.

55) "Metal chelates as flame retardants and smoke suppressants for thermoplastic polymers", C.F. Cullis, A.M.M. Gad and M.M. Hirschler, Europ. Polymer J., 20, 707-11 (1984).

56) "Combinations of titanium (IV) oxide, iron (III) oxide and molybdenum (VI) oxide as flame retardants and smoke suppressants for thermoplastic polymers", C.F. Cullis, M.M. Hirschler and T.R. Thevaranjan, Europ. Polymer J. 20, 841-7 (1984).

57) "Red phosphorus as a flame retardant for a thermoplastic nitrogen-containing polymer", J.R.A. Broadbent and M.M. Hirschler, Europ. Polymer J. 20, 1087-93 (1984).

58) "The role of diffusion in the rapid combustion of cellulose", M.M. Hirschler and R.P. Townsend, Proc. Royal Soc. (London), A 396, 119-30 (1984).

59) "Carbon monoxide from cigarette paper combustion", M.M. Hirschler and Y.R. Shashoua, Chemical and Physical Processes in Combustion, Eastern Section Combustion Inst., 1984 Fall Tech. Mtg, Clearwater Beach (FL, U.S.), p. 104/1-4, Dec. 3-5 1984.

60) "A novel engine-free dilution tunnel for the collection of particulate matter formed during combustion", C.F. Cullis, M.M. Hirschler and M.A.M. Stroud, J. Phys. E: Sci. Instrum., 17, 317-22, (1984).

61) "The combustion of deuterium-labelled decane", D. Herron and M.M. Hirschler, Oxidation Communications, 7, 321-32 (1984).

62) "Environmental implications of energy strategies (Transportation) Chapter 5: Diesel engines and Fuels", C.F. Cullis and M.M. Hirschler, O.E.C.D., Paris, 1984.

63) "Environmental implications of energy strategies (Transportation) Chapter 6: Two-stroke engines", M.M. Hirschler, O.E.C.D., Paris, 1984.

64) "Environmental implications of energy strategies (Transportation) Chapters 1-8", M.M. Hirschler (Editor), O.E.C.D., Paris, 1984.

65) "Diesels: Increased air pollution vs. energetic and economic advantages", C.F. Cullis and M.M. Hirschler, Eighth Int. Clean Air Conf., Clean Air Society of Australia and New Zealand, Melbourne (Australia), May 1984.

2) "Oxidation of Organic Compounds. Solvent Effects in Radical Reactions", N.M. Emanuel', G.E. Zaikov and Z.K. Maizus, translators: A.K. Henn and I.G. Evans, translation editor: M.M. Hirschler, Pergamon Press, Oxford, 1984.

1985

66) "Effects of magnesium oxide/hydroxide on flammability and smoke production tendency of polystyrene", M.M. Hirschler and T.R. Thevaranjan, Europ. Polymer J., 21, 371-5 (1985).

67) "Simultaneous thermal analysis of PVC compounds", M.M. Hirschler, Ninth Europ. Conf. Flammability and Fire Retardants, Alena Enterprises of Canada, Bad Hofgastein (Austria), May 9-10, 1985.

68) "The effects of red phosphorus on the flammability and smoke-forming tendency of organic polymers", C.F. Cullis, M.M. Hirschler and Q.M. Tao, Ninth Europ. Conf. Flammability and Fire Retardants, Alena Enterprises of Canada, Bad Hofgastein (Austria), May 9-10, 1985.

69) "Efficiency of Metal-Containing Compounds in the Flame Retardance and Smoke Suppression of Polymers", M.M. Hirschler, Am. Chem. Soc., Central Regional Meeting, paper 133, p. 54, June 5-7, Akron, (OH, U.S.A.) 1985.

70) "Update on vinyl flammability, smoke and toxicity issues", M.M. Hirschler, Eighth Vinyl Formulators Tech. Seminar, Sept. 24-27, Bolton Landing (NY, U.S.A.), 1985.

71) "Hazards in a house fire: example of a chair", M.M. Hirschler and G.F. Smith, Chemical and Physical Processes in Combustion, Eastern Section Combustion Institute, 1985 Fall Tech. Mtg, Philadelphia (PA, U.S.A.), p. 59/1-4, Nov. 4-6, 1985.

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Chapter 5

FLAME RETARDANT MECHANISMS: RECENT DEVELOPMENTS

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SUMMARY

The principal mechanisms by which flame retardance is conferred on polymeric substrates are reviewed in the light of the most recent experimental work. The six elements which are the active constituents of the most widely used flame-retardant systems are chlorine and bromine (Group VII), phosphorus and antimony (Group V) and boron and aluminium (Group III).

Flame retardance involves the interference with one or more of the various stages involved in the complex process of polymer combustion. This action may be purely physical in nature, although it is most likely to be effective if the rate and course of some of the constituent chemical reactions are also altered.

Gas-phase mechanisms may involve the destruction of those species which propagate the flame reactions or simply the absorption of heat with an accompanying reduction in gas temperature.

Condensed-phase mechanisms usually involve changes in the rates of pyrolytic or thermo-oxidative breakdown of the polymeric structure.

1. INTRODUCTION

Natural organic polymers, principally cellulosics, have been an important part of man's environment for many centuries. They have complex structures which in general withstand well prolonged exposure to the atmosphere. Synthetic polymers are relatively new materials which have been in commercial production for only about 50 years. They are relatively simple materials composed of few different monomeric units and they have been designed for applications where some combination of mechanical properties, and perhaps colour, is vital to their effectiveness. They are however in general more susceptible to oxidative attack than natural polymers.

The prevention of the loss of the attractive properties of polymers during use is usually termed stabilisation. The processes responsible for deterioration may consist of photo-oxidative, thermo-oxidative, hydrolytic, solvolytic or other chemical degradation reactions resulting from normal exposure. They do not, in general, involve an extensive breakdown of the polymeric structure; the materials lose their effectiveness long before they have broken down completely. The additives (stabilisers) normally used for this purpose must inhibit processes which are slow but which should not be allowed to occur to any significant extent.

Although only synthetic polymers normally need stabilisation, both natural and synthetic polymeric materials are inherently flammable. The inhibition of polymer combustion involves substrates which are to be employed either under conditions where they may be exposed to local high temperatures or in applications where their breakdown may produce undesirable hazards. The conferment of flame retardance is the process by which polymers are either protected from undergoing a rather more complete destruction of the material than simple loss of mechanical properties or are forced to change the course of this decomposition so as to form products which are less hazardous.

It is not surprising that interest in treatments to reduce the flammability of organic polymers, which are entirely different from those used for their stabilisation, can be traced back to ancient times. The empirical application of additives started with the use of compounds of aluminium, which is still a constituent of one of the most widely used flame retardants. Solutions of alum (potassium aluminium sulphate) are known to have been used by the Egyptians to inhibit the combustion of wood, while nowadays many synthetic thermoplastics are treated with aluminium oxide trihydrate.[1]

Gay-Lussac carried out in France one of the first detailed systematic studies of the flame retardance of cellulosic textiles[2] and Perkin continued this work in England towards the end of the nineteenth century, although many of his results were not published until after his death.[3-6] These researches were, of necessity, largely empirical and it is only in the last 20 years or so that attempts have been made to elucidate the fundamental mechanisms of flame retardance. Some reviews have dealt with several aspects of this subject[7-12] and the next chapter deals with one aspect in some depth. The remainder of this chapter will present some recent developments.

2. COMBUSTION OF POLYMERS

The burning of a polymer is a complex process which involves several interrelated and interdependent stages. To understand the mechanism of flame retardance it is essential to outline these stages, even if superficially. The heat supplied to the polymer is responsible for bringing about its thermal decomposition. This can occur by several different mechanisms: scission of the main polymer chain, i.e. polymeric backbone, scission of the bonds linking the polymer chain to substituents, or cyclisation processes. If polymer chain scission takes place at the terminal unit, i.e. end-chain-scission, the result is depolymerisation to yield identical monomer-type molecules. The other modes of decomposition yield different small molecules or fragments which are liberated into the gas phase. These volatile products may subsequently ignite in admixture with the surrounding gaseous oxidant. This combustion liberates more heat which is then fed back to the solid phase of the polymer causing its further breakdown. This model of burning polymer will be discussed in more detail in Chapter 6.

Smouldering combustion occurs as an ignition of the solid char formed as a consequence of the initial thermal or thermo-oxidative decomposition, at temperatures which are frequently lower than those required for the ignition of the gaseous products. Glowing combustion is distinguished from smouldering combustion in that it is usually accompanied by a pale blue flame characteristic of the conversion of CO to CO_2.

In principle it is possible to affect each one of the separate stages individually. In practice, however, the technology of flame retardance usually involves either the use of additives or the replacement of monomers by less flammable analogues. These compounds do not very often confine their action to one of the separate stages involved in polymer combustion. Many, if not most, flame retardants may function simultaneously by several different mechanisms, often depending on the nature of the organic polymer. It is, therefore, more systematic to deal with individual classes of additives, according to the principal element they include, and explain their mechanisms of action, rather than to discuss in depth the different mechanisms by which a flame retardant may operate. Before this is attempted, however, some of the possible mechanisms of flame retardant action will be outlined.

3. FLAME RETARDANCE

Two distinct types of flame retardant must be recognised.

Reactive flame retardants are compounds usually containing a heteroelement which can be used to substitute one or more of the normal comonomers. This substituent then becomes an integral part of the repeating structural unit of the polymer. Reactive flame retardants can also be chemically incorporated, in smaller proportions, usually during the polymerisation process, so that only partial replacement is effected and only occasional structural units are altered.

Additive flame retardants are incorporated into polymers by being physically mixed with the polymer, normally after the polymerisation is complete. They may be more or less uniformly distributed in the bulk of the condensed polymer phase or coated on its surface but they do not affect the chemical structure of any of the monomeric units.

When the combined effect of two or more flame retardants is larger than the sum of the effects of each of the individual compounds, synergism is said to occur. Antagonism results when the combined effect of two or more flame retardants is smaller than the sum of their individual effects. Synergistic or antagonistic flame retardance can also occur as a result of the interaction of an additive with a heteroelement already present in the polymer structure.

The ideal flame-retardant polymer is one which is completely thermally stable and which does not break down at all. Although many polymers have been developed which have considerable thermal stability[13–18] they all eventually burn if they are basically organic in nature.[19] The great advantage that these materials offer is, of course, that they are very unlikely to be the material first ignited. If their decomposition products can form a flammable mixture, however, they will then eventually fuel the flames of an already existing fire. These polymers are generally very expensive to produce and do not normally possess the engineering properties which make the present high-tonnage polymers so attractive. It is therefore probable that the production of thermally stable polymers will in future remain a process of rather more academic than industrial interest, except for specific applications.

The most obvious effect of an additive is to retard the thermal decomposition of the polymer. This is, of course, similar in its effects to the preparation of an intrinsically thermally stable polymer. It is also possible, and sometimes desirable, to affect the breakdown of a polymer by increasing its rate of decomposition and thus forming a non-ignitable mixture, either because the latter is too fuel-rich or because the products formed are now intrinsically non-flammable.

The use of 'fillers' represents another flame-retardant mechanism. The inert compounds generally used are introduced into the polymer and may act as heat sinks, so that the temperature never reaches levels high enough for the polymer to suffer significant breakdown.

Another possible mechanism of action is the creation of a non-flammable protective layer which then insulates the polymer from the source of heat or excludes the gaseous oxidant from the polymer surface. If such a coating is formed only by the decomposition of the additive at high temperatures and if the char resulting from these condensed-phase reactions can trap the evolved gases and use them to cause expansion into a carbonaceous foam, then an intumescent coating results. Direct external application of a non-flammable protective surface layer results in a non-intumescent coating.

All the treatments mentioned affect mainly the thermal decomposition of the polymer. The inhibition of the flame reactions can be brought about either by chemical or by physical means. Chemical action usually involves the replacement of reactive species by less reactive ones (see Chapter 6). A physical mechanism could be the production of small non-gaseous particles (i.e. mists) which can increase the rate of chain-termination by acting as 'third bodies' or 'walls' for the destruction of radicals or may even 'smother' the flames by excluding the gaseous oxidant. Another physical mechanism involves the release from the additive of inert gases which may produce a mixture too fuel-lean to be flammable.

It should, at least in principle, be possible to inhibit the transfer of heat back from the flame to the solid polymer phase. This can be achieved in practice as a result of the endothermic decomposition of the additives or the promotion of melting and dripping following depolymerisation or by the process known as ablation where entire burning sections of the polymer 'drop off'. In all these cases a large proportion of the heat of combustion is removed from the critical zone.

The inhibition of smouldering or glowing combustion is slightly more complex than that of flaming combustion because it is more difficult to envisage well-defined separate stages. The alteration of the initial breakdown process is analogous to the action in the case of flaming combustion, i.e. the mechanism may involve chemical inhibition, fillers or coatings. On the other hand, the burning of the char is usually inhibited by specific additives which have very little effect on luminous flames and vice versa.

The information that is most frequently sought about the mechanisms of action of specific flame retardants relates to whether they act primarily in the gas phase or in the condensed phase. It is still a matter of some controversy whether oxidative surface reactions are important in the combustion process. For some polymers (e.g. polypropylene) oxygen in the surrounding atmosphere is claimed to be involved in the initial breakdown.[20,21] For other polymers (e.g. polystyrene) radiant pyrolysis studies have shown that it makes no difference whether or not the surrounding atmosphere contains oxygen.[22]

It is widely believed that, when the action of the flame-retardant additive is affected by the structure of the polymer substrate but not by the nature of the gaseous oxidant, then the mechanism is likely to involve an alteration in the condensed-phase decomposition of the polymer. If, however, the flame-retardant action changes when the oxidising atmosphere is varied, then, although it would be expected that the additive acts in the gas phase, it may only be influencing surface oxidative reactions while acting from the condensed phase. The mechanism of action may be assumed to be predominantly gas-phase if additionally the nature of the polymer does not influence the effect of the flame retardant.

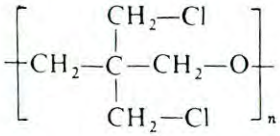
The action of those additives used for the retardation of smouldering can occur both in the gas phase (i.e. halogens or sulphur dioxide[23,24]) and in the condensed phase (i.e. borates or phosphates[25]).

One of the tools most frequently used for elucidating flame retardant mechanisms is the determination of the limiting oxygen index (LOI), which corresponds to the minimum percentage of oxygen needed in an otherwise inert atmosphere to sustain the combustion of a polymer.[26] This is the basis of standard tests (ASTM D2863, BS 2782-141, ISO draft version) but is also of great value for fundamental research on account of the variety of parameters which can be altered. Typically oxygen is replaced as the oxidising gas by nitrous oxide to investigate whether there is a gas-phase mechanism of action of flame retardants.

In the following sections the effects of the most important elements with a flame-retardant action will be discussed. These are boron and aluminium (Group III), phosphorus and antimony (Group V) and chlorine and bromine (Group VII). Other elements have also been found to confer flame retardance but they are either much less widely used or have less well-defined effects. Among these other elements mention will be made of nitrogen, molybdenum, zirconium, titanium, tin and sulphur.

