FLAME RETARDANTS

1. Introduction

Each year, Americans report nearly 2 million fires leading to 22,000 injuries and 4000 deaths (1). The direct property losses exceed $11 billion (1) and the total annual cost to our society has been estimated at nearly $200 billion (2). Personal losses occur mostly in residences where furniture, wall coverings, and clothing are frequently the fuel. Large financial losses occur in commercial structures such as office buildings and warehouses. Fatal and otherwise costly fires also occur in automobiles, airplanes, buses, and trains.

Fires occur when an ignition source, such as a match, cigarette, or stove burner, meets a flammable product such as a chair, wall, or scattered papers. The heat from the source breaks down polymer strands in the material, creating (generally endothermically) chemical fragments that vaporize. At a sufficiently high temperature, these fragments react with the oxygen in the air to release more heat. Some of this heat radiates or convects back to the product, breaking down more polymeric strands, yielding more gas-phase fuel, etc. Life- and property-threatening fires result when the rate of heat feedback to the product exceeds the sum of the heat dispersed from the combustion environment and the marginal enthalpy required to produce a steady stream of vapor-phase pyrolyzate.

Understanding of fires dates to the nineteenth century. The advent of modern fire fighting techniques and equipment has meant less destruction of cities or whole buildings. Additionally, fire-resistant building design usually contains fires to only parts of structures. The widespread installation of smoke detectors and the increasing use of automatic sprinklers have contributed significantly to the reduction in the number and severity of fires. However, a high fuel load in either a residence or a commercial building can overwhelm even the best of building construction.

2. Terminology

A number of adjectives have been used to describe a product having an apparently low contribution to a fire. Nonquantitative terms such as fireproof, flameproof, self-extinguishing, nonburning, and noncombustible have been used and have often led to confusion regarding the relative fire safety of different materials. Additionally, a product is sometimes improperly described by a component material rating under a fire test (eg, a “V-0 material” referring to one with a V-0 rating in the UL 94 test) or a building code provision (eg, a “25 flame spread product” referring to the result of a test for wall coverings using the ASTM E84 method.)

These ambiguities eventually led the Federal Trade Commission to take action in the case of cellular plastics and to restrict the use of such terminology (3). This action, in addition to the prohibition placed on the use of certain terminology, requires the use of a caveat whenever the results of burning tests are cited. Much of the older literature, however, as well as some of the more recent publications, still use this restricted terminology.

Some pertinent definitions include *fire retardant (flame retardant)*, used to describe polymers in which flammability has been reduced by some modification as measured by one of the accepted test methods; *fire-retardant chemical*, used to denote a compound or mixture of compounds that when added to or incorporated chemically into a polymer serves to slow or hinder the ignition or growth of fire, the foregoing effect occurring primarily in the vapor phase; *materials*, single substances of which things are constructed; and *products*, consumer items made of one or more materials that may be composed of single or blended polymers, may be layered or fiber-reinforced, and generally contain a variety of additives.

3. Measuring the Fire Performance of Products

Laws have been promulgated to improve the fire performance of individual combustibles. Traditionally, these require meeting a particular level of performance on a prescribed fire test. Passing the test enables the product to be sold. There is rarely a commercial benefit of outperforming the pass–fail criterion.

The past decade has seen major advances in formalizing engineered fire safety, alternatively called performance- or objective-based design. In this approach, a fire safety objective is set, eg, all people leave the building safely or the damage is contained such that the building is returned to service within a week. The flammability properties of all combustibles are combined with the capability of fire detection and containment systems, the properties of the escape routes from the facility, the capabilities of the occupants, etc, in a manner that ensures that the fire safety objective will be met. Individual products do not pass or fail; rather their inclusion–exclusion is considered within the safety context of the overall facility design.

