Newsletter n°25 – Septembre 2022

FR & Fire risk

FR & Toxicity

he debate related to the toxicological and environmental risks of flame retardants (FRs) has been dynamically in charge of research and industrial attention in recent years. Some halogenated FRs (HFRs) have already been banned by specific regulations such as the RoHS directive and/or the REACH regulation. However, opinions are still fuzzy in regard to HFRs, especially brominated ones. Some researchers consider that the risks should be assessed on a case-by-case basis, while others recommend a general ban of HFRs. In addition, some studies question the usefulness of FRs, at least in certain areas where lower risks are recognized. The debate deserves to be conducted on the basis of rigorous data, whether they come from statistics provided by organizations in charge of fire safety or from scientific studies carried out in the laboratory. The present issue "PolyFlame N°25" is devoted to two articles with two opposing opinions. The first article titled "Could Flame Retardants in Furniture be Increasing the Fire Risk?" was written by Joseph M. Fleming (Fire and Life Safety Consulting). The second article titled "Flame Retardants and the Associated Toxicity" was written by Marcelo M. Hirschler (GBH International) and was already published in our newsletter N°9 in May 2016. The articles published in this issue engage only these opposing outlooks. We hereby confirm that they do not necessarily reflect the views or opinions of the PolyFlame editorial team. In addition, we are open to any suggestions for articles, answers or comments that would allow this discussion to continue and reach maturity.

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In French :

Le débat lié aux risques toxicologiques et environnementaux des retardateurs de flamme a fait couler beaucoup d'encre depuis quelques années. Quelques retardateurs de flamme halogénés ont déjà été interdits par des réglementations spécifiques telles que la directive RoHS et/ou le règlement REACH. Les avis sont encore partagés sur ces retardateurs halogénés, notamment bromés. Certains chercheurs considèrent que les risques doivent être évalués au cas par cas tandis que d'autres sont pour une interdiction générale des retardateurs de flamme halogénés. Par ailleurs, certaines études remettent en cause l'utilité des retardateurs de flamme au moins dans certains domaines, et pointent du doigt le faible rapport bénéfice/risque.

Le débat mérite d'être mené en s'appuyant sur des données rigoureuses, qu'elles proviennent de statistiques des organismes en charge de la sécurité incendie ou d'études scientifiques réalisées en laboratoire. Le numéro présent «PolyFlame N°25» est consacré à deux articles avec deux avis opposés. Le premier article intitulé "Could Flame Retardants in Furniture be Increasing the Fire Risk?" a été rédigé par Joseph M. Fleming (Fire and Life Safety Consulting). Le deuxième article intitule "Flame Retardants and the Associated Toxicity" a été rédigé par Marcelo M. Hirschler (GBH International) et a déjà été publié dans notre newsletter N°9 en mai 2016.

Les articles publiés dans ce numéro n'engagent que leurs auteurs. Ils ne reflètent pas nécessairement les vues ou les opinions de l'équipe rédactionnelle de PolyFlame. Par ailleurs, nous sommes ouverts à toutes propositions d'articles, de réponses ou de commentaires qui permettraient de poursuivre cette discussion.

Bonne lecture





Could Flame Retardants in Furniture be Increasing the Fire Risk?

Joseph M. Fleming Fire and Life Safety Consulting

I had the privilege of serving as a fire fighter, on the Boston (US) Fire Department, for over 40 years. During part of that career, I served as the Fire Marshal for the City of Boston for 8 years (1993 — 2001). In that role, I enforced flammability standards for public spaces that were the strictest in the United States. (This was due to a tragic night club fire in 1942 that killed 492 people.) [1] As a consequence, the furnishing and fabrics in public spaces also contained the most flame retardants in the United States. I became troubled at research indicating health risks from the use of flame retardants. I conducted an in-depth study into the benefits of flame retardants to reduce fire risk, in order to justify these regulations.