4. CHLORINE

The fact that chlorine exerts some kind of flame-retardant action can be deduced from the relatively low flammability of polymers containing this halogen chemically bound in their structure. The chemical nature of the environment surrounding the bonded chlorine is very important as is apparent from plots of limiting oxygen indices of chlorinated polyethylenes and polypropylenes against the chlorine content (Fig. 1).[26-29] When the chlorine atom is attached to a tertiary carbon atom, as in polypropylene, a large flame-retardant effect is found at very low levels of chlorine (0–5 wt %; slope 2·0). When the chlorine is attached to secondary carbon atoms, as in chlorinated polyethylene, in chlorinated alkanes used as additives incorporated into polyethylene, in poly(vinyl chloride) or in poly(vinylidene chloride), the flame retardant effect is much smaller. There is also a clear change of slope, so that at low loadings the chlorine is much less effective (slope 0·2) than at high loadings (slope 1·0). The change in slope occurs at a chlorine level which would roughly correspond to a structure such as C_4H_7Cl. For comparative purposes the limiting oxygen index of Penton (a chlorinated polyether with chlorine attached to primary carbon atoms and with the following structural formula



$$\left[-CH_2-\overset{\overset{\displaystyle CH_2-Cl}{|}}{\underset{\underset{\displaystyle CH_2-Cl}{|}}{C}}-CH_2-O- \right]_n$$

is plotted in the same Figure. It can be seen that the LOI is much smaller than that where the bond is to a secondary carbon atom. This strongly suggests that the mechanism of action is predominantly chemical. When hydrogen chloride or chlorine have been added to the oxidising atmosphere above burning polyethylene[26] and polypropylene[29] and found to have virtually no effect, the inference has clearly been that the action is confined to the condensed phase. Comparative studies of the LOI and of the limiting index when the oxidising gas is nitrous oxide (LNOI) have shown both curves to be parallel,[27] again suggesting no gas-phase effect.

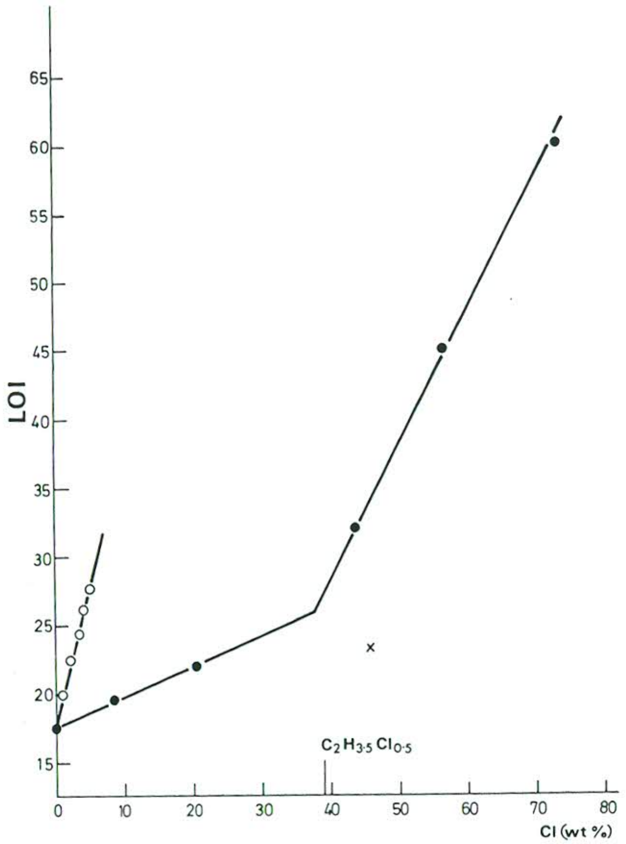


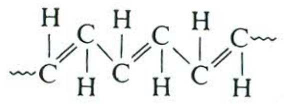
FIG. 1. Effect of chlorine, present in polymers, on their flammability: ○ polypropylene; ● polyethylene, poly(vinyl chloride) or poly(vinylidene chloride); × Penton. (Data taken from refs. 26–29.)

It has traditionally been assumed that chlorinated additive flame retardants act by virtue of their ease of elimination of hydrogen chloride.[30] This is borne out by the finding that, e.g. for polypropylene, aliphatic chlorinated hydrocarbons are ineffective flame retardants; their decomposition is so fast that they evolve hydrogen chloride during processing of the polymer.[31] Analogously chlorinated biphenyls or biphenyl ethers have a very strong Cl—C bond so that their decomposition is too slow to be effective. Thus compounds such as perchloropentacyclodecane with intermediate Cl—C bond strengths are found to be the most useful flame retardants for this polymer.[31] In general, aromatic chlorine-containing compounds are said to perform poorly as additive flame retardants,[32] although little evidence is found in the literature for this statement. Thermogravimetric studies of the decomposition of liquid and solid chlorinated alkanes frequently used as flame retardants have shown that hydrogen chloride is in fact evolved, at least in the absence of polymer.[33,34] This suggests that HCl is later effective as a gas-phase flame inhibitor. Thus the flame chain-carriers would react with HCl and transform reactive radicals into relatively unreactive ones such as chlorine atoms. The mechanism of this action will be discussed more fully in conjunction with brominated flame retardants. Hydrogen bromide is a very efficient flame inhibitor, e.g. for polypropylene some five times more so than hydrogen chloride (on a molar basis).[29] When additive flame retardants containing chlorine are compared with their brominated analogues, in terms of their efficiency in reducing the LOI of polypropylene, the relative slope values are less than or equal to 2·2.[29]

It can thus be concluded that, although there may be some gas-phase action for chlorine compounds, it is relatively inefficient and the bulk of the flame-retardant effect takes place in the condensed phase.

An alternative theory[35–38] has been proposed which assumes the operative mechanism to be a purely physical dilution of the flammable mixtures or a 'blanketing' of the flames by volatile chlorinated species. This mechanism would explain the action of the large number of inorganic chlorides and oxychlorides used, particularly for cellulosic materials. These additives are usually hygroscopic and thus liberate non-flammable gases including HCl.

Before studying other flame retardant elements, it is of interest to look at the mechanism of combustion of the most important chlorinated polymer: poly(vinyl chloride) (PVC). It decomposes principally by a chain-stripping process liberating hydrogen chloride, so that a polyenic residual structure remains:



This dehydrochlorinated charry residue can be cyclised to yield benzene, a process which occurs intramolecularly and not intermolecularly.[39] It is also possible for some main-chain C—C scissions to occur and small C_2 and C_3 products to be formed which later yield carbon oxides as the sole oxygenated products. The formation of the char and of the aromatic products is the reason why combustion of PVC produces large amounts of smoke.

5. BROMINE

The most widely accepted mechanism for the action of bromine-containing compounds as flame retardants involves the release of volatile species, mainly hydrogen bromide, into the gas phase, where it then inhibits the flame reactions.[30,32,40–48] Hydrogen bromide is produced by the thermal decomposition of many organic bromine compounds; it thus interacts with the highly reactive free radicals which are the chain carriers responsible for the propagation of combustion, e.g. by reactions 1 and 2.

$$OH^{\cdot} + HBr \longrightarrow H_2O + Br^{\cdot} \tag{1}$$

$$H^{\cdot} + HBr \longrightarrow H_2 + Br^{\cdot} \tag{2}$$

The bromine atoms formed are relatively unreactive but can still eventually abstract hydrogen from the polymeric fuel or its combustible decomposition products (RH) to regenerate hydrogen bromide by reaction 3.

$$RH + Br^{\cdot} \longrightarrow R^{\cdot} + HBr \tag{3}$$

Hydrogen bromide may also be regenerated by termination reactions, either by the bimolecular reaction 4 at relatively low temperatures,[47]

$$HO_2^{\cdot} + Br \longrightarrow HBr + O_2 \tag{4}$$

or by the termolecular reaction 5, involving a 'third body'.[45]

$$Br^{\cdot} + H^{\cdot} + M \longrightarrow HBr + M^{*} \tag{5}$$

This mechanism reduces the concentration of the oxidising hydroxyl radicals and inhibits the normal flame reactions 6 and 7, as well as the subsequent oxidation of CO to CO_2 (reaction 8). In the case of gaseous

$$RH + H^{\cdot} \longrightarrow H_2 + R^{\cdot} \tag{6}$$

$$RH + OH^{\cdot} \longrightarrow H_2O + R^{\cdot} \tag{7}$$

$$CO + OH^{\cdot} \longrightarrow CO_2 + H^{\cdot} \tag{8}$$

premixed flames, this mechanism, or some slight variation, is well established.[40] Unfortunately, however, the flames above burning polymers are not premixed, although the presence of oxygen very near the surface of

some polymers, such as polypropylene,[20,21] and of inert gases from the atmosphere in the pre-flame region of burning poly(methyl methacrylate)[49] means that polymer flames may not be purely diffusional. The amount of bromomethane needed to extinguish pure diffusion and premixed flames has been found to be the same.[41] It is therefore reasonable to assume that, although very few studies have been made of diffusion flames, polymer flames may be very similar to fuel-rich premixed flames.[47]

This simple chemical mechanism suffers from the disadvantage that it does not take into account the well-known fact that, for many organic fuels, the concentration of inhibitor needed to extinguish a flame is much greater when the halogenated compound is introduced from the fuel side rather than from the oxidant side.[41,50,51] Any bromine introduced directly into a polymer should thus be assumed to be fairly ineffective as compared with the presence of HBr in the gas phase. In fact, however, considerable evidence suggests that the bromine present in the condensed phase which is then volatilised as hydrogen bromide has a much greater effect on flammability than if it were introduced, as hydrogen bromide or as bromine, into the gas phase from the start. For example, although it has been calculated that almost 50 wt % hexabromocyclohexane should be required to confer flame retardance on polystyrene,[51] it has been found experimentally that *ca* 2% is sufficient.[52] These discrepancies have been attributed to simple failures in the application of the appropriate aerodynamic corrections[53] but it may also be that the premixed character of polymer flames is much greater than is generally assumed.

It has been shown that, in the combustion of brominated polystyrenes,[51] brominated polyurethanes,[54] brominated polyethylene and polypropylene[31,55,56] and polyesters containing additive brominated flame retardants,[57] the evolution of hydrogen bromide is an essential initial step. The rate of formation of hydrogen bromide is dependent on the C—Br bond strength, as is indicated by the difference between the efficiencies of *o*- and *p*-bromostyrene comonomers in conferring flame retardance on unsaturated polyesters.[58] It is therefore to be expected that aromatic bromine compounds, which cannot easily split off HBr, would be much poorer flame retardants than aliphatic compounds. It has been claimed repeatedly that the liberated hydrogen bromide affects in some way the mechanism of the thermal decomposition of the polymer in the condensed phase; this is not yet altogether established. Bromine chemically incorporated into the condensed phase of polyethylene has no effect on the rate of mass loss of the polymer (Fig. 2) nor on the limiting pressure change (Fig. 3) during thermal oxidation.[56] It does, however, decrease the pressure

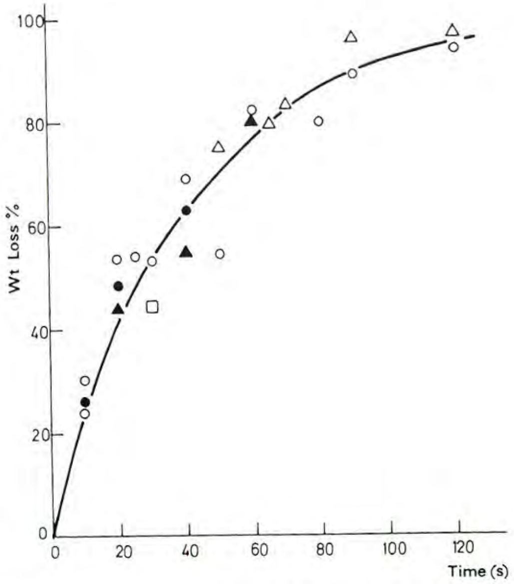


FIG. 2. Effect of chemically incorporated bromine on the rate of weight loss of polyethylene during oxidation: temperature 703 K; atmosphere 5·3 kPa O_2 + 21·3 kPa N_2; sample weight 6·4 mg; ○ untreated polymer; ● Br content 1·7 wt %; △ Br content 2·2 wt %; ▲ Br content 2·6 wt %; □ Br content 6·6 wt %. (After ref. 56, reproduced by permission of The Royal Society and of Professor C. F. Cullis.)

change during the initial stages of the reaction. When, on the other hand, hydrogen bromide is added to the oxidising atmosphere, it decreases the rate of mass loss of the polymer.[59] Simultaneously, HBr also increases the pressure change during the initial stages of the thermo-oxidative decomposition, so that the erstwhile limiting value is reached much more rapidly, and thereafter it decreases the accompanying pressure change (Fig. 3). These findings, coupled with the fact that virtually all the hydrogen bromide can be recovered from the gas phase after a very short time, suggest that the inhibition reactions do occur mainly in the gas phase. The effects on pressure change are consistent with a rapid elimination of hydrogen bromide, which then leaves 'weak' positions in the main polymer chain, so that 'random' chain scission now occurs principally at these bonds. In this way, rather high molecular weight and relatively involatile products will be formed initially. These compounds will subsequently decompose further and form the same products which would have originated from polyethylene in the absence of bromine, i.e. low molecular weight alkanes and alkenes. When HBr is already present in the gas phase, it is likely to contribute to an initial attack on the polymer chain and produce scissions which lead to gaseous products in addition to those formed by the reaction of the fuel with oxygen (reaction 9).

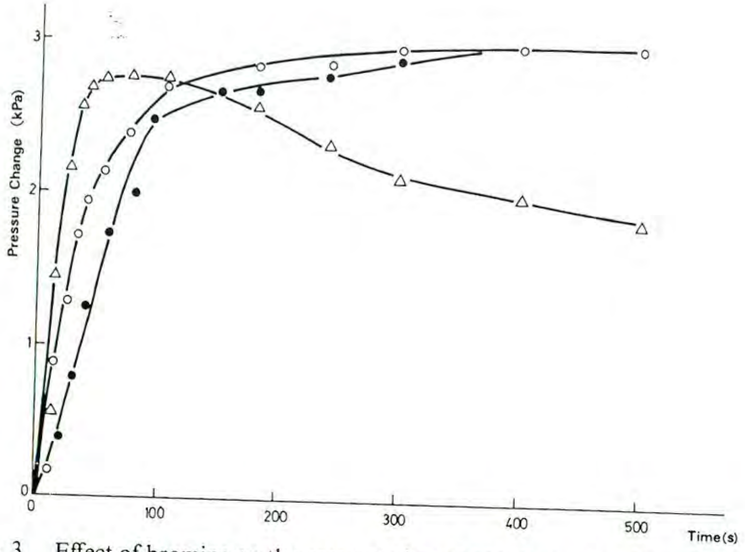
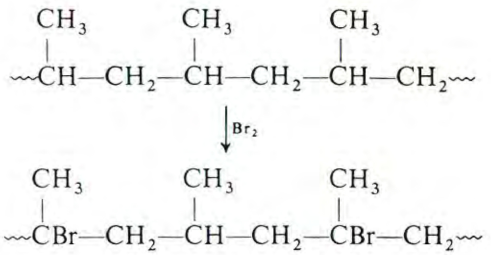


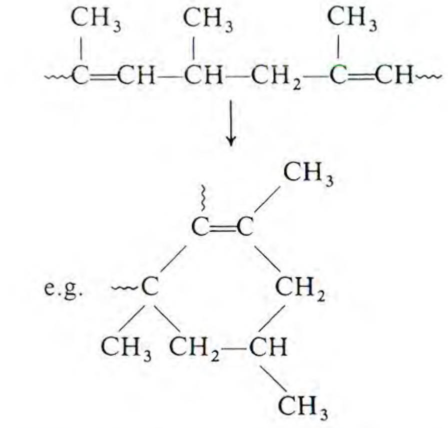
FIG. 3. Effect of bromine on the pressure change accompanying the oxidation of polyethylene: temperature 703 K; sample weight 6·4 mg; ○:atmosphere 20·0 kPa O_2 + 6·6 kPa N_2, untreated polymer; ●:atmosphere 20·0 kPa O_2 + 6·6 kPa N_2, polymer containing 12 wt % Br; △:atmosphere 20·0 kPa O_2 + 5·3 kPa N_2 + 1·3 kPa HBr, untreated polymer. (After ref. 56, reproduced by permission of The Royal Society and of Professor C. F. Cullis.)