The assessment of the contribution of a product to the fire severity and the resulting hazard to people and property combines appropriate product flammability data, descriptions of the building and occupants, and computer software that includes the dynamics and chemistry of fires. This type of assessment offers benefits not available from stand-alone test methods: quantitative appraisal of the incremental impact on fire safety of changes in a product; appraisal of the use of a given material in a number of products; and appraisal of the differing impacts of a product in different buildings and occupancies. One method, HAZARD I (4), has been used to determine that several commonly used fire-retardant–polymer systems reduced the overall fire hazard compared to similar nonfire retarded formulations (5).

Most of the fire test methods in regulations have been developed by consensus standards organizations in response to a particular fire hazard. The two leading U.S. based entities are ASTM International and NFPA International. International Organization for Standardization (ISO) is the predominant non-U.S. based fire standards organization. In the United States, the methods are then referenced in the model building codes. Formerly, these were the Standard Building Code, the Basic Building Code, and the Uniform Building Code. Currently, the two major building codes are the ICC Building Code and NFPA 5000. The methods are also cited in fire codes, such as the National Electrical Code and the Life Safety Code. These code structures are in turn adopted, often with modification, by governmental jurisdictions. In addition, there are a number of voluntary practices. For example, Underwriters Laboratories (UL) allows the use of its endorsement on products that meet their test criteria, and the upholstered furniture industry has adopted voluntary cigarette ignition-resistance standards.

Fire test methods attempt to provide correct information on the fire contribution of a product by exposing the whole product or a small sample of it to conditions intended to replicate the fire scenario(s) of concern. The tests most often measure the resistance of the specimen to ignition, whether the specimen continues to burn beyond an initial ignition, the rate at which the specimen burns, and/or the composition and quantity of the combustion products.

Clearly, fewer ignitions would reduce the number of fires. The susceptibility of a product to an ignition source can be measured by flame or heat impingement tests, such as UL 94 (6) or NFPA 260/261 (7), or by ignition delay times in an apparatus such as the Cone Calorimeter (8). In UL 94, a vertical strip of a material is ignited at the bottom and after the burner is removed, one observes whether burning is sustained. This finding is an example of a material test that results in a simple flammability class assignment. The NFPA cigarette ignition tests are examples of similar tests for a product. There, a cigarette is laid on a reduced-scale mockup of a seat cushion to see whether ignition occurs. The Cone Calorimeter is an apparatus used to measure flammability properties of a product. A specimen representative of the product is exposed to radiant energy typical of a fire of concern. While the principal measurement is that of the rate of heat release, the time to ignition can also be determined and used as an indication of ignition susceptibility.

Once ignited, an ignition-resistant material may burn with a higher intensity than a more easily ignited counterpart (9). Moreover, successful ignition-resistance test performance is not proof of fire prevention. The real world situation may be more severe than the test design, larger ignition sources may occur, or thermal radiation from other burning objects could increase the ease of ignition. Thus many elements of fire protection practice presume that ignition can occur. It is then desirable that products burn sufficiently slowly that the fire does not grow rapidly to threatening size, does not ignite adjacent items, and can be readily and simply extinguished. Therefore the controlling characteristic variable is the rate of heat release of the product. Methods have been developed for accurate measurement of rate of heat release (8,10). There is also research relating these rates to the performance of products (11–13).

Fire science has progressed markedly since the older test methods were developed, and it is now known that the basis for many of these tests is doubtful. Thus, to obtain a true impression of the likely fire performance of a product, the results from older tests must be used with great care.

4. Methods for Improved Performance

The materials of attention in promoting fire safety are generally organic polymers, both natural [eg, woods (qv), papers and wools (qv)] and synthetic [eg, nylons (see POLYAMIDES), polyurethanes, and rubbers (qv)]. Less fire-prone products generally are inherently more stable polymeric structures or contain fire-retardant additives. The former are usually higher priced engineering plastics (qv) that achieve increased stability at elevated temperatures by incorporating stronger (often aromatic) chemical bonds in the backbone of the polymer (14). Examples are the polyimides, polybenzimidazoles, and polyetherketones. There are also some advanced polymers, such as the polyphosphazenes and the polysiloxanes, that have strong inorganic backbones. Thermally stable pendent groups are also necessary. Strongly bonded polymers may, however, be brittle or difficult to process.