To my surprise, I could not find any compelling evidence to indicate that there was a benefit. To make matters worse, the research that I was able to find seemed to indicate that the use of flame retardants possibly increased the risk to occupants in a fire. The use of flame retardants creates more smoke and creates it more quickly. Thus, occupants are potentially trapped sooner in a fire involving flame retardants than in one without flame retardants. These chemical flame retardants are particularly dangerous to fire fighters. When they burn, they create toxic smoke containing dangerous combustion byproducts like dioxins and furans. A recent paper highlighted the need to consider smoke production when measuring the benefits of flame retardants. [2]

There is a need to assess the benefits of flame retardants by considering both their effect on heat release rate and smoke production rate.

This possibility was mentioned in the 1975 report, "America Burning." [3] This report was issued by a special Presidential Commission due to the tremendous fire loss in the United States at that time, which was far higher than comparable countries.

"The hazards of flames have been studied and regulated to some extent, but recognition of the hazards of smoke and toxic gases has come belatedly. Ironically, efforts to make materials fire-retardant may have increased the life hazard, since the incomplete combustion of these materials often results in heavy smoke and toxic gases."

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The National Aeronautics and Space Administration (NASA) also warned about the failure to account for smoke in 1975. [4]

"To date, the major concern of those engaged in the development of fire-retardant materials has been the reduction of the ease of ignition and of flame propagation.

There has been less concern for other fire induced characteristics such as smoke emission and increased toxicity of combustion products. Few, if any, of the flamespread retardants are also smoke suppressants; the mechanisms employed in retardants tend to increase smoke production in many situations. For example, smoke generation is usually greatest at the thermal degradation stage just prior to ignition. Flame retardants do not alter the thermal degradation but simply delay ignition of the gas phase; and the longer ignition is retarded the more smoke is produced."

The importance of smoke when looking at the benefit of flame retardants, has been forgotten Most research measures the impact on heat release rate. I would like to make the case that smoke is equal to if not more important than heat release rate when considering survivability in a fire. This paper will justify my concerns.

Part One – Has the use of flame retardants in the US impacted the fire problem?

The Flame Retardant Industry will often make the following claim.[5]

"Since the introduction of strict fire safety standards in the U.S. — including the use of flame retardants — fires have been reduced by nearly 50 percent, from 734,000 in 1980 to 379,500 in 2020.

I am not sure what "including the use of flame retardants" means?" After 40 - 50 years of experience, couldn't the supporters of flame retardants, particularly in furniture, come up with better data to support the usefulness of flame retardants?





It is interesting to note that, in the United States, prior to the *"introduction of strict fire safety standards*," that the fire death per 100,000 people was decreasing for the 40 years. (See Figure 1.) In fact, they appear to have levelled off after 2000. There are obviously many causes for the reduction fire and fire deaths: fewer people smoking, better emergency care for fire victims, newer housing, etc. There is no reason to assume that a significant portion of that reduction was due to the use of flame retardants.



FIGURE 1 – Fire dearth rate for 100,000 people in USA [6] Another problem with attributing the reduction in fire deaths from furniture fires to the use of fire retardants is that TB117, a furniture fire test put in place in California (US) in 1975 and repealed in 2013, measured a propensity to small flame ignition, while most fatal furniture fires involve non-flaming ignition.

In a paper titled, "White Paper on Upholstered Furniture Flammability [7], the NFPA, estimate the historical benefits of flame retardants. They concluded.

"Fire retardants applied to polyurethane foam filling materials have been used to pass tests for small-open-flame resistance of filling materials since the introduction of such tests in 1975. The small-open-flame ignitions that motivated the introduction of fire retardants constitute a modest share of total upholstered furniture fatal fire deaths (about 10-15%) and always have. For

other fire scenarios – notably the large open flame ignitions involving fire spread from another burning item – available test evidence has not shown a significant effect, and one would not expect an effect because the treatments were never designed

to resist such large ignition heat sources. Either way, the evidence suggests the past impact of historically favored fire retardant treatments on fire deaths could not have been very large, even if they reliably performed as intended in all fires."