$$RH + O_2 \rightarrow R^{\cdot} + HO_2^{\cdot} \qquad (9)$$

These reactions will soon be inhibited by the mechanism proposed earlier, so that the pressure rise decreases, i.e. there is inhibition of the flame reactions. No important condensed-phase effect can be attributed to gaseous HBr for this polymer. For polypropylene, however, gaseous hydrogen bromide accelerates thermal decomposition in inert atmospheres,[55] but not thermo-oxidative decomposition,[56] so that oxygen must react with the polymer in the condensed phase. In this same polymer, the initial pressure rise due to bromine incorporated by bromination of the substrate is identical to that of the unbrominated sample but the pressure eventually reaches a lower limiting value. This can be interpreted by assuming that bromination occurs predominantly at the tertiary carbon atoms (reaction 10) and that these positions will be less 'weakened' by the elimination of HBr because of the positive inductive effect of the methyl group. The resulting polymer, however, after elimination of HBr, will be more susceptible to cyclisation reactions typical of polydienes (reaction 11) and will thus give rise to fewer molecules of volatile products.



$$\sim CH(CH_3)-CH_2-CH(CH_3)-CH_2-CH(CH_3)-CH_2\sim \xrightarrow{Br_2} \sim CBr(CH_3)-CH_2-CH(CH_3)-CH_2-CBr(CH_3)-CH_2\sim \quad (10)$$



(11)

Other studies have shown that it is only the bromine content and not the type of additive which is relevant to the degree of flame retardance conferred on polyesters,[60] poly(methyl methacrylate) and polystyrene[61] (Fig. 4). Many halocarbons, such as CF_3Br or $C_2F_4Br_2$, are extensively used as fire suppressants,[62,63] although they are in fact thermally very stable. In a CF_3Br–CO–H_2–Ar flame, hydrogen bromide appears before bromine atoms,[64] but normally it is difficult to find reactions leading to the formation of HBr from these compounds; they are however much more efficient flame suppressants than HBr itself.[45] To explain this mode of action it may be useful to consider an alternative purely physical theory.[35-38] On re-examination of literature data, it was found that the peak effectiveness of halogen-containing organic compounds acting as flame retardants was dependent on a minimum weight of halogen of *ca* 70 % in the fuel-additive mixture.

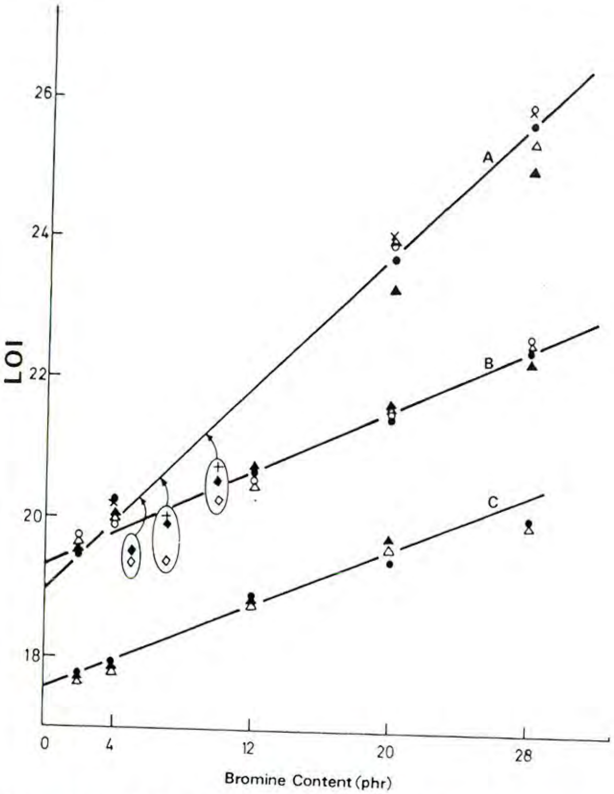


FIG. 4. Effect of bromine additives on the flammability of organic polymers: ○ tetrabromoxylene; ● 1,1,2,2-tetrabromoethene; △ tetrabromoethane; ▲ pentaerythrityl tetrabromide; × tetrabromobutane; + bis(2,3-dibromopropyl) ether; ◇ tribromoneopentyl alcohol; ◆ decabromobiphenyl ether. A, unsaturated polyester resin; B, high impact polysystryrene; C, poly(methyl methacrylate). (After refs. 60 and 61, reproduced by permission of Heyden & Son Ltd.)

$$k = \frac{\text{wt halogen}}{\text{wt fuel} + \text{wt flame retardant}} \times 100 = 69{\cdot}8 \pm 3{\cdot}5$$

This percentage was found to be completely independent of the nature of the halogen present, so that all four halogens would then have a relative effectiveness which is in direct proportion to their atomic weights, i.e.

I : Br : Cl : F :: 6·7 : 4·2 : 1·9 : 1·0

This theory assumes that the principal role of the halogens is to increase the total mass of material that must be introduced into the gas phase per unit time, without at the same time producing an increase in the heat flux back from the flame to the polymeric fuel.[38]

The effectiveness of halogens, particularly bromine, as flame retardants appears to be enhanced by free-radical initiators.[65] It was in fact later shown that the action of the free-radical initiators was quite independent of that of the bromine.[66,67] The free radicals promote depolymerisation of the polymeric fuel which then melts and drips away, taking with it a large proportion of the heat evolved. There is thus no real combined effect of the free-radical promoters and bromine.

Nitrogen does increase the effect of bromine, as for example when ammonium bromide is used as an additive,[68] or when brominated alcohols are incorporated into polyurethane foams.[54] The elimination of HBr usually occurs via the formation of an electron-deficient centre. The electron-rich nitrogen atom can act as a nucleophile and stabilise the resulting intermediate structure, thus increasing the ease of elimination of hydrogen bromide.

It can be concluded that, although there may be some effect on the condensed-phase decomposition of the polymer, bromine probably acts mainly by a free-radical mechanism in the gas phase.

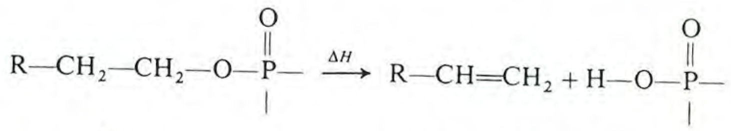
6. PHOSPHORUS

6.1. General

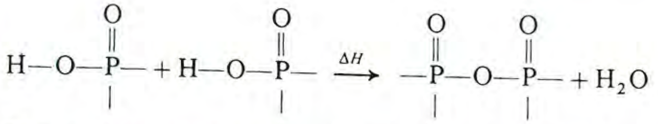
Phosphorus is one of the elements, the flame-retardant action of which is most difficult to understand. Different phosphorus compounds, or indeed even the same phosphorus compound in association with different polymer substrates, may exert modes of action ranging from condensed-phase to gas-phase and from physical to chemical mechanisms.

6.2. Hydroxylated Polymers

The most carefully studied systems are those where the substrate is cellulose. Phosphoric acid and its esters decompose thermally yielding polyphosphoric acids (12) and water (13).

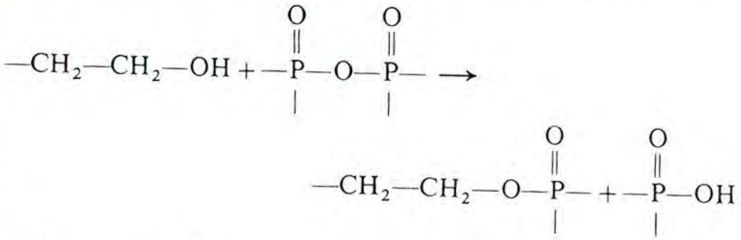


$$R{-}CH_2{-}CH_2{-}O{-}\overset{\overset{O}{\|}}{\underset{|}{P}}{-} \xrightarrow{\Delta H} R{-}CH{=}CH_2 + H{-}O{-}\overset{\overset{O}{\|}}{\underset{|}{P}}{-} \qquad (12)$$



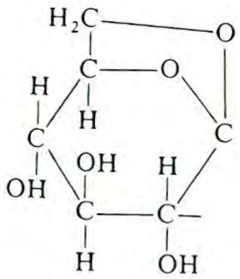
$$H{-}O{-}\overset{\overset{O}{\|}}{\underset{|}{P}}{-} + H{-}O{-}\overset{\overset{O}{\|}}{\underset{|}{P}}{-} \xrightarrow{\Delta H} {-}\overset{\overset{O}{\|}}{\underset{|}{P}}{-}O{-}\overset{\overset{O}{\|}}{\underset{|}{P}}{-} + H_2O \qquad (13)$$

These reactions are followed first by substitution of the free hydroxyl groups in cellulose by phosphate groups and the concurrent regeneration of phosphoric acid (reaction 14) and finally by dehydration of the resulting organic phosphates to yield an alkenic structure by reaction 12.



$$\begin{aligned}&{-}CH_2{-}CH_2{-}OH + {-}\overset{\overset{O}{\|}}{\underset{|}{P}}{-}O{-}\overset{\overset{O}{\|}}{\underset{|}{P}}{-} \longrightarrow \\ &\qquad {-}CH_2{-}CH_2{-}O{-}\overset{\overset{O}{\|}}{\underset{|}{P}}{-} + {-}\overset{\overset{O}{\|}}{\underset{|}{P}}{-}OH \qquad (14)\end{aligned}$$

Account should be taken of the fact that cellulosic polymers usually decompose by two parallel routes. One of these involves depolymerisation to yield *laevo*-glucosan (**I**), which, in turn, breaks down to give flammable gaseous products. The other mechanism is a chain-stripping reaction whereby the substituents on the carbon chain, mainly hydroxyl groups, are eliminated, as water, and the residue becomes an unsaturated char which smoulders or glows instead of undergoing flaming combustion. Thus, if phosphorus-containing flame retardants act by a condensed-phase mechanism such as that proposed, an increase in the amount of char would be expected. This in fact happens with cellulosic polymers.[69,70]



(I)

Simultaneously, however, water must be evolved. This has been shown to act, in the gas phase, to decrease the heat liberated during combustion.[71] Plots of the limiting oxygen index (LOI) against phosphorus content for phosphoric acid-treated cellulose have the same slope as those for the limiting nitrous oxide index (LNOI).[72] This suggests, then, that the effect of the water produced by reaction of phosphoric acid and cellulose, even if it occurs in the gas phase, is purely physical and will not be affected by a change in the nature of the gaseous oxidant. Further evidence in support of chemical action in the condensed phase comes from the fact that, as the level of phosphoric acid is increased, there is a steady decrease in the temperature at which the endothermic decomposition of cellulose occurs[73] (Fig. 5). Phosphoric acid is shown to introduce an additional stage, which is probably the phosphorylation of the hydroxyl groups in cellulose.

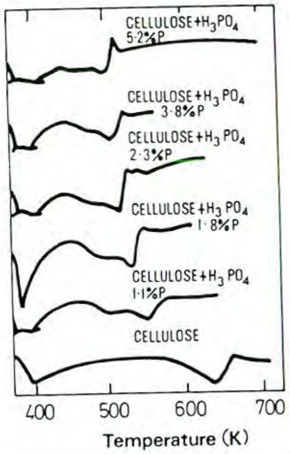


FIG. 5. Thermal analysis of cotton fabrics treated with increasing amounts of phosphoric acid. (After ref. 73, reproduced by permission of John Wiley & Sons Ltd.)

Work carried out on the thermal decomposition of other hydroxylated polymers shows that phosphorylation accelerates also the chain-stripping process as a result of the dehydration and formation of conjugated double bonds; in consequence the scission of polymer chains is inhibited.[74,75] The differential thermal analysis curves for poly(vinyl alcohol) and for the same polymer after phosphorylation (Fig. 6) show the various changes which phosphorus has produced in the rate of thermal degradation of the polymer, e.g. in the activation energies for the various steps.[74]

The mechanism of this mode of flame-retardant action by phosphoric acid and its esters on hydroxylated polymers is probably ionic, since it is a well-established fact that the hydroxyl groups in cellulose are extensively attacked by acidic catalysts, while they are not affected by neutral salts.[10] Acid catalysts can also induce scission of one of the two C—O bonds in epoxides. A further confirmation of this mechanism is therefore provided by the fact that studies of the LOI and LNOI of epoxy resins have shown that triphenyl phosphine does not chemically affect the gas-phase flame reactions: triphenyl phosphine produces only condensed-phase effects on the decomposition of these resins.[76] Epoxy coatings, modified with phosphorus esters, show an increased char-forming tendency and intumescence,[77] also signs of condensed-phase reactions.

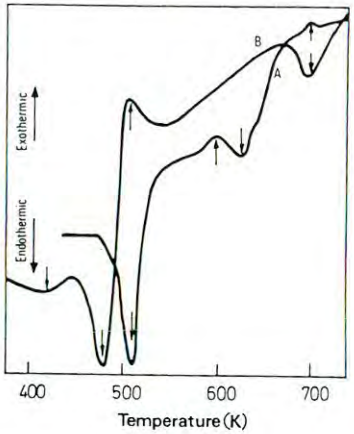


FIG. 6. Thermal analysis of poly(vinyl alcohol) (A) and phosphorylated poly(vinyl alcohol) (B). (Reproduced from ref. 74, by permission of the publishers, IPC Business Press Ltd ©.)

The effect of phosphorus on the flame retardance of cellulosic compounds is considerably enhanced by nitrogen bases, such as urea, guanidine or dicyanodiamide. One of the main advantages of the use of nitrogen is the clearly increased ease of attachment of the phosphorus to the polymeric fabric. This reduces loss of the additive due to its solubility in water. There is abundant evidence that the minimum amount of phosphorus needed to make cotton flame-retardant decreases with increasing amounts of nitrogen.[78,79] It is not clear whether this is simply an effect of the better durability of the phosphorus finish, or whether it is an additive or even synergistic effect.[9] The most pronounced effects have been found with nitrogen compounds containing relatively non-basic N—H groups.[79] The flame-retardant action is dependent, however, on various factors, such as the mode of application of the phosphorus and nitrogen compounds.[80] A systematic study was undertaken of nitrogen bases added to a cellulose–triphenyl phosphate system.[81–82] The char yields obtained increased with nitrogen content. The nitrogen compounds were also shown to interact exothermically with *laevo*-glucosan in a manner similar to that in which acids act. Transphosphorylation takes place and it was concluded that phosphoramides were formed as intermediates. The nitrogen compounds thus probably act by a nucleophilic attack on the phosphate, which results in the formation of numerous P—N bonds.[72] These bonds, being more polar than the original P—O bonds, result in increased electrophilic character of the P atom and the rates of acid-catalysed dehydration of cellulose are thus also higher. In this way char formation is increased at the expense of that of flammable *laevo*-glucosan. When various phosphoramides are used directly as additives, the slopes of the plots of the proportion of cellulose converted into char ($Y(1-X)$), against the logarithm of the phosphorus content, are all the same, irrespective of N content, while the slope for phosphoric acid is much smaller (Fig. 7).[83] When a phosphoramide is cross-linked with a melamine resin, the slope still does not change but the effect is much larger. This is due to a physical rather than chemical cause: the volatility of the phosphoramide is decreased and thus more of the reagent is in contact with the cellulose during the pyrolysis. When the amido group is replaced by a methyl ester (not containing nitrogen) or by a nitrile (which is non-nucleophilic and cannot, thus, form P—N bonds), the resulting slope is the same as that for phosphoric acid. This tends to give support to the mechanism proposed.