Fire-retardant additives are most often used to improve fire performance of low-to-moderate cost commodity polymers. These additives may be physically blended with or chemically bonded to the host polymer. They generally effect either lower ignition susceptibility or, once ignited, lower flammability. Ignition resistance can be improved solely from the thermal behavior of the additive in the condensed phase. Retardants such as inorganic hydroxides [aluminium trihydroxide ($Al(OH)_3$, ATH)] and magnesium hydroxide [$Mg(OH)_2$] add to the heat capacity of the product, thus increasing the enthalpy needed to bring the polymer to a temperature at which fracture of the chemical bonds occurs. The endothermic elimination of water can be a significant component of the effectiveness of this family of retardants (15). Other additives, such as the organophosphates, change polymer decomposition chemistry. These materials can induce the formation of a cross-linked, more stable solid and can also lead to the formation of a surface char layer. This layer both insulates the product from further thermal degradation and impedes the flow of potentially flammable decomposition products from the interior of the product to the gas phase where combustion would occur (16).

Flame retardants function in the vapor phase where the enthalpy-generating combustion reactions occur. Halogen-containing species, eg, can be selected to vaporize at the same temperature as the polymer fragments. Coexisting in the reactive area of the flame, the halogens are effective at decreasing the concentrations of the free radicals that propagate flames, thus reducing the flame intensity, the enthalpy returned to the product, and the burning rate, in that order. For small ignition sources, the use of flame retardants can produce self-extinguishment. More intense sources may overwhelm the flame retardant, necessitating either a higher concentration or an alternative choice of additive.

Useful materials incorporating fire-retardant additives are not always straightforward to produce. Loadings of 20% are common, and far higher levels of flame retardants are used in some formulations. These concentrations can have a negative effect on the properties and functions for which the materials were originally intended. Product-specific trade-offs are generally necessary between functionality, processibility, fire resistance, and cost.

Nonetheless a large number of fire-retardant additives are possible. The development of the field of fire-retardant additives has its origins in three efforts: the nineteenth century systematic studies of Gay-Lussac, Perkin's discovery that stannates and tungstates helped make treatment with ammonium salts water-resistant, and the discovery in the 1930s of the effect of mixing antimony oxide with organic halogen compounds (17).

Research has since led to a diversity of additives and a thriving market. Fire retardants are now the second most used plastics additives, exceeding 25% of a $4.5 billion U.S. market in 2000. This market is expected to continue to increase as the use of plastics continues to grow (18). Table 1 gives the principal groups of chemicals and their relative use.

In addition to these groups, a new class of non-halogen based flame retardant has recently emerged from the nanotechnology field (20). These are

Table 1. **Consumption of Flame Retardants (2001 data) (19)**

	United States	Western Europe	Japan	Other Asia	Total (metric tons × 10^3)	Total ($M U.S.)
brominated compounds	60	42	47	90	239	774
organophosphorus compounds	58	83	26	20	187	465
chlorinated compounds	17	51	5	25	98	108
aluminum trihydroxide	285	168	40	10	503	219
antimony oxides	30	25	14	30	99	265
magnesium hydroxide	15	12	4	3	34	69
others	28	27	7	8	70	102
total (metric tons × 10^3)	493	408	143	186	1230	
Total ($M U.S.)	627	556	373	446		2002

organo-modified layered silicates (or clays) that are surfactant functionalized, 1-nm thick mica-type plates with 100–200-nm lateral dimensions. When these organoclays are mixed (exfoliated) with polymers, the heat release rate is significantly reduced. However, this new class of flame retardants does not improve ignition resistance and must be compounded with other conventional flame retardants to pass standard fire tests. A variety of publications and patents have been published on this concept (21).