Flame retardants do not appear to have had a large impact on fires and fire deaths, but the industry also claims that flame retardance increase "escape time." If this is true, then the Fire Death Rate (Deaths per 100 Fires) should have decreased over the last 40 years. The opposite occurred. [8]

Fire	Death Rate for Fur	niture Fires (1980	– 2009) NFPA
Year	Fires	Deaths	Fire Death Rate
1980	36,900	1,360	3.685
1985	23,100	930	4.026
1990	16,400	870	5.305
1995	13,300	660	4.962
2000	9,300	580	6.373
2005	7,100	540	7.605
2009	5,900	450	8.036

Table 1 - Fire Death Rate for Furniture Fires (1980-2009) in USA

This increase in the Fire Death Rate for furniture fires, occurred despite a massive increase in the use of smoke alarms over that period (Table 1). According to the NFPA, this same trend, although not as dramatic, occurred in all home fires. This data can only make sense if either: 1) flame retardants do not impact heat release rate in a meaningful way, and/or 2) heat release rate is not the key variable to impact "escape time.

Part Two – Did the Use of Flame Retardants Reduce Furniture Flammability?

United States Test Results

In the past, in the United States, flame retardants were added to furniture in order to pass the California Fire Tests: TB117 (a small flame), for residential furniture and TB133 (a more robust test), for "public spaces" furniture. [9] Unfortunately, the "small





flame" TB117 Test does not seem to have been a good predictor of fire behavior in real fires. America Burning [2] also warned against this possibility. Unfortunately, this warning, similar to the warning on flame retardants acting as "smoke accelerators," was ignored.

"Existing large- and small-scale tests suffer from an inability to predict exact consequences of a real fire, particularly those involving foamed plastics. Improvement of test methods is dependent, to a large degree, on a better understanding of the basic processes of ignition and combustion and the mechanisms of fire retardancy and smoke generation and correlating these with actual fire experiences"

In 2013, Underwriters Labs tested FR and Non-FR furniture [10] and concluded –

"2. Substitution of TB 117 flame retardant treated foam (frPU) in place of untreated foam (OU):

- Fire growth behaviour was unchanged – rapid development with a high peak release rate

- Average peak heat release rate was reduced by 15% for corner ignition and side/back location, and unchanged for the back bottom ignition

- Elapsed times for the heat release rate to reach 1000 kW (flashover) were comparable"

In 2012, the Consumer Product Safety Commission tested furniture [11] and concluded –

"Overall, the results demonstrated that the addition of a fire barrier markedly increased the fire safety of the furniture. The data indicated that the fire sizes were smaller and the time to reach the peak fire size was slower with fire barriers, regardless of the fabric or foams used. Among the other effects examined,

a relative difference was noticed in the foams, but the fireretardant foams did not offer a practically significantly greater level of open-flame safety than did the untreated foams."

It would appear that there is little research from independent labs nor fire data that supports the claim that, "flame retardants have been a major contributor to the reduction in fire deaths and injuries over the past 40 years.

United Kingdom Test Results

In a study [12] comparing furniture that contained flame retardants (UK) and furniture that did not contain flame

retardants (FR & US) data was collected on HRR and smoke production (Figures 2).



Figure 4. Heat release for all three country configurations using crib 4 ignition source in an oxygen consumption calorimeter measured in kW over the duration of the each burn.



Figure 8. Smoke generation for French, US and British room configurations using crib 4 ignition. Smoke is measured in m^2/s over the duration of the test.

FIGURES 2 – Heat release rate and smoke generation for three country configurations using crib 4 ignition source [12]

These results indicate the use of flame retardants, delayed the increase in HRR by about 15 minutes. But that does not answer the question, "Do flame retardants provide extra time for occupants to escape?" This study also shows that the rapid increase in smoke is also delayed by 15 minutes. For an alert occupant, the 5 minutes escape time should be more than adequate to escape. For a sleeping occupant, who is relying on a smoke alarm to alert them to the fire, the operation of the smoke alarm may also be delayed by 15 minutes. The same fire scenario occurs, the clock just starts later. The smoke from a piece of furniture may also be more irritating, due to the additional chemicals, causing a smaller amount of smoke to trap the occupants. If this occurs then the addition of flame retardants, even if it delays the time to flashover could decrease the Available Safe Egress Time (ASET). In addition, a large percentage of fires that occur while occupants are sleeping have





an extended non-flaming period, during which copious amounts of smoke can be produced and this data provides no insight into that phenomenon.