Summing up, then, phosphorus compounds confer flame retardance on hydroxylated polymers, by a condensed-phase esterification of the hydroxyl groups as a result of acid catalysis. Water is then liberated which acts as a physical agent in the gas phase. The incorporation of nitrogen which can form P—N bonds increases the effectiveness of the esterification process.

6.3. Other Polymers

In the case of thermoplastic polymers, a significant proportion of the phosphorus added is lost by volatilisation prior to the breakdown of the polymer itself, so that evidently any condensed-phase action is relatively small.[84] Phosphorus-containing compounds are known to be gas-phase flame inhibitors,[47] and this is confirmed by the finding that various non-halogenated phosphorus compounds with the phosphorus in different oxidation states have roughly the same effect on the LOI of polyethylene,[27] and of poly(ethylene terephthalate) (PET).[85] The mechanism of action may involve the formation of heavy vapour clouds which effectively 'smother' the flame by excluding oxygen.[86] During the combustion of polystyrene[86] and of poly(ethylene terephthalate),[87] for example, most of the phosphorus is volatilised and almost none remains in the solid residue.

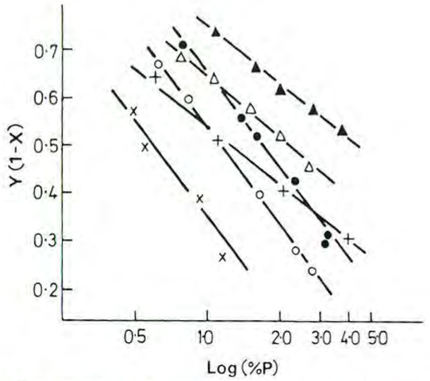
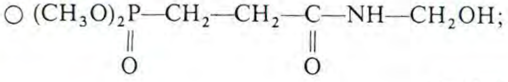
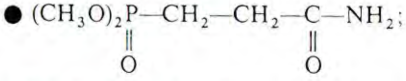
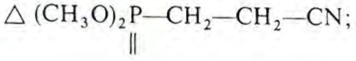
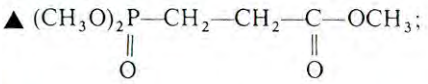


FIG. 7. Effect of different phosphorus-containing additives on the proportion of cellulose converted into char ($Y(1-X)$). Additives:


○ $(CH_3O)_2\underset{\underset{O}{\|}}{P}—CH_2—CH_2—\underset{\underset{O}{\|}}{C}—NH—CH_2OH$;


● $(CH_3O)_2\underset{\underset{O}{\|}}{P}—CH_2—CH_2—\underset{\underset{O}{\|}}{C}—NH_2$;


△ $(CH_3O)_2\underset{\|}{P}—CH_2—CH_2—CN$;


▲ $(CH_3O)_2\underset{\underset{O}{\|}}{P}—CH_2—CH_2—\underset{\underset{O}{\|}}{C}—OCH_3$;

× $(NHCH_3)_3P{=}O$ + melamine; + H_3PO_4. (After ref. 83, reproduced by permission of the Swiss Federations of Dyers and of Chemist-Colourists and of Professor R. H. Barker.)

Tricresyl phosphate, which increases the limiting oxygen index of several thermoplastic polymers (polyethylene, polyoxymethylene, poly(methyl methacrylate)) to similar extents (8–15 %), has a much greater effect on the LOI of poly(ethylene oxide) (+40 %).[27] This is an indication of the importance of the substrate. Poly(ethylene oxide) is amenable to acid catalysis due to the presence of the ether oxygen atom and its rate of decomposition is therefore probably affected by phosphorus in the condensed phase. The other polymers are, however, affected only as a result of effects on the gas-phase reactions of their decomposition products.

The combined action of phosphorus and nitrogen on the combustion of thermoplastics is occasionally antagonistic: this is the case with polymers such as polyethylene, polypropylene and poly(methyl methacrylate).[9] This can be explained if the acidic phosphate species changes the pattern of breakdown of poly(methyl methacrylate) (PMMA) so that it suffers chain-stripping, instead of depolymerisation to monomer, and thus yields large proportions of char.[88] The addition of nitrogen bases would then decrease the effectiveness of this catalytic action. In fact, however, in blends of PMMA with ammonium polyphosphate, no reaction occurs between the two components of the blend, but the organic polymer reacts with polyphosphoric acid, the breakdown product of its ammonium salt.[89] This chemical explanation of P–N antagonism is inconsistent with the mechanism of action proposed for thermoplastic polymers, which is mainly physical and takes place in the gas phase.

Phosphorus-based flame retardants are fairly extensively used in many nitrogen-containing polymers such as polyacrylonitrile,[90] natural[91] and synthetic[92] polyamides and polyurethanes,[93] but the mechanism of action is not yet well understood.

Studies of the combined action of phosphorus and halogens on the combustion of polyesters and polyurethanes have shown that the reaction occurs mainly in the condensed phase.[87,94–96] There is, generally, increased formation of char and a large proportion of the phosphorus remains in the solid residue. The main function of the halogen in halogenated phosphates is probably to prevent the volatilisation of the additive.[87] Thus, while trihexyl phosphate, which is non-volatile, is just as effective a flame retardant for poly(ethylene terephthalate) as a brominated phosphate, tripropyl phosphate does not significantly affect the LOI of the polymer. It is also interesting that tris(chloromethyl-2-chloroethyl) phosphate is a very much more efficient flame retardant than tris(2,3-dichloropropyl) phosphate, the only significant structural difference between the two compounds being the tertiary carbon atom in the former; this compound is thus less volatile. The suggested mechanism of action in the condensed phase involves an acid-catalysed aldol condensation. Tris(2,3-dibromopropyl) phosphate also acts in the condensed phase when conferring flame retardance on polystyrene, but the mechanism is not yet clear.[97] Another phosphorus–halogen system widely used, but so far little studied, comprises the phosphate plasticisers for PVC.

TABLE 1

EFFECT OF RED PHOSPHORUS ON LIMITING INDICES OF POLYETHYLENE TEREPHTHALATE

Additive wt (%)	*LOI*	*LNOI*
0·0	20·4	46·4
1·0	23·6	47·9
2·0	25·1	48·7
3·0	27·6	49·3
4·0	30·3	49·9
Slope (LI ÷ wt %)	3·57	1·64

(After ref. 100.)

Finally it is of considerable interest to mention a compound which is surprisingly a very effective flame retardant, viz. red phosphorus, a polymeric form of elemental phosphorus which is quite distinct from the more common white P_4 molecules. It is obviously the most economical way in which phosphorus can be made to give maximum yields of the acid catalyst for condensed-phase action. Significantly, in the case of polyurethanes, the action of red phosphorus is enhanced by the presence of small amounts of halogen compounds.[98,99] Less easy to explain is the combined effect of red phosphorus and halogens for thermoplastic polymers such as polyolefins or PVC.[99] In the case of poly(ethylene terephthalate), red phosphorus is a very good flame retardant in its own right and it acts partly in the gas phase. This conclusion is confirmed by the

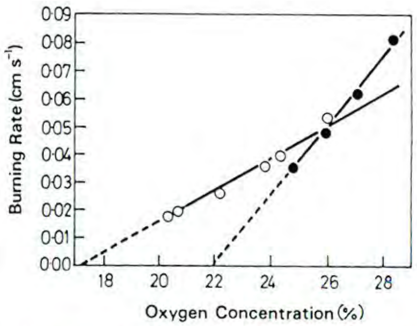


FIG. 8. Effect of oxygen content on the burning rate of poly(ethylene terephthalate): ○ untreated polymer; ● polymer + 2% red P. (After ref. 100, reproduced by permission of John Wiley & Sons Inc.)

different slopes of plots of LOI and LNOI versus phosphorus content, as described by the equation

$$LI_P = LI_0 + \text{slope} \times P^{1/2}$$

where LI_P is the limiting index (LOI or LNOI), at an additive concentration of phosphorus of P wt %, and LI_0 is the same index when no phosphorus has been added[100] (Table 1). The presence of red phosphorus does also affect, however, the rate of burning of the polymer, so that there is probably a considerable proportion of condensed-phase action (Fig. 8).

7. ANTIMONY

The use of metal oxides as flame retardants had already been suggested by Sir William Perkin at the turn of the century. It was not, however, until World War II that antimony trioxide began to be used[101-103] and it was soon shown that Sb_2O_3 (or more accurately Sb_4O_6) is generally ineffective in the absence of halogens, a finding borne out by most later studies.[8,9,68,102-105] In some isolated cases, however, antimony oxide may provide some degree of flame retardance on its own.[106-108] It is however the apparent synergism between antimony and halogens which has been the cause of the wide use of antimony as a flame retardant. The mechanism of action of antimony–halogen systems has been the subject of much research and is the butt of deep controversies. The greatest amount of work has been devoted to the identification of the active species and to the determination of the phase in which the flame-retardant action takes place.

The optimum atomic ratio for the Cl–Sb or the Br–Sb systems can now be safely assumed to be 3:1.[68,102,105,109] This does not however necessarily imply that volatile antimony trihalide is the active intermediate. The initial assumption made[102,103] was that antimony oxyhalide was the species responsible for the flame-retardant action. Studies of the thermal decomposition of antimony oxychloride (SbOCl)[110] do in fact show that this compound decomposes yielding, in three endothermic steps, gaseous antimony trichloride and a solid residue of Sb_2O_3. The thermogravimetric pattern of decomposition of SbOCl has a substantial overlap with that of various flexible polyurethane foams for which the Sb–Cl system had been shown to be a good flame retardant. Several other flame-retardant systems (or putative flame-retardant systems) were also studied and it was seen that those additives which had considerable thermogravimetric overlap with the foam were effective combustion inhibitors, while those which decomposed at either substantially lower or higher temperatures than the polymer had little or no flame-retardant action. This led to the conclusion that SbOCl is formed *in situ* and then produces $SbCl_3$, which is the actual flame retardant.[105] Antimony trichloride is too unstable to be incorporated into a polymer and cannot therefore be used as a flame retardant. This means, of course, that the theory cannot be tested directly. There was, however, some earlier evidence for the gas-phase action which was taken as support for this mechanism: thus the limiting oxygen index of chlorinated polyethylene is improved by antimony trioxide but the limiting nitrous oxide index is unaffected.[26,27]

However, mass spectrometric studies of the flames above polymers containing antimony + chlorine have indicated that there is no $SbCl_3$ in the flame zone,[47] although solid antimony monoxide (SbO) and even metallic antimony (Sb) can be detected. A sequence of reactions is therefore suggested, including 15 and 16. The active species proposed are thus solid

$$SbCl_3 + H_2O \longrightarrow SBOCl + 2HCl \tag{15}$$

$$SbOCl + H \longrightarrow SbO + HCl \tag{16}$$

antimony monoxide and gaseous hydrogen chloride, the inhibitory action being at least partly heterogeneous. Triphenyl stibine is oxidised to SbO, probably explaining why it is effective, in the absence of halogens, in reducing the flammability of epoxy resins.[76]

The fact that at least 50 % of the antimony is volatilised from polymers also including halogens,[111] while 95 % of the antimony remains in the solid residue when halogen-free polymers are burnt,[27] is further evidence for a gas-phase mechanism.

Thermal analysis of antimony oxide–halogen systems in the absence of an organic polymer provides no evidence for the formation of SbOCl, but nevertheless indicates that volatilisation of chlorine and antimony[33,34,112-114] and indeed of bromine and antimony[33,112-114] occurs in a 3:1 ratio. This does not, however, appear to be the complete solution of the mechanistic problem. Thus, for instance, the synergistic effect of Sb_2O_3 is much larger with solid chlorinated waxes than with liquid compounds with the same chlorine content.[33,112-114] This can be explained by the fact that the temperatures of decomposition of the solid additives to form HCl are much lower than their temperatures of volatilisation. The liquid additives on the other hand distil unchanged and do not decompose until fairly high temperatures are reached (Fig. 9). Antimony oxide can affect the rate of formation of volatile products (V) from the chlorinated additives and the Sb–Cl systems can alter V for the polymeric substrate. When

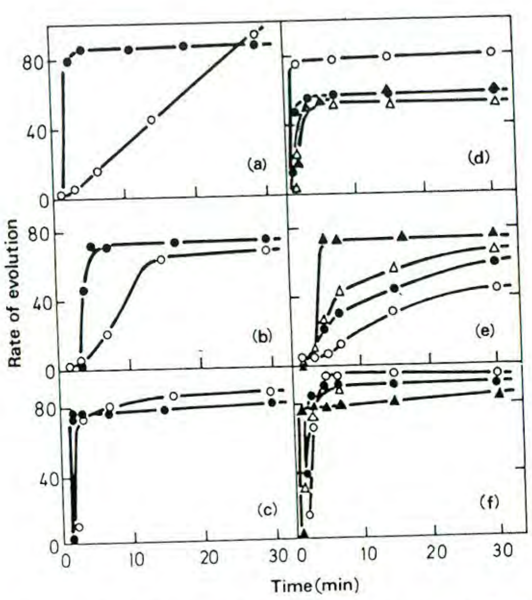


FIG. 9. Rate of formation of gaseous products from various mixtures of polyester, chlorinated paraffins and antimony trioxide: (a) ○ Dechlorane 4070; ● Dechlorane 4070 + Sb_2O_3 (at 683 K); (b) ○ Cereclor 70; ● Cereclor 70 + Sb_2O_3 (at 583 K); (c) ○ Cereclor 70; ● Cereclor 70 + Sb_2O_3 (at 683 K); (d) ○ Cereclor 70 + Sb_2O_3; ● Cereclor 70L + Sb_2O_3; △ Cereclor 65L + Sb_2O_3; ▲ Cereclor S52 + Sb_2O_3 (at 583 K); (e) ○ polyester; ● polyester + 15 wt % Sb_2O_3 + 15 wt % Cereclor 70 (incorporated into the substrate); △ polyester + 15 wt % Sb_2O_3 + 15 wt % Cereclor 70 (physically mixed with the substrate); ▲ Cereclor 70 + Sb_2O_3 (at 583 K); (f) as in (e), but at 733 K. (After ref. 33, reproduced by permission of Dr. G. S. Learmonth.)

different chlorinated paraffins are compared, a much higher temperature is required for a significant increase in the case of the liquid Dechlorane 4070 than for the solid Cereclor 70; for some liquid additives the rate always remains very low. The Sb–Cl system increases V for the polymer if the experiment is carried out at a temperature below the ignition point of the resin (723 K), while it decreases V at a higher temperature when enough flammable products would otherwise be formed from the polymer for ignition to occur. Analysis of the thermogravimetric curve of the polymer shows that the second stage of its decomposition, i.e. that in which the unsaturated polyester resin gives off most of the volatile products, is the one most affected. This is clear evidence for condensed-phase action, which probably occurs before the gas-phase reactions.

The antimony–halogen system has been found to enhance the condensed-phase formation of char, which then insulates the bulk of the polymer by the formation of a physical barrier.[32,115] Although the difference in thermal dehydrochlorination rates of chlorinated polyethylene in the presence and in the absence of antimony trioxide can be attributed to a condensed-phase reaction,[116] the opposite conclusion can be drawn from the lack of effect of Sb and Cl on the thermal decomposition of polypropylene in nitrogen.[117]

The system chlorinated paraffins + Sb_2O_3 is very much less effective in reducing the extinction times of glass-reinforced polyester resins than pentabromotoluene (PBT) with Sb_2O_3.[118] If, however, even a small proportion of PBT is added to the chlorine-containing system, an effect is found which is as large as that of PBT–Sb_2O_3 system. This has led to the interpretation that the mechanisms of action of antimony oxide with bromine and with chlorine are qualitatively different.