As can be seen from Table 1, brominated retardants are a significant fraction of the market. However, there is an ongoing debate over the possible risks of halogenated, especially brominated, fire retardants (17,22). One brominated flame retardant has been banned in Europe and others are the focus of heated debate over their removal from the market. The issues under debate are

1. The burning of halogenated combustibles produces toxic smoke, and epidemiological studies show that most fire victims die from smoke inhalation (23). The smoke from all fires is noxious. It has been shown that if the fire retardant significantly decreases the burning rate of the product, the reductions in smoke and heat yields are more important to survivability than a modest increase in the toxic potency of the smoke (5).
2. The burning of halogenated combustibles produces corrosive smoke, which results in additional damage to electronic components, etc. The smoke from nonhalogenated polymers is also corrosive and the fire safety community is in the process of developing methods to characterize this property of smoke.
3. The incineration of halogenated combustibles may produce significant amounts of dioxin- and furan-like species. Laboratory combustion experiments need to be compared with measurements of the effluent from properly designed and operated incinerators.

Another factor potentially affecting the market for halogenated fire retardants is the waste disposal of plastics (see WASTES, INDUSTRIAL). As landfill availability declines or becomes less popular, two alternatives are incineration and recycling (qv). The nature of the combustion products from halogenated products requires careful construction and maintenance of incinerators (qv) to avoid damage to the incinerator itself and a public health problem from the exhaust. The ease of recycling used products also has a potential effect on fire retardants. A recent report concluded that incineration of organobromine flame retardants does not lead to emission of significant concentrations of dioxins or furans if the incineration is carried out under the proper, optimal, combustion conditions (24). In general all classes of flame retardants, organohalogen, organophosphorus, nitrogen based, inorganic and mineral compounds are coming under increase scrutiny, both in Europe and in the United States. The concern is their impact on both human health and the environment (22). This ongoing analysis of flame-retardant chamicals is paralleled by life cycle analyses, which compare the risks and hazards of using organohalogen flame retardants to using no flame retardant throughout the life of the products (25).

Flame-retardant additives are capable of significant reduction in the hazard from unwanted fires, with techniques now available to quantify these improvements. Combined with an understanding of fire-retardant mechanisms, polymer-retardant interactions, and reuse technology, formulations optimized for public benefit and manufacturing practicality can be selected.

BIBLIOGRAPHY

"An Overview" under "Flame Retardants" in *ECT* 4th ed., Vol. 10, pp. 930–936, by R. G. Gann, National Institute of Standards and Technology; "Flame Retardants, Overview" in *ECT* (online), posting date: December 4, 2000, by Richard G. Gann, National Institute of Standards and Technology.