The type of data produced in this type of study, as well as seriously flawed assumptions that 1) the smoke alarm is irrelevant and 2) that occupants are not impacted by smoke, leads to the following illustration (Figure 3). [13]





FIGURE 3 – Illustration from [13]

When analyzing data from fire tests, involving furniture, flame retardant advocates typically focuses on heat release rate and ignore smoke. "Smoke toxicity and heat release are key factors in fire hazard, together with flame spread and ignitability." [14] The problem with using this metric for safe egress in a residential setting is that it is visibility that is usually the first tenability criteria that is reached. According to the SFPE Handbook. [15]

"Table 63.1 lists the acute physiological fire hazards affecting escape capability. These tend to be encountered more or less in the order shown, with exposure first to smoke, which is likely to be irritant, followed by asphyxia or burns, depending upon the type of fire scenario and the proximity of the person to the fire. Once a victim has become trapped or incapacitated in a fire, then conditions usually become lethal within a further few seconds or minutes. This is because flaming fires grow exponentially, so concentrations of smoke and toxic gases, and the heat intensity, increase rapidly, resulting in death either from asphyxiation or heat exposure. The key determinant of survival is therefore incapacitation so that the lethal potency of fire effluent is of limited relevance."

Part Three – Flame Retardant Impact on Tenability and Smoke Alarm Response.

While the most research focuses on heat release rate, one researcher in New Zealand look at all of the various tenability criteria using computer simulation. [16] Here is a comparison between Standard Foam and FR Foam with a wool cover (Table 2).

Table 2 – Time to Reach Untenable Levels of radiant Heat and Smoke in [16]

Time to Reach Untenable Levels	ofı	radiant He	at and Smok	е
		Lounge	Hall	Bedroom
Time to Reach Tenability for Radiant Heat				
Standard Foam		140	250	>600
FR Foam with a Wool Cover		360	760	>600
Time to Reach Tenability for Smoke (Visibility)				
Standard Foam		35	50	80
FR Foam with a Wool Cover		25	55	90

If one focuses on Radiant Heat the FR Foam looks much safer. If one looks at Smoke (Visibility), which is the key determinant for escape the FR Foam is essentially equivalent or worse.

This researcher also estimated the smoke alarm response time (Tables 3).



Tables 3 – Time to Untenable Condition for two items in [16]

	Tir	me to untenable condition ((sec)
Tenability Criterion	Lounge 4	Hall 1	Bed 2
Visibility < 2 m	35	50	80
@ 2 m above floor			
FED inc (gases)	>600	>600	>600
FED inc (rad)	140	250	>600
Smoke alarm activation	20	35	45
time			

Table 5-1. Chair L21 (standard polyurethane foam with polypropylene cover), no sprinkler

Table 5-3. Chair J22 (fire-retardant polyurethane foam with wool cover), no sprinkler

	Tin	ne to untenable condition (sec)
Tenability Criterion	Lounge 4	Hall 1	Bed 2
Visibility < 2 m	25	55	90
@ 2 m above floor			
FED inc (gases)	>600	>600	>600
FED inc (rad)	360	>600	>600
Smoke alarm activation	13	29	47
time			

In this study, the flame retardants did increase the time to reach tenability for heat, but decreased the time to reach untenability for smoke (visibility). The use of flame retardants also slightly decreased the time to smoke alarm activation, due to an increase in smoke.

Conclusion

I hope that I provided enough evidence to justify a position that smoke, both toxicity and visibility, are just as important as heat release rate when gauging the effectiveness of flame retardants. When considering the use in residential settings the response of a smoke alarm should be factored into any "escape time" estimate, considering whether occupants are awake or asleep. I am not suggesting that flame retardants may not provide a benefit in certain circumstances. I am suggesting that when balancing any potential fire safety benefit against potential environmental and health risks, that all relevant criteria be measured.

Addendum

The highly questionable benefit of flame retardants in furniture applies as well to vehicle upholstery. This is particularly applicable to child car seats.

US Federal regulations governing flammability of vehicle interiors took effect in 1972 as Federal Motor Vehicle Safety Standard (FMVSS) 30. It prescribes burn resistance requirements for materials used in vehicle passenger compartments, the purpose of which, according to NHTSA, "is to reduce deaths and injuries to motor vehicle occupants caused by vehicle fires, especially those originating in the interior of the vehicle from sources such as matches or cigarettes...." [17] How do occupants die from vehicle fires started by cigarettes involving upholstery? How do children die from vehicle fires started by cigarettes involving upholstery? How does the use of flame retardant in vehicle upholstery improve the survivability from a fire that starts in the engine area, or from spilled fuels? If the heat flux is high enough to ignite the upholstery, how could a person sitting on the upholstery not be seriously injured? How could a child in a car seat survive?