In conclusion, it now seems probable that some reaction takes place in the condensed phase to produce the antimony trihalide, via the intermediate formation of a Lewis acid.[119] The use of Friedel–Crafts alkylation reagents in conjunction with an antimony oxide–chlorine Lewis acid precursor has, in fact, been shown to promote *in situ* charring of polystyrene.[120] It is however important that the halogen compound for the Sb–halogen system is one that does not volatilise prematurely. If this happens, the polymer structure would in fact be weakened and its flammability increased.[111,121] Once antimony halide is formed, it volatilises and breaks down rapidly in the hot pre-flame zone to produce SbO and hydrogen halide, which are the active species reaching the flame zone. It is probably the existence of the additional heterogeneous scavenging action of SbO, reminiscent of the effect of lead oxide formed from lead alkyls added to motor gasolines, that is the key factor which allows the drastic reduction in the proportion of halogen required to render a polymer flame-retardant.

8. BORON

Four different mechanisms of action can be attributed to additives containing boron:

(a) Formation at the surface of the solid polymer of 'glassy' inorganic deposits which act in a similar fashion to intumescent coatings.

(b) Enhancement, with hydroxylated polymers, of char production at the expense of the formation of flammable gaseous products; this involves a condensed-phase mechanism whereby the boron-containing compound is first converted into boric acid and subsequently forms borate esters.

(c) Release of water vapour into the gas phase by hydrated boron compounds (or of ammonia by ammonium borates); the water released acts both as a heat sink, reducing the amount of heat transferred back to the polymer for its continued decomposition, and as a diluent of the gaseous fuel, thus removing the composition and temperature of the gaseous mixture from within the flammability limits.

(d) Chemical inhibition of oxidation reactions at the gas–solid interface by acting as free-radical scavengers.

Boric acid and its hydrated salts were among the first inorganic compounds to be used as flame retardants for cellulosic textiles.[2] They have low melting points and their thermal decomposition occurs according to the general scheme 17:[8]

$$\underset{\text{boric acid}}{H_3BO_3} \xrightarrow{400\text{–}470\,K} \underset{\text{metaboric acid}}{HBO_2} \xrightarrow[13\cdot3\,kPa]{533\text{–}543\,K} \underset{\text{boric oxide}}{B_2O_3} \qquad (17)$$

Boric oxide becomes 'glassy' at *ca* 600 K and starts flowing above 775 K. The mixture of boric acid and borax ($Na_2B_4O_7 . 10H_2O$), which has very little tendency to crystallise out, starts losing water of hydration when contained in a cellulosic polymer at a temperature intermediate between that of the softening point of the polymer and that at which extensive thermal decomposition starts. The inorganic residue traps part of the evolved water and a portion of the polymer will expand so as to produce a surface layer which is similar to an intumescent coating and which insulates the bulk of the polymer from the external heat source. Borax, in the absence of boric acid, is an excellent inhibitor of flaming combustion, but is a catalyst for the afterglow of char residues.[122] This is very symptomatic because it has been found that, for cellulose, the borax added is not uniformly distributed throughout the polymer but tends to remain near the surface.[123] Boric acid is normally thought of as a rather poor flame retardant, which is however very effective in suppressing glowing combustion. This may be a misconception because the efficiency of boric acid in increasing the limiting oxygen index and limiting nitrous oxide index for wool passes through a maximum at *ca* 0·5 wt % of boron, while no such

effect is found for borax, a boric acid–borax mixture or ammonium fluoroborate (Fig. 10).[124] In none of these cases is there an apparent chemical effect in the gas phase since the LOI and LNOI vary in a similar fashion. The borax-treated wool melts and chars while no melting is observed for the boric acid-treated samples. The action of the fluoroborate has been attributed to the action of liberated boron trifluoride in the gas phase[68] and to a dehydration and cross-linking mechanism similar to that of borax. The results on wool tend to suggest, however, that neither mechanism is entirely correct. Several water-soluble borates have been used as flame retardants and are quite effective, their efficiency being largely dependent on the associated cation and on the ratios of metal oxide to boric oxide and of inert gases to boric oxide. In this connection, ammonium salts, e.g. ammonium pentaborate, should be mentioned because they yield additional non-flammable gases (ammonia, reaction 18) which are volatilised instead of depositing metal oxide residues.

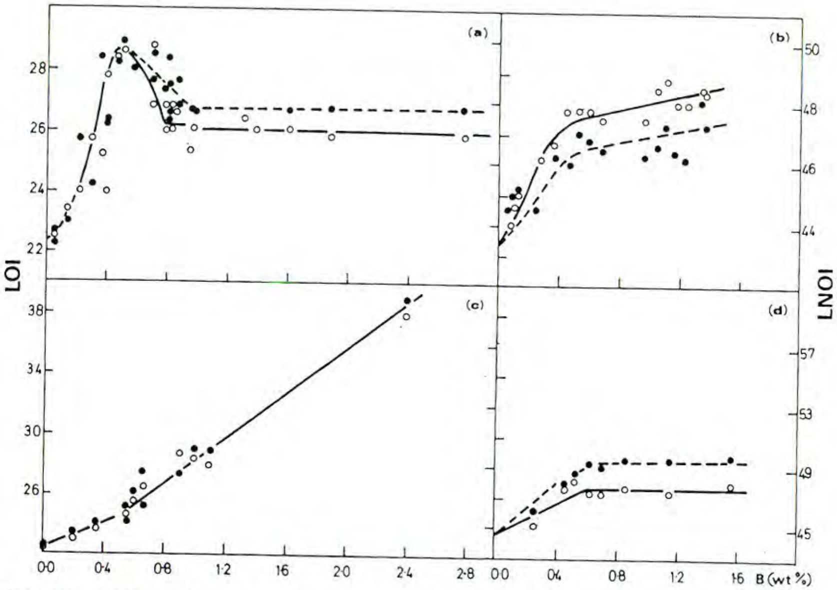


FIG. 10. Effect of boron on the flammability of wool: ○ oxidant, O_2; ● oxidant, N_2O; (a) boric acid; (b) borax; (c) ammonium fluoroborate; (d) borax + boric acid (7:3). (After ref. 124, reproduced by permission of the Textile Research Institute.)

$$(NH_4)_2O . 5B_2O_3 . 8H_2O \longrightarrow 5B_2O_3 + 9H_2O + 2NH_3 \qquad (18)$$

The mechanism of char enhancement by borates for hydroxylated polymers is very similar to that exhibited by phosphates: the free hydroxyl groups are esterified, forming borate esters, and this is followed by loss of water.[125] Thus, in cellulose, char production is favoured at the expense of the formation of *laevo*-glucosan. Hydrated borates are more effective than the anhydrous salts,[126] so that the release of inert gases also occurs with borate flame retardants. Boron itself remains in the condensed phase, analysis of cellulosic char residues showing that 90% of the boron added has not volatilised.

The temperature at which the flame retardant action occurs (*ca* 535 K) is perfectly adequate for cellulose, which does not start to decompose significantly below 620 K. Another hydroxylated polymer, however, poly(vinyl alcohol), is not a good substrate for borate flame retardants, because it starts to decompose at *ca* 475 K[127] so that, when boric oxide is formed, the polymeric hydroxyl groups have already been eliminated. Phenolic resins are hydroxylated polymers for which borates are very efficient flame retardants.[128,129]

Fused boric oxide has been used as a flame retardant for cotton fabrics[130] and it has been found that smouldering combustion is inhibited only when the source of heat is placed above the material and not when the cellulose is heated from below. The resulting chars have been found to have a free-radical content some 2–3 times lower than those from cotton treated with lithium hydroxide or sodium chloride. This has led to the suggestion that some 'active sites' in the char are blocked chemically by volatile species acting heterogeneously by a free-radical mechanism. If an analogy were sought with other flame retardants, the action of SbO is the one that comes most clearly to mind.

Finally, the action of zinc borates (and some other insoluble borates) deserves mention. They have been extensively used as partial or total replacements for antimony oxide in conjunction with halogens.[131–133] The mechanism of action is probably different from that of Sb_2O_3 but not much is yet known about it despite the fact that a number of studies have been made. There may be some interaction between the boron and the zinc.

9. ALUMINIUM

Aluminium oxide trihydrate is the flame retardant most abundantly used for plastics during the last few years (representing almost 44% of the total in the United States in 1978[1]). This implies a phenomenal rise since hydrated alumina was introduced only around the mid-1960s as a flame retardant for unsaturated polyester resins, on account of its low cost.[134]

Studies of its effect on the limiting oxygen index of epoxy resins showed that, while anhydrous alumina did not markedly affect this measure of polymer flammability, the hydrated oxide produced a significant increase in the LOI and a parallel one in the LNOI (Fig. 11).[76] This suggests that the predominant inhibiting action occurs in the condensed phase and involves principally an endothermic dehydration. The alumina thus acts as a heat sink and prevents the flammable gases from reaching temperatures at which they would ignite, while the water vapour released simultaneously dilutes the gaseous fuel.

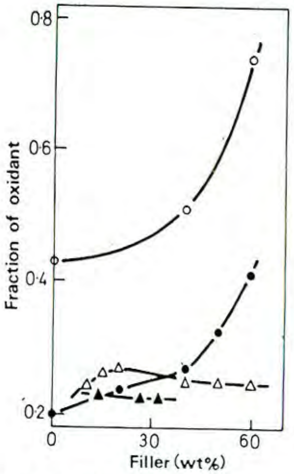


FIG. 11. Effect of alumina on the flammability of epoxy resins: ○ $Al_2O_3.3H_2O$ (oxidant, N_2O); ● $Al_2O_3.3H_2O$ (oxidant, O_2); △: Al_2O_3 (Norton 389001) (oxidant, O_2); ▲ Al_2O_3 (Linde A) (oxidant, O_2). (After ref. 49, reproduced by permission of Dr. C. P. Fenimore.)

These experiments have thus shown that the effect of hydrated alumina does not consist merely in the dilution of the solid combustible polymer by a non-flammable filler material. It thus became of interest to determine the heat that alumina trihydrate needs to absorb to lose its water of hydration. Early measurements of this heat of hydration[135] suggested a value of 1970 $J g^{-1}$,[136–140] but more recent results[141–143] indicate that this figure is probably too high and an average value of 1170 $J g^{-1}$ has been obtained,[143] which is almost independent of particle size.[144,145]

An early source of interest in alumina trihydrate was its effect on smoke.[76] The hydrated material has a significantly greater effect on the reduction of smoke, as well as on flammability, than is the case for the anhydrous compound,[28] although the injection of water as such into the oxidant gases does not affect the amount of smoke produced.[146] Comparison with other fillers (e.g. hydrated silicates) shows that alumina is very much more effective than any of the others in increasing the time to reach a critical obscuration from styrene–butadiene rubber (SBR).[147] If another smoke parameter is analysed, i.e. maximum smoke density, alumina is not much better than other fillers.[147] This suggests that what is occurring is a decrease in the rate of formation of smoke, i.e. the alumina has a chemical effect on the condensed-phase mechanism of thermal decomposition. This is further confirmed by results with other polymers. The distribution of products from burning polystyrene is markedly changed by hydrated alumina, there being, for example, a considerable increase in the amount of toluene formed.[148] Smoke formation is thus decreased as a result of the formation of less smoky volatile intermediate products. In unsaturated polyester resins, the amounts of unburnt hydrocarbons produced are increased and the rate of smoke generation is reduced.[149] This decrease in the rate of smoke formation, even in the presence of smoke-enhancing brominated additives, is, as with SBR,[147] a much more pronounced effect than the decrease in maximum smoke density.

It having been established that alumina probably acts chemically in the condensed phase, its possible interaction with halogens will be considered. Some early evidence for a chemical mode of action has remained largely unnoticed. A combination of 16·8% alumina trihydrate and 3·4% tris(2-chloroethyl) phosphate gives excellent flame retardancy to rigid polyurethane foams,[150] while 20% $Al_2O_3 . 3H_2O$ alone is ineffective in reducing the flammability of both rigid and flexible polyurethane foams.[93] Similarly, while the addition of fillers, such as glass fibre or calcium carbonate, increases the burning rates of chlorendic acid-based unsaturated polyester resins, this is not the case for hydrated alumina.[151] It has been suggested, albeit without much supporting evidence, that the reduction by alumina of the flammability of SBR rubbers in the presence of chloroparaffins is due to a formation of $AlCl_3$ which catalyses in the solid phase the elimination of halogen radicals.[8] Thermogravimetric studies of mixtures of anhydrous alumina with chlorinated wax showed no volatilisation of aluminium chloride.[34] This only served to confirm that alumina is unlikely to act in the gas phase. Perhaps more important is the

fact that no apparent effect is found on the thermal decomposition pattern of the chlorowax. The addition of $Al_2O_3 . 3H_2O$ to unsaturated polyester resins treated with a brominated additive was found to decrease the amount of hydrogen bromide liberated into the gas phase, as measured in a smoke chamber (Fig. 12).[149] In other work, samples of acrylonitrile–butadiene–styrene copolymer (ABS) containing decabromobiphenyl and of high density polyethylene (HDPE) containing chlorinated wax, in both cases in conjunction with either anhydrous alumina, alumina monohydrate or alumina trihydrate, were heated in the source of a mass spectrometer and the volatile products were analysed.[152] In no case were Al–Cl or Al–Br species found, which is further confirmation that the alumina acts primarily in the condensed phase.

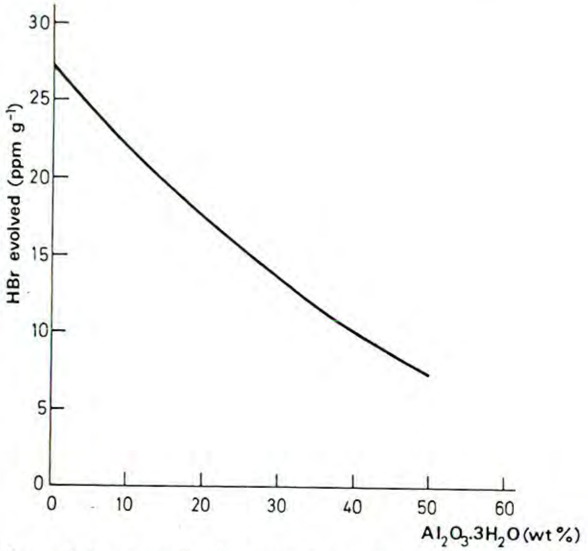


FIG. 12. Effect of alumina trihydrate on the evolution of hydrogen bromide from unsaturated polyester resins. (After ref. 149, reproduced by permission of the Society of the Plastics Institute, Inc., and of Dr. D. P. Miller.)

The limiting oxygen indices of ABS treated with decabromobiphenyl (DBB) and with each of the aluminium oxides show very definite signs of synergism (Table 2).[152] The LOI of the polymer containing the mixture is compared, in Fig. 13, with the LOI which would correspond to an additive effect of the flame retardants (LOI_{add}):

$$LOI_{add} = LOI_{Br} + LOI_{Al} - LOI_p$$

TABLE 2

EFFECT OF DECABROMOBIPHENYL ON THE LIMITING OXYGEN INDEX OF ABS COPOLYMER TREATED WITH ALUMINA

DBB[a] (*phr*)	*LOI*		
	Al_2O_3	$Al_2O_3 . H_2O$	$Al_2O_3 . 3H_2O$
0	19·2	18·9	18·8
5	21·5	19·7	19·7
10	22·9	20·9	20·6
15	24·4	21·5	21·4
20	25·8	22·2	22·2
25	26·6	23·1	23·1
30	27·9	23·8	24·2
35	29·5	24·7	25·7
40	30·9	25·3	27·5
45	33·0	25·9	29·0
50	36·4	26·4	30·1
0[b]	18·6	18·6	18·6

(After ref. 152.)