CITED PUBLICATIONS

1. M. J. Karter, Jr., *NFPA J.* **95**(5), 81 (2001).
2. J. R. Hall, Jr., *The Total Cost of Fire in the United States*, NFPA International, Quincy, Mass., 2000.
3. *Fed. Reg.* **40**(12), 255 (1975).
4. R. D. Peacock, W. W. Jones, R. W. Bukowski, and C. L. Forney, *HAZARD I—Fire Hazard Assessment Method*, version 1.1, NIST Handbook 146, National Institute of Standards and Technology, Gaithersburg, Md., 1991.
5. V. Babrauskas and co-workers, *Fire Hazard Comparison of Fire-Retarded and Non-Fire-Retarded Products*, NBS Special Publication 749, National Bureau of Standards, Gaithersburg, Md., 1987.
6. *Tests for Flammability of Plastic Materials for Parts in Devices and Appliances*, UL-94, Underwriters Laboratories, Northbrook, Ill., 1991.
7. "Cigarette Ignition Resistance of Components of Upholstered Furniture," NFPA 260, and "Resistance of Mockup Upholstered Furniture Material Assemblies to Ignition by Smoldering Cigarettes," NFPA 261, NFPA International, Quincy, Mass., 1998.
8. *Standard Test Method for Heat and Visible Smoke Release Rates for Materials and Products Using an Oxygen Consumption Calorimeter*, ASTM E1354-99, ASTM International, West Conshohocken, Pa., 2001.
9. J. W. Rowen and J. W. Lyons, *J. Cell. Plast.* **14**(1), 25 (1978).
10. *Standard Test Method for Heat and Visible Smoke Release Rates for Materials and Products*, ASTM E906-99, ASTM International, West Conshohocken, Pa., 2001.
11. V. Babrauskas, *SFPE Technology Report 84-10*, Society of Fire Protection Engineers, Boston, Mass., 1984.
12. R. G. Hill, T. I. Eklund, and C. P. Sarkos, *DOT/FAA/CT-85/23*, Federal Aviation Administration Technical Center, Atlantic City, N.J., 1985.
13. B. Sundström, ed., *Fire Safety of Upholstered Furniture—the Final Report on the CBUF Research Programme*, Interscience Communications Ltd., London, 1995.
14. R. G. Gann, R. A. Dipert, and M. J. Drews, in J. I. Kroschwitz, ed., *Encyclopedia of Polymer Science and Engineering*, 2nd ed., John Wiley & Sons, Inc., New York, 1986, pp. 154–210.
15. W. E. Horn, Jr., *Inorganic Hydroxides and Hydroxycarbonates: Their Function and Use as Flame-Retardant Additives*, in A. F. Grand and C. A. Wilkie, eds., *Fire Retardancy of Polymeric Materials*, Marcel Dekker, Inc., New York, 2000, pp. 285–352.
16. J. Green, *Phosphorus-Containing Flame Retardants*, in A. F. Grand and C. A. Wilkie, eds., *Fire Retardancy of Polymeric Materials*, Marcel Dekker, Inc., New York, 2000, pp. 147–170.

17. S. J. Ainsworth, *Chem. Eng. News* **70**, 34 (Aug. 31, 1992).
18. *Additives for Plastics*, Business Communications Company (BCC) Inc., Report P-169, May 2001, http://www.buscom.com/plastics/P169.html
19. Fire Retardant Chemicals Association, Lancaster, Pa., 2002.
20. J. W. Gilman, C. L. Jackson, A. B. Morgan, R. Harris, Jr., E. Manias, E. P. Giannelis, M. Wuthenow, D. Hilton, and S. Phillips, *Chem Mater.* **12**, 1866 (2000).
21. J. W. Gilman and T. Kashiwagi, *Polymer-Layered Silicate Nanocomposites with Conventional Flame Retardants*, in T. J. Pinnavaia and G. Beall, eds., *Polymer-Clay Nanocomposites*, Wiley and Sons, Ltd., West Sussex, U.K., 2000, pp. 193–206.
22. A. Beard, B. Dero, and D. Drohmann, *The Issues and Threats for Flame Retardants in Europe and The Industry Response*, International Fire Safety Conference, FRCA, San Francisco, CA, March 2001, http://www.cefic-efra.org/code/FRCA_Paper.html
23. R. G. Gann, V. Babrauskas, R. D. Peacock, and J. R. Hall, Jr., *Fire Mater.* **18**, 193 (1994).
24. *Report in Incineration of Products Containing Brominated Flame Retardants*, Waste Management Policy Group, Organization for Economic Co-operation and Development (OECD), http://www.olis.oecd.org/olis/1997doc.nsf/LinkTo/env-epoc-wmp(97)4-REV3
25. M. Simonson, P. Blomqvist, A. Boldizar, K. Moller, L. Rosell, C. Tullin, H. Stripple, and J. O. Sundqvist, Fire-LCA Model: TV Case Study, SP Report 2000:13. http://www.sp.se/fire/Eng/Research/Fire_LCA_TV.htm

RICHARD G. GANN
JEFFREY W. GILMAN
Fire Research Division,
National Institute of Standards and Technology