Motor vehicle fire safety is changing. More plastics are being used to make vehicles lighter and electrical vehicles create unique fire problems. I suspect that there will be a lot of research justifying the use of flame retardants to address these new technologies. Any new fire test standards should measure the impact on occupants from the effects of: fire, heat, smoke, and toxic gases.

In the past, we have assumed that flame retardants improve survivability in a fire. At the same time, those who were concerned about possible health effects had to "prove" the risk to a scientific certainty. Given the track record of these "forever chemicals," I think it is time we held both fire safety and health/environmental concerns to the same evidentiary standards and burdens of proof.





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Flame Retardants and the Associated Toxicity

Marcelo M. Hirschler (GBH International)

Flame retardants are incorporated into materials, to improve their fire performance, normally by slowing fire development. They are either added into an existing polymeric material (natural or synthetic) or reacted with other raw materials to create a new material so that the resulting material exhibits improved fire performance. This typically results in a decrease in the amount of combustion products released in a fire [1].

Smoke toxicity and heat release are key factors in fire hazard, together with flame spread and ignitability. In fact, "inhalation of combustion products" is listed as the cause of death for some 2/3 of all fire victims. It is rare for multiple fire fatalities to occur in fires that have remained small. In the United States more than 83% of fire deaths in building fires happen in fires that have become very large. Such fires are large enough that they extend beyond the room of origin, and thus generate too much toxic smoke for survival [2]. The inherent toxic potency of smoke resulting from burning most combustible materials falls within a narrow range, so that there is no non-toxic smoke. Therefore, releasing lower mass of combustibles is essential to lower the overall toxicity of a fire atmosphere.

Moreover, the key fire property controlling the loss of human tenability in fires is the heat release rate of the burning materials [3], which governs the intensity of a fire and can vary by orders of magnitude for common combustibles [4]. Thus, toxic hazard is a more direct function of heat release rate rather than of the toxic potency of the smoke.

Table 1 [3] shows predicted survival time from an upholstered chair fire in a standard room. The data show the different results from varying toxic potency of smoke versus heat release and the dramatic survival time declines for the latter. This is a very important concept, because it puts into perspective the importance (or lack of it) of smoke toxic potency data in terms of fire hazard assessment, or simply of fire safety.



Table 1. Effects of Fire Properties on Survival Time

Product	Survival time
Chair (base case)	> 10 min
Chair igniting twice as fast	> 10 min
Chair with twice as high toxic potency	> 10 min
Chair with twice as high heat release rate	3 min

During the 1970'S and 1980's there was a belief that burning plastic materials produced smoke that was far more toxic than smoke from burning natural products such as wood, wool, or cotton. A number of studies have been done to compare the amount of carbon dioxide, carbon monoxide, and hydrogen cyanide produced by natural and synthetic materials under flaming and nonflaming conditions in order to model smoke toxicity. This work resulted in the development of multiple smallscale smoke toxicity test methods, all of which gave varied and narrow rankings for materials, resulting in limited applicability to predicting outcomes of fire events. Toxicologists studying toxicity data consider that ranges of toxicity are measured in orders of magnitude step changes, while most combustible materials produce data that are comparable and differences between materials is generally of minor importance to the overall toxicity of smoke [5]. In other words, the smoke toxicity of virtually all materials, natural or synthetic, is almost identical, within the margin of error.

Effects of Individual Combustion Products on Fire Victims

A pair of studies involving over 5,000 fatalities (between fire victims and non-fire victims or carbon monoxide (CO) inhalation) addressed: (a) a period between 1938 and 1979 in a localized area (Cleveland, OH) and (b) a countrywide study in the early 1990s [6]. They found remarkable similarities between the populations of victims: they all died primarily of CO asphyxiation. Other studies have shown that the fraction of any combustible converted into CO in a large (typically flashover) fire is approximately 0.2 g/g [7-8]. By combining the conclusions of the studies above and others it can be concluded [9] that:

- There is excellent correlation between fire fatalities and the concentration of carbon monoxide absorbed in blood as carboxyhemoglobin (COHb).
- COHb concentrations in blood are the same (when comparing populations of the same type) in fire and non-fire CO deaths (e.g. defective space heater incidents).