[a] 10 phr alumina added in all cases.

[b] No additives.

where LOI_{Br} is the LOI value of the polymer containing bromine, LOI_{Al} is that of the polymer containing Al_2O_3 or $Al_2O_3 . 3H_2O$ and LOI_p is that of the untreated polymer. It can be seen that with ABS a very pronounced synergism occurs between decabromobiphenyl and anhydrous alumina. This is slightly less marked with the trihydrate, where the effect occurs principally at high loadings of Br ($Br:Al > 3:1$), and is much less noticeable with the monohydrate. An increase in the concentration of metal oxide does not apparently affect the LOI, when the amount of halogen is kept constant (Table 3). With HDPE some synergism is also found between anhydrous alumina and decabromobiphenyl but the effect is much smaller since the individual flame retardants are also much less effective for this polymer. Chlorinated wax does not seem to have any clear-cut synergistic effect with these metal oxides in the case of HDPE. In fact the order of effectiveness of the aluminium oxides is the order of increasing water content, the anhydrous compound being perhaps even slightly antagonistic towards the chlorinated wax.

The results with Al and Br suggest that there may be three mechanisms by which flame retardance may be conferred on the polymer. Until the

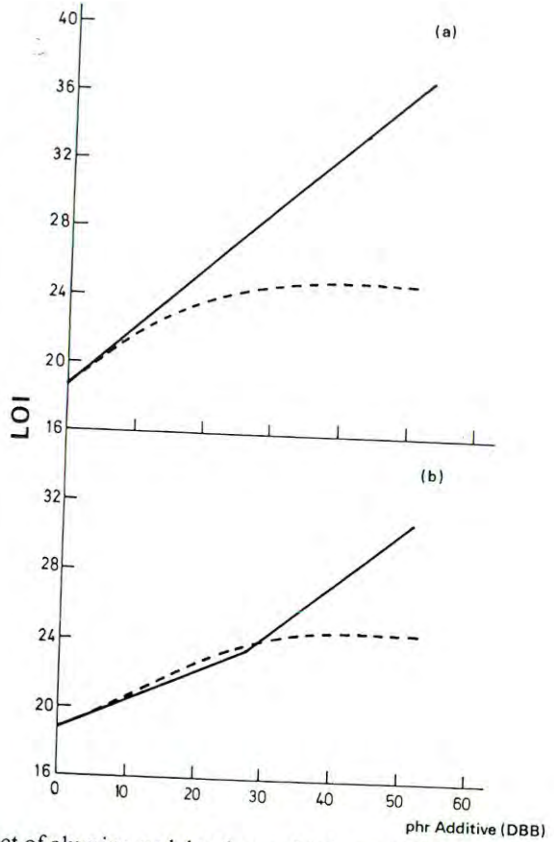


FIG. 13. Effect of alumina and decabromobiphenyl (DBB) on the flammability of acrylonitrile–butadiene–styrene copolymer: —— experimental; ---- calculated assuming additive behaviour; (a) Al_2O_3; (b) $Al_2O_3 . 3H_2O$.

TABLE 3

EFFECT OF ALUMINA ON THE LIMITING OXYGEN INDEX OF ABS COPOLYMER TREATED WITH DECABROMOBIPHENYL

Alumina[a] (*phr*)	*LOI*		
	Al_2O_3	$Al_2O_3 . H_2O$	$Al_2O_3 . 3H_2O$
0	20·5	20·5	20·5
10	22·9	20·9	20·6
15	22·9	20·9	20·6
20	22·9	20·9	20·6

(After ref. 152.)

[a] 10 phr decabromobiphenyl added in all cases.

bromine content is such that Br:Al > 3:1 with the anhydrous oxide, there is a condensed-phase reaction between Al and Br which probably inhibits the decomposition of the polymer. As the concentration of bromine increases, there is additionally an elimination of hydrogen bromide which acts in the gas phase and thus increases the slope of the variation of the LOI. With the trihydrate, the water of hydration probably partly inhibits the condensed-phase mechanism between Al and Br but exerts a positive overall flame-retardant effect on account of its own direct diluent action. The monohydrated oxide also liberates water of hydration which can inhibit the reaction between Br and Al but its overall effect is smaller than that of the trihydrate due to its lower water content.

Even though alumina seems to have a chemical mechanism of action, its efficiency in the absence of bromine is relatively low so that fairly high concentrations must normally be used as compared with those of other flame retardants. This limits its use to polymers where considerable proportions of other materials can be incorporated without causing an unacceptable alteration in the physical or mechanical properties. Its abrasiveness may also be a disadvantage during the processing of the polymer. In conjunction with bromine, addition of 10 phr of anhydrous alumina can, however, cause a significant improvement as compared with the effect observed in the absence of the metal oxide.[152]

Finally, aluminium oxides have also been found to be possible partial replacements for antimony oxide in the system Sb_2O_3–Br–ABS.[153] At equal loadings the cost is significantly reduced and the LOI is, under certain conditions, even slightly improved. The monohydrate appears to be the most effective of the three oxides.

10. OTHER ELEMENTS

Various other elements may also prove beneficial in inhibiting polymer combustion, apart from the six already mentioned. They are however either less widely used or employed only for specific polymers, or relatively little understood as regards their mechanism of action.

Nitrogen is an element whose presence in a polymer appears to confer some degree of flame retardance, as shown by the rather low flammability of polyamides, both natural and synthetic. This may however be partly due to the ease of melting of these polymers so that the heat of combustion tends to be carried away from the flame. Many nitrogen-containing compounds are also used as reactive flame retardants, e.g. triazines, urea derivatives or cyanuric acid derivatives, and it has been suggested that their action may be simply the eventual release of nitrogen which dilutes the gaseous products.[11] The action of ammonium salts and of nitrogen–phosphorus systems has already been mentioned.

Ammonium sulphates and ammonium sulphamates are also ammonia-releasing flame retardants by reactions 19 and 20. Their mechanism of

$$2NH_4SO_3NH_2 \xrightarrow{475-565\,K} (NH_4SO_3)_2NH + NH_3 \qquad (19)$$

$$(NH_4SO_3)_2NH \xrightarrow{575-775\,K} 3NH_3 + 2SO_3 \qquad (20)$$

action is probably very similar to that of phosphates or borates, when used in conjunction with hydroxylated polymers like cellulose, since sulphate esters are formed in the condensed phase. Some other organic complexes have also been used for the sulphonation of cellulose, although this involves partial destruction of the polymer structure.[154] The effect of other inorganic sulphur-containing salts, including alum, with historical connotations, is probably not due to the sulphur but rather to the evolved gases. Many other inorganic salts have also been used such as, for example, carbonates or chromates. Those which do not yield gaseous products (NH_3, H_2O, CO_2) are probably only inert fillers which dilute the solid combustible polymer and act as heat sinks. Some of them may act as catalysts for oxidative decomposition of the polymer, e.g. causing increased charring of cellulose.

Molybdenum compounds, such as molybdenum oxide or ammonium molybdate, are said to exhibit flame-retardant synergism with halogens,[155,156] as well as being very effective smoke suppressants. In the case of MoO_3, the metal has been found virtually quantitatively in the char, rather than in the gas phase.[157] The effect of molybdenum oxide on the combustion and pyrolysis of PVC is particularly interesting. Molybdenum oxide decreases the temperature for the start of the dehydrochlorination of the substrate by an ionic mechanism.[158] After dehydrochlorination, the additive acts as a Lewis acid to promote the isomerisation of the *cis* double bonds (formed from isotactic PVC) to *trans* double bonds.[159-161] In this way, the formation of aromatic products, which occurs by an intramolecular mechanism,[39] is inhibited. No flammable volatile products are thus formed if the heat supplied to the polymer is low, so that the molybdenum compound acts as a flame retardant. This effect does not, however, occur at the higher temperatures involved in real fires, because other volatile flammable products are then formed, mainly aliphatic straight-chain hydrocarbons; the action of the molybdenum is then reduced to that of a smoke suppressant.[161] Molybdenum compounds are useful as partial replacements for antimony oxide in the presence of bromine, both for polyesters[162] and for ABS,[153] although there is probably no synergism between Sb and Mo. In the case of cotton fabrics, it has been found that for sodium molybdate the limiting oxygen index and the limiting nitrous oxide index show the same slope when plotted against molybdenum content, while for ammonium molybdate the slopes are different (Fig. 14).[72] Over 90% of the molybdenum added to PVC is recovered from the char remaining after the polymer has burnt.[156] These findings suggest that the flame-retardant action takes place in the condensed phase but that there is some additional gas-phase effect of ammonia, particularly in nitrous oxide atmospheres. This is, of course, consistent with the other, earlier, results presented for PVC.

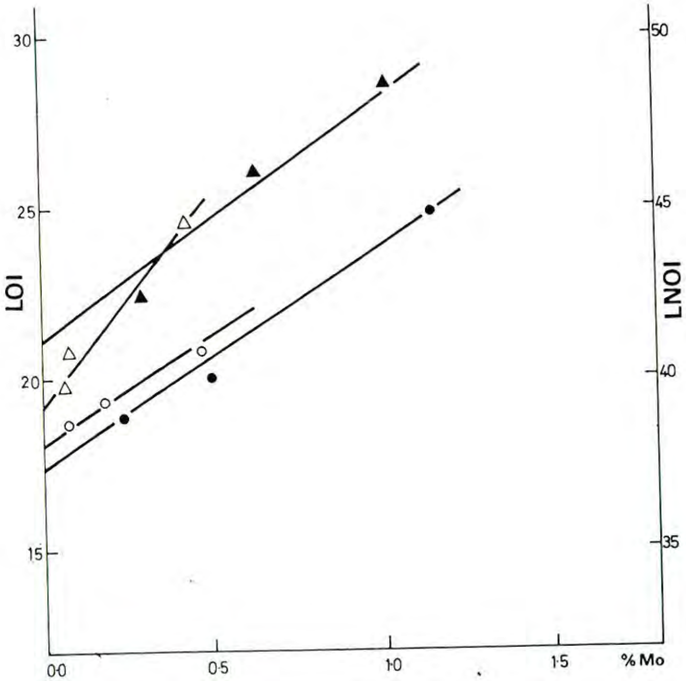


FIG. 14. Effect of molybdenum on the flammability of cotton fabrics: ○ ammonium molybdate (oxidant, O_2); ● sodium molybdate (oxidant, O_2); △ ammonium molybdate (oxidant, N_2O); ▲ sodium molybdate (oxidant, N_2O). (Reproduced from ref. 72, by courtesy of Marcel Dekker, Inc.)

Hydrated tin(IV) oxide has been proposed as a good substitute for antimony oxide.[163] It is possible that its effect is caused simply by the release of the water of hydration. The tin chloride is only partially volatilised[34] and, when used as a partial substitute for Sb_2O_3, is much less effective in increasing the LOI of ABS or of HDPE. Tin has also been used as a flame retardant for wool, particularly in the form of hexafluorostannates.[124,163,164] In this connection it is of interest to examine the effects of titanium and zirconium, which are also widely used for inhibiting the combustion of wool as the corresponding hexafluorometallate salts.[91,165-167] Titanium, zirconium, tin and chromium compounds exert their effects mainly in the condensed phase, as the results are largely independent of the oxidising atmosphere.[124,168] It is probable however that it is not the metal oxide itself but a complex of the metal oxide which has adsorbed oxygen which provides the catalytic species. This would explain why nitrous oxide has a greater effect on the titanium system than on the zirconium system, both metals being very similar in all respects.[124]

Ferrocene is a good smoke suppressant for thermoplastic polymers such as poly(vinyl alcohol)[169] or ABS,[170] where the gas-phase mechanism involves the total volatilisation of the iron. If butadiene is replaced by chloroprene in ABS to yield the chlorinated elastomer, volatilisation of the metal is still virtually total but the smoke-suppressant efficiency decreases considerably.[170] In PVC, however, the mechanism is a condensed-phase Lewis-acid type catalysis of dehydrochlorination,[169] analogous to that for the system PVC–MoO_3.

This review is necessarily not comprehensive since it is almost impossible to cover all the compositions that have been claimed to be effective as flame retardants in the numerous natural and synthetic polymers. An attempt has been made to deal with only those systems where the results are relatively well documented and directly amenable to interpretation.

11. CONCLUSIONS

Many different mechanisms of action have been proposed for flame retardants but these can be reduced, in principle, to a few important types, at least for the active elements most widely used in this context.

All additives which decompose thermally to yield inert gases (water, ammonia, carbon dioxide, nitrogen) will affect the flame reactions as a result of the physical dilution of the gaseous fuel and of the consequent reduction in gas temperature. Thus, of course, less heat is fed back to the condensed polymer phase. Hydrated metal oxides or salts, ammonium salts, phosphates, borates, sulphates or carbonates can act in this way.

Some additives may also function by a chemical mechanism in the gas phase; highly reactive free radicals responsible for flame propagation being replaced by less reactive species. The prime example of this behaviour consists of brominated additives, which yield gaseous hydrogen bromide. Chlorine-containing additives, although much less effective, may also act by this mechanism. Antimony trioxide, which feeds antimony monoxide into the flame zone, similarly acts by heterogeneous 'scavenging' of radicals, although it generally requires the presence of halogens to facilitate its volatilisation.

Phosphorus compounds, when added to polymers not susceptible to acid catalysis, are flame inhibitors acting partly by chemical mechanisms and possibly partly by 'blanketing' the flame to exclude oxygen. In the presence of halogens, however, the mechanism, although it may also include a 'blanketing' effect, involves mainly condensed-phase reactions.

When the substrates are hydroxylated polymers (e.g. cellulose), the mechanism of action of phosphorus-, boron- or sulphur-containing additives is an acid-catalysed esterification, which alters the condensed-phase mechanism of decomposition by enhancing char formation at the expense of volatile products. The presence of nitrogen bases, which can form $\mathrm{P{-}N}$ bonds, improves the efficiency of phosphorus esters.

Chlorine and, to a much smaller extent, bromine alter the rate of thermal decomposition of the polymer, as does the antimony oxide–halogen system, before the gas-phase inhibitors (respectively HCl, HBr and $\mathrm{SbO{-}HX}$) are liberated. Alumina also affects the condensed-phase decomposition reactions, particularly in the presence of bromine, an effect inhibited by water. Condensed-phase effects are also found with red phosphorus, molybdates and some other metals (e.g. titanium or zirconium).

Boron can also act by two additional mechanisms: a free-radical inhibition at the gas-solid interface and the formation at the surface of the polymer of inorganic $\mathrm{B{-}O}$ deposits which insulate the substrate from the heat source.

All the mechanisms described in the section are necessarily over-simplifications, although in practice these are the modes of action used to describe the flame-retardant compounds concerned. The outline presented in Section 2 has shown polymer combustion to be a complex process involving various concurrent and consecutive stages. It is therefore to be expected that an unusual selection of properties would be required for any combination of compounds to constitute a good flame retardant. It is thus very difficult, in the present state of our knowledge, to predict successfully what future developments are likely to be involved in the formulation of new efficient flame retardant systems.

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Benefits of Flame Retardants – Marcelo M. Hirschler - January 2016

Some of the benefits of flame retardants can be seen from the following facts.

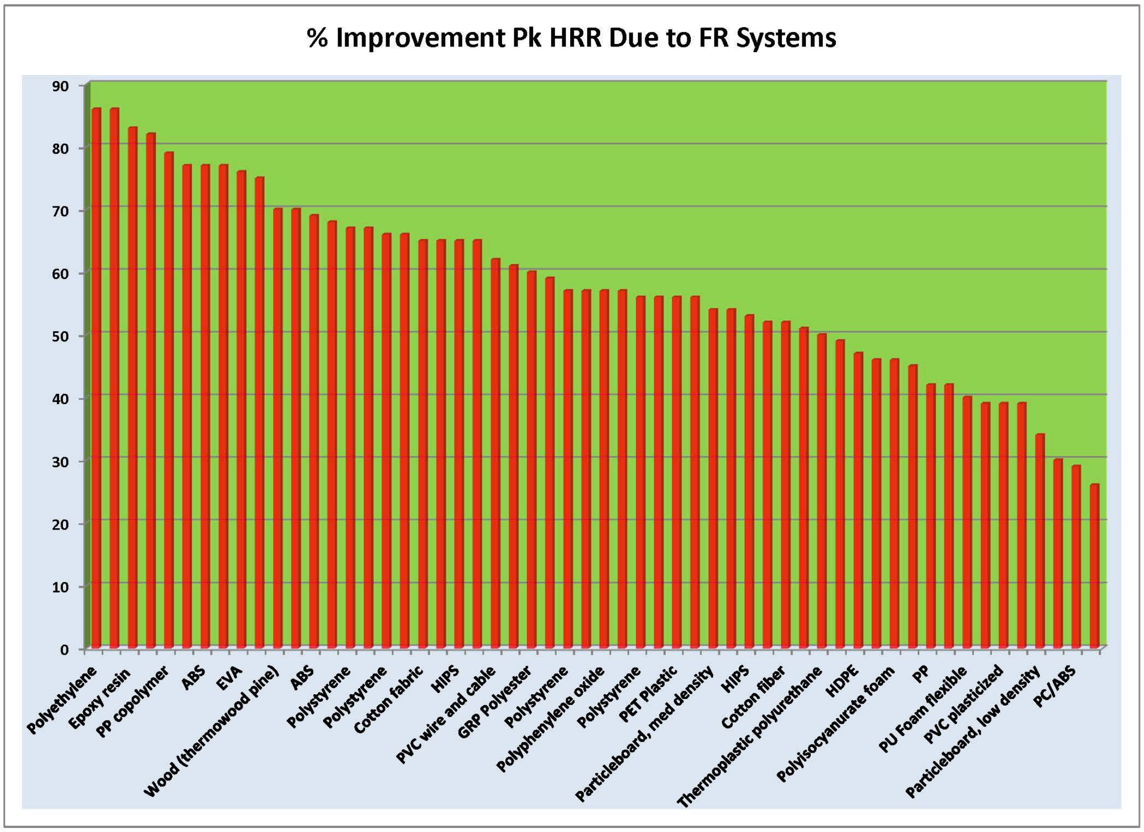
1. The use of flame retardants in combustible materials leads to a decrease in the heat released in fires.
2. The use of the correct type and amount of flame retardants improves the fire performance of the associated materials.
3. Fires with properly flame retarded products result in much fewer toxic products than fires with the same products without flame retardants.
4. Fires with properly flame retarded products result in much less destruction than fires with the same products without flame retardants.
5. Fires with properly flame retarded products result in much less flame spread to nearby products than fires with the same products without flame retardants.
6. Fires with consumer products have decreased significantly over the last 30 years or so, partially because of the increased use of flame retardants.

1. Flame retardants and heat release.

Flame retardants can be used to significantly decrease heat release rate of polymers, and the effectiveness of such systems can be extremely high. A set of studies [1-3] of the effects of flame retardants on the heat release of natural and synthetic combustible materials showed the effectiveness of flame retardants on heat release. The figure below [1] shows a large number of systems (a total of 56 systems) and the percentage improvement in peak heat release rate due to the addition of various flame retardant systems. The improvement can be higher than 80%.

Another study investigated the fire performance of 5 non-flame-retarded products and compared it with that of properly flame retarded alternate products [4]. The full sets of non-flame-retarded and flame retarded products were ignited in a room-corridor arrangement and the heat released by the non-flame-retarded products was 4-5 times higher than that released by the flame retarded products (1,640 kW vs. 345 kW).

The emphasis on heat release is presented because it has been demonstrated that the peak heat release rate is the key property governing the intensity of a fire [5]. Heat release rate is critical because as the heat release rate becomes greater 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.



2. Flame retardants and improved fire performance.

As discussed above, the most important means to describe fire performance is based on heat release. However, it is also clear that fire growth and flame spread are predicted by heat release rate. Two extensive research programs dealing with fire growth on combustible wall lining materials tested several wall lining materials in bench-scale and large-scale fire tests and both showed that fire growth (for example measured as flame spread) was much lower for materials that generated lower heat release [6, 7]. This led to the development of models predicting whether full room involvement (also known as flashover) results as a function of the heat released by the materials. Therefore, since flame retardants decrease heat release they also improve fire performance. including fire fatalities, fire injuries and significant property loss) and (b) the actual "cause of death" for a fire fatality. The two are different.

It is essential to note, a flame retardant system must be tailored to the substrate (or polymer) that it is used with. It is an essential requirement for an adequate flame retarded polymeric system to exhibit adequate fire performance that the flame retardant additive system appropriately improves the heat release rate of the substrate. This often requires extensive research to ensure that the right system is used for each substrate. Typically, flame retardants that are effective with a specific substrate are ineffective with alternate substrates (even if they are similar in chemical composition).

3. Flame retardants and toxic product release.

In order to understand this it is important to review the concept of flashover, which is that 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 practice fire statistics classify any fire that goes beyond the room of origin as a "flashover fire" [8], 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, any discussion of "flashover fires" includes all fires that are either known to have gone to flashover or known to have gone beyond the room of origin, without distinction. In the US 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 [8]). 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 fire atmospheres are much more toxic after flashover [8].

On the other hand, the "cause of death" (in the US) 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. It is important to note that it is now consensus in the fire safety community that the smoke toxicity of virtually all common products, whether they contain flame retardants or not and irrespective of the combustible substrate involved, have very similar smoke toxic potencies [9, 10, 11].

In the study comparing flame retarded and non-flame retarded products discussed above [4] the results showed that none of the test specimens produced smoke of extreme toxicity. The smoke from both sets of products was similar in potency and comparable to the potency of the smoke produced by materials commonly found in buildings. However, in terms of the total quantities of toxic gases produced in the room fire tests, expressed in 'CO equivalents,' the quantities produced by the flame retarded products were one third of the amounts of toxic products produced by the non-flame-retarded products. With regard to the overall fire hazard the study indicated that the impact of flame retardant materials on the survivability of the building occupants was also assessed by comparing the time to untenability in the burn room, which is applicable to the occupants of the burn room. The results showed that the average available escape time was more than 15-fold greater for the flame retarded products than for the non-flame-retarded products.

4. Flame retardants and total amounts burnt.

Multiple studies have shown that when properly flame retarded products are involved in a fire, the fire is much less likely to spread to other products and much more likely to remain small. This means that the amount of products burnt will be much smaller. In the study discussed above [4] it was found that three of the five flame retarded products assessed would not ignite (and thus would not burn) when exposed to the same fire source that caused any one of the non-flame-retarded products to burn and be destroyed completely. Thus, the only way that the five flame retarded products could be made to burn is by using an auxiliary burner to avoid finding no flame propagation at all. The study found that the amount of material consumed in the fire tests for the flame retarded products (in spite of the additional burner) was less than half the amount lost in the tests for the non-flame-retarded products.

Interestingly, when products produce significantly lower heat release (and thus much less material destroyed or burnt) there is also usually lower smoke released, leading to better visibility for victims trying to escape or first responders trying to initiate rescue from a fire. In the study above, the amount of smoke generated from both tests was not significantly different but in 90% of studies of room-corner fire tests (where flame propagation, heat release and smoke release are assessed) the products with lower heat release also had lower smoke release [12].

5. Lower flame spread for properly flame retarded products.

This has been explained earlier. The lower heat release resulting from properly flame retarding products has as a consequence, lower flame spread [6, 7]. For example, building interior finishes, principally wall and ceiling coverings, can have a major impact on both fire growth and ultimate fire size [13]. Wall and ceiling coverings may act like a "fuse," spreading flames away from fire origin to involve other objects, causing the fire to grow to large size. Interior finishes may also provide a large, unbroken surface over which flame spreads. As the wall or ceiling covering exhibits higher heat release rate, the flame spreads faster to involve greater surface area and the fire size increases. If the interior finish exhibits poor fire performance, the flames from the interior finish may release sufficient energy to cause the formation of a hot gas layer. If the wall or ceiling covering is well flame retarded the fire will stop spreading and cease being a problem. NFPA fire loss statistics show that interior wall coverings are responsible for being the item first ignited in homes in many fires and for an even larger proportion of civilian fire fatalities. The most recent statistics on home structure fires were published in 2015 [14].

6. Fire statistics show that fewer fires are starting at consumer products now.

Fires associated with a variety of consumer products have decreased significantly over the last 30 years or so, as shown in the following list (based on NFPA statistical data in various reports). One of the reasons for this decrease (but, of course not the only one) is the use of flame retardants improving the fire performance of consumer products.

Fires starting in various consumer products

	1980	2010-2011	Decrease (%)	Reference
Heating Equipment	230,300	53,600	77	15
Electrical	75,000	47,700	36	16
Washers & dryers	25,000	16,800	33	17
Refrigerators, freezers, ice makers	3,040	1,680	45	18
Electronic equipment rooms	1,600	190	88	19
Office equipment (non-home)	1,720	600	65	20
Office equipment (home) *	540	640	-19	20

* Note that the use of office equipment (computers) in homes has increased from less than 2% in 1980 to more than 75% in 2010, meaning that the proportion of fires to computers in homes has decreased

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Flame Retardants and Heat Release

by

Marcelo M. Hirschler

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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.

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KEY WORDS: heat release; flame retardants; fire hazard; polymers

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

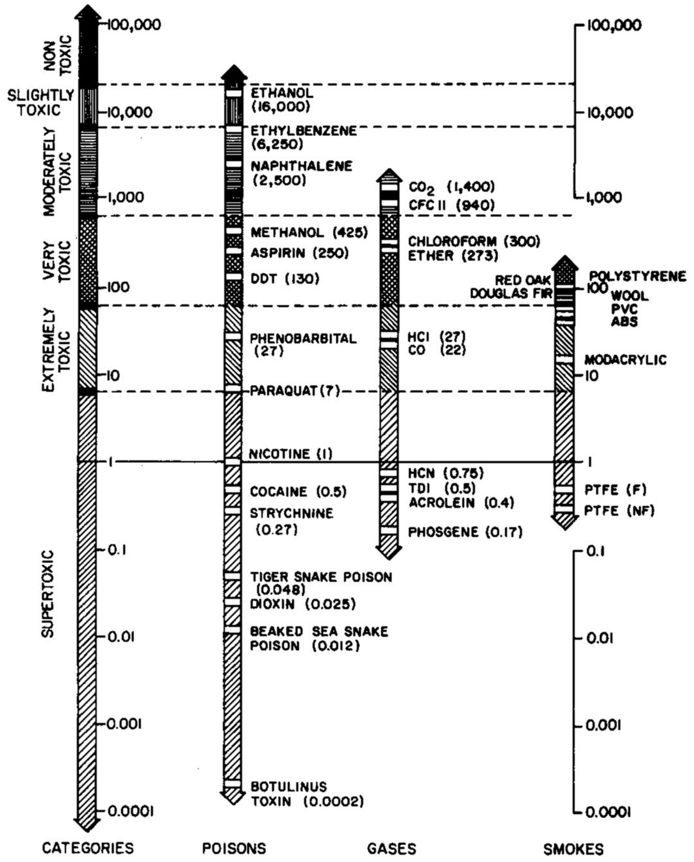

Figure 1. Levels of smoke toxicity (in orders of magnitude) [10].

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

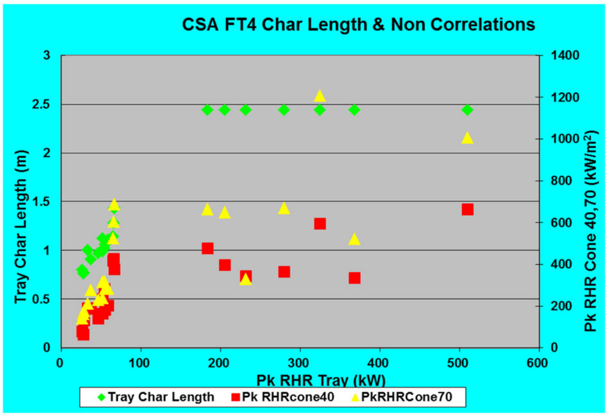

Figure 2. Char length for cables in the vertical cable tray test (UL 1685/CSA FT4) and peak heat release rate in the cone calorimeter as a function of cable tray peak heat release rate [13].

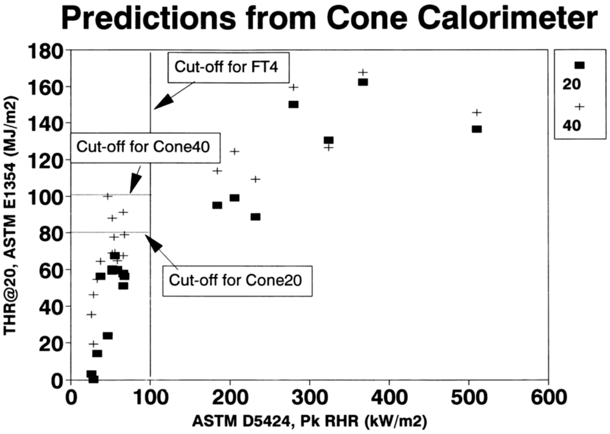

Figure 3. Comparison of flame spread in tray tests with char length and heat release rate [17].

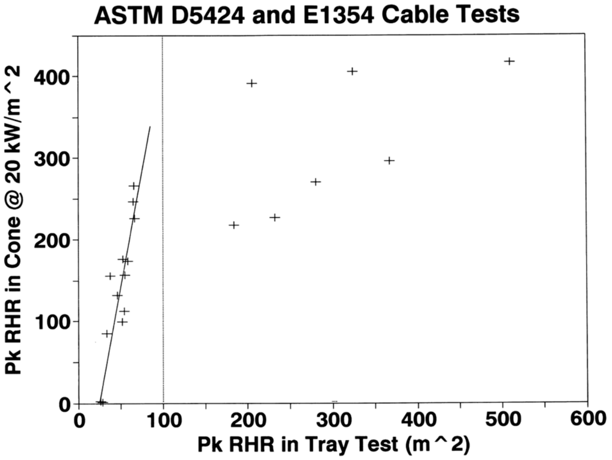

Figure 4. Comparison of peak heat release rate in cone and vertical cable tray test [17].

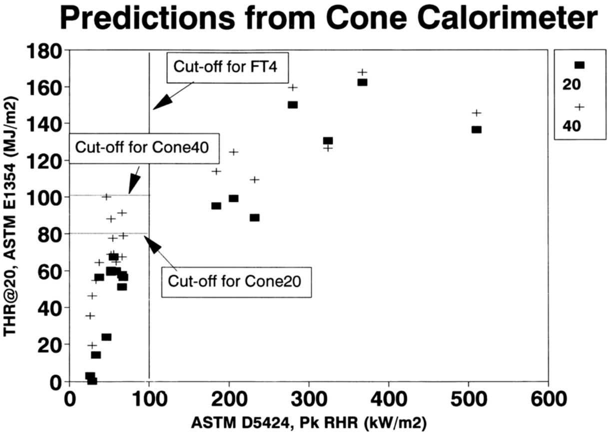

Figure 5. Indication of vertical cable tray test results predicted from cone test results [17].