• Fatalities can be linked to COHb levels as low as 20%, and any COHb level above 30-40% is usually lethal.

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• The toxicity of fire atmospheres is determined almost solely by the amount of CO, since there is no difference in the COHb levels in blood of victims of poisoning by pure CO or in fire victims, once other exposure factors have been considered.

• The concentration of CO in fire atmospheres is roughly 20% [10], irrespective of what materials have burnt.

• It is rarely important to measure individual toxic gases for hazard assessment purposes, for any materials, including flame retardant additives.

• The primary usefulness of measuring toxic gases issued by burning materials is usually in terms of material development so as to understand its fire performance.

• The most immediately dangerous chemicals produced during all fires are those that behave as chemical asphyxiants, such as CO, responsible for most deaths in fires, and hydrogen cyanide, along with smaller contributions by irritants such as hydrogen halides or oxides of nitrogen.

 Moreover, the smoke toxicity of virtually all materials is almost identical [9-10].

The overall conclusion from a large body of research is clear fire fatalities are overwhelmingly associated with heat release since when heat release rate increases it leads to more CO generated. Thus, as fires become bigger, they have higher smoke toxicity, while other causes of fire deaths are of minor importance.

Types of Flame Retardants and their Effects

Seven key chemical elements are known to interfere or disrupt combustion: chlorine, bromine, phosphorus, aluminum, boron, antimony and nitrogen [11]. These elements are not used as such but provide the essential functionality into substances known as flame retardants. A flame retardant could contain one or more of these elements. Flame retardants act by various mechanisms, including free radical gas phase quenching, physical barrier formation by charring or contribution of water. Flame retardants improve fire performance by interfering with the availability of fuel, oxygen or ignition source (fire triangle components). Effective flame retardant designs are rarely composed of a single flame retardant and may (depending on the substrate) contain a multiplicity of chemicals.





Two of the elements mentioned (chlorine and bromine) are known as halogens (another halogen exists, fluorine, which is not used in flame retardant additives but is found as part of polymers known as fluoropolymers). Halogenated flame retardants are generally considered the most effective and can be used at some of the lowest concentrations. During combustion free radicals containing bromine or chlorine guench the fuel source in the gas phase. On the other extreme, some purely inorganic materials (such as metal hydroxides: alumina trihydrate or magnesium hydroxide) are used to provide water, released during combustion to lower gas phase temperatures. Such flame retardants are the highest volume products used commercially but have limited applicability because they need to be used at very high concentrations, often resulting in deleterious effects to properties of the substrate material, such as flexibility. Between these extremes are phosphoruscontaining materials, which can form protective char barriers on the surface of a burning material. Their performance and applications is often improved by including other elements, such as nitrogen or a halogen. Flame retardants are also used in combination with other additives (to improve the functionality of the base flame retardant) that affect fire performance or lower smoke release. They include materials based on molybdenum, tin, zinc and sulfur compounds.

Flame retardants cannot make materials "fire proof". Flame retardants are an important first line of defense in the case of fire by slowing the combustion process (or even preventing it) and by lowering the resulting heat release and flame spread. A large and sustained heat input can overwhelm the effect of flame retardants and the material can still burn. Flame retardant materials are being developed continually, and the total number of flame retardant additives that have been used commercially can be counted in the thousands, since the first one used commercially in the 1700s [12-14].

Smoke Toxicity of Flame Retarded Materials

The overall smoke toxicity of materials containing flame retardants is not significantly different from that of materials that do not contain flame retardants (as discussed above). In fact, properly flame retarded materials will generate less mass of smoke and combustion products, thus causing fire atmospheres to be less toxic (as shown in a famous NBS study [15]). Thus, the use of flame retarded materials will not alter the smoke toxicity in fire atmospheres. The basic function of flame retardants in interfering with the combustion process means that there will be more incomplete combustion. However, as discussed above