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.

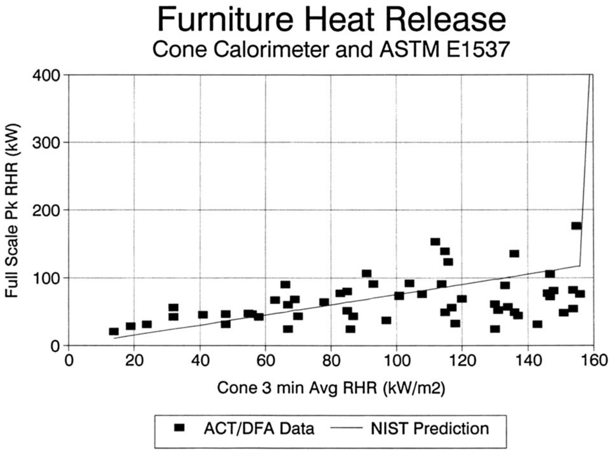

Figure 6. Prediction of CA TB 133 test results from cone calorimeter [17].

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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 ≤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]).

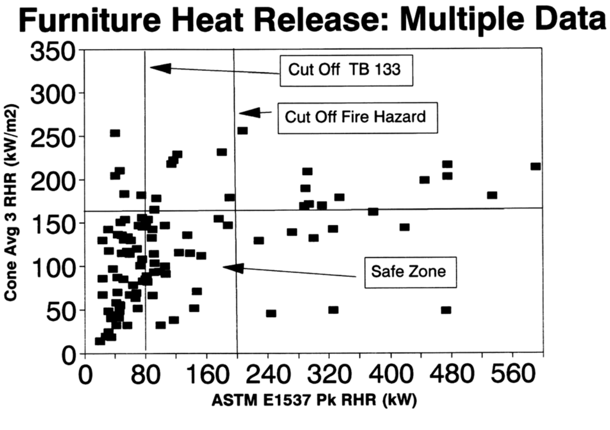

Figure 7. Predictions of full-scale furniture test data showing safe zone [17].

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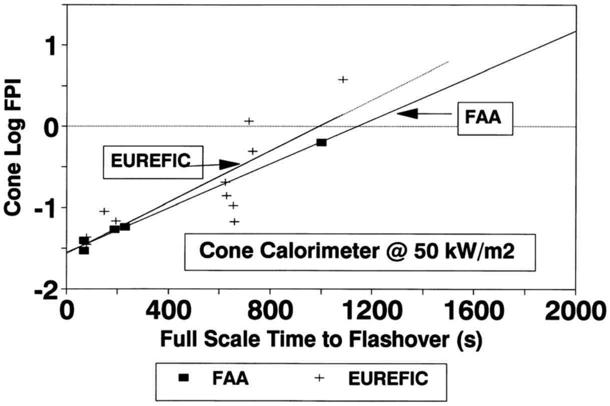

Figure 8. Comparison of wall linings (EUREFIC) and aircraft panels (FAA) full-scale test results with fire performance index predictions from cone calorimeter [28].

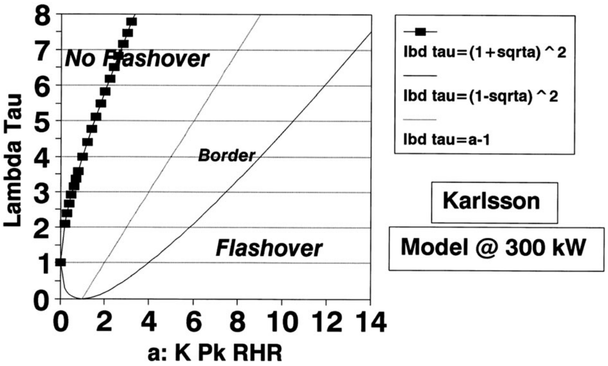

Figure 9. Safe zone predictions in wall linings based on Karlsson model and cone calorimeter data [28].

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.

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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.

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(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.

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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

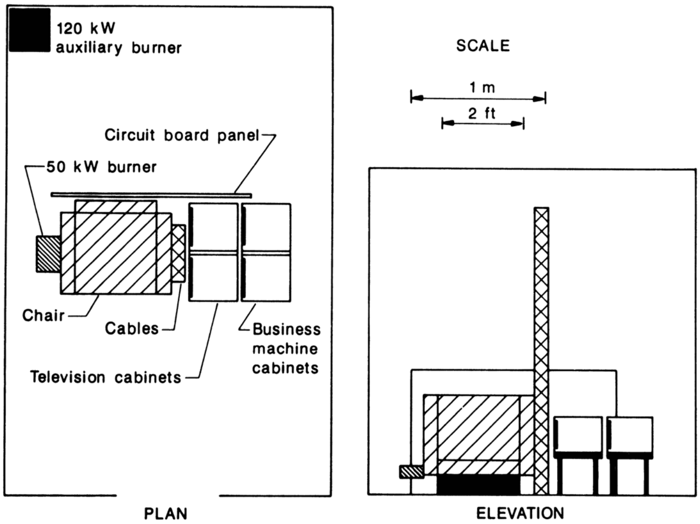

Figure 10. NBS/NIST layout of full-scale product burns for non-FR products [48].

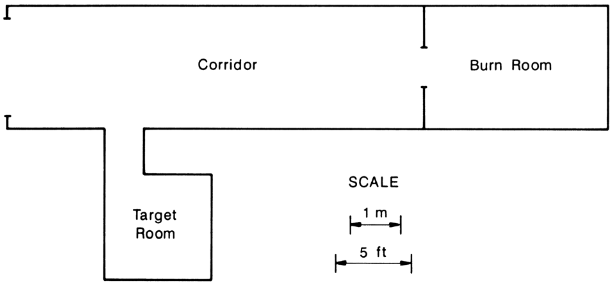

Figure 11. NBS/NIST room–corridor layout of full-scale product burns for non-FR products [48].

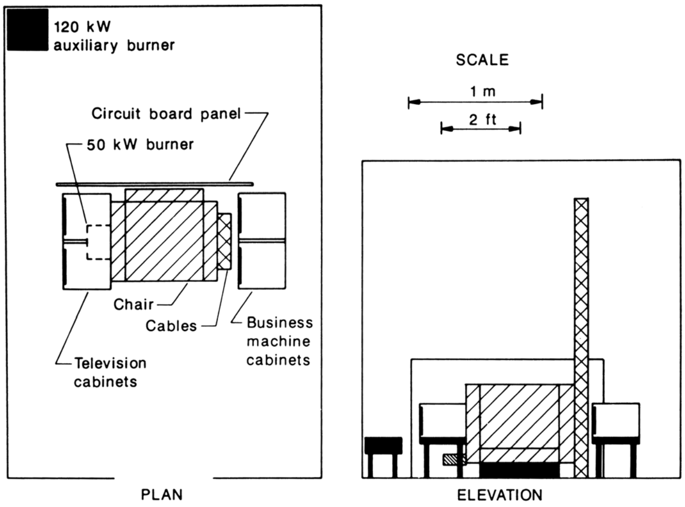

Figure 12. NBS/NIST layout of full-scale product burns for FR products [48].

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

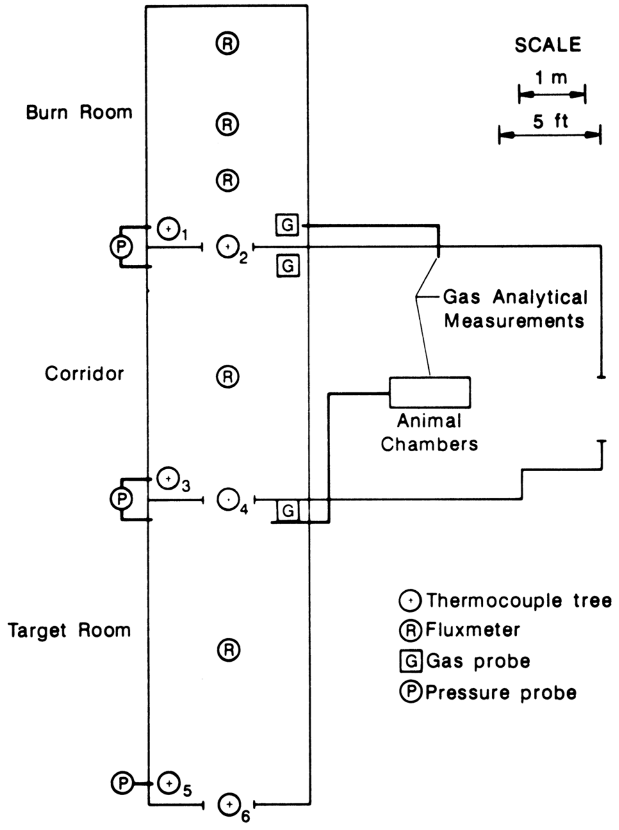

Figure 13. NBS/NIST room–corridor layout of full-scale product burns for FR products [48].

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

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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

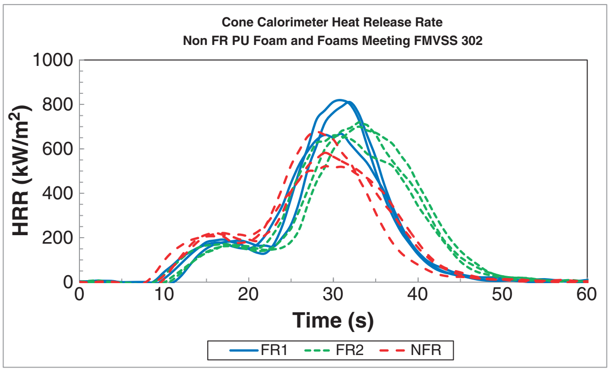

Figure 14. Alexander Morgan cone calorimeter: polyurethane foam treated for FMVSS 302 [54].

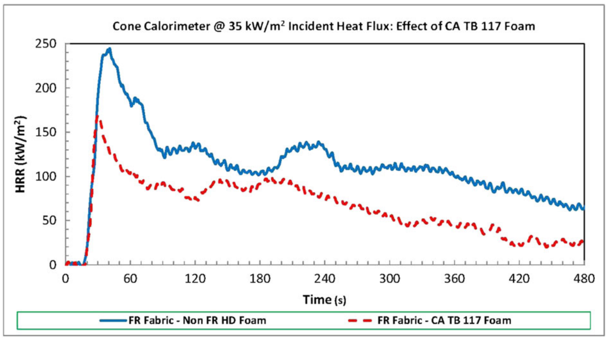

Figure 15. NIJ cone calorimeter comparison of polyurethane foam treated for CA TB 117 and non-FR with an FR cotton fabric treated for NFPA 701 [56,58].

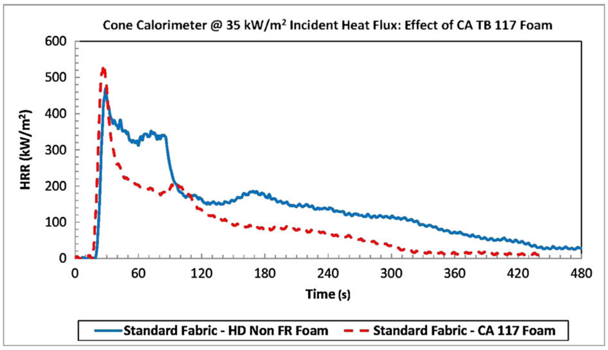

Figure 16. NIJ cone calorimeter comparison of polyurethane foam treated for CA TB 117 and non-FR with a non-FR cotton fabric [56,58].

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

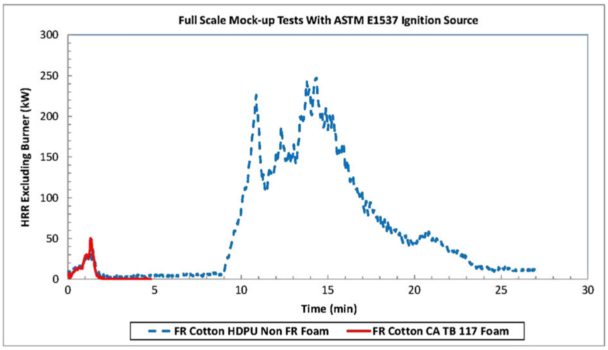

Figure 17. NIJ full-scale (ASTM E1537, one seat sofa) comparison of polyurethane foam treated for CA TB 117 and non-FR with an FR cotton fabric treated for NFPA 701 [56,58].

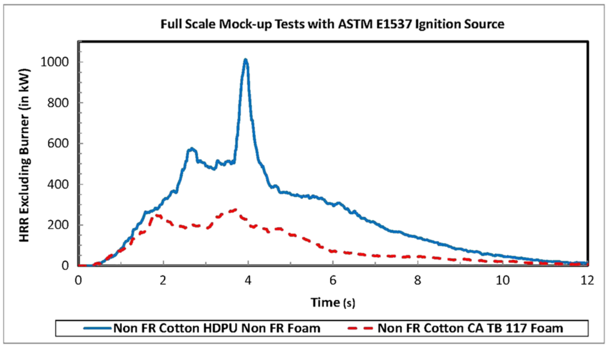

Figure 18. NIJ full-scale (ASTM E1537, two seat sofa) comparison of polyurethane foam treated for CA TB 117 and non-FR with non-FR cotton fabric [56,58].

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.

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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.

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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

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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

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

EVA	TTI s	Pk HRR kW/m^2	FPI (m^{2}skW^{-1})	Avg HRR kW/m^2	THR 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 s	Pk HRR kW/m^2	FPI m^{2}skW^{-1}	Avg HRR kW/m^2	THR 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].

	TTI	Pk HRR	FPI	Avg HRR
EVA cable jacket compound	s	kW/m^2	m^{2}skW^{-1}	kW/m^2
30 kW/m^2				
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/m^2				
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/m^2				
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/m^2

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

	TTI	Pk HRR	FPI	Avg HRR	THR
HDPE at 35 kW/m^2	s	kW/m^2	m^{2}skW^{-1}	kW/m^2	MJ/m^2
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/m^2	m^{2}skW^{-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/m^2 at an incident heat flux of 40 kW/m^2. 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^2skW^{-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

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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 s	Pk HRR kW/m^2	FPI m^{2}skW^{-1}	THR 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/m^2	TTI	Pk HRR	FPI	THR
	s	kW/m^2	(m^{2}skW^{-1})	MJ/m^2
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].

	TTI	Pk HRR	Av HRR 3 min	Eff. Ht Comb	FPI
Cone at 40 kW/m^2	s	kW/m^2	kW/m^2	MJ/kg	m^{2}skW^{-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	$(\text{m}^2\text{skW}^{-1})$	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	$(\text{m}^2\text{skW}^{-1})$	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].

	TTI	Pk HRR	FPI
Foamed EPS at 35 kW/m^2	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 s	Pk HRR kW/m^2	FPI	THR MJ/m^2	Ht Comb 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	TTI	Pk HRR	FPI
With P plasticizers	s	kW/m^2	(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.

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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

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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).

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

	TTI	Pk HRR	FPI	Eff. Ht Combust
Cone testing of cotton	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].

	TTI	Pk HRR	FPI	Euroclass
Cone at 50 kW/m^2	s	kW/m^2	m^{2}s kW^{-1}	
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.

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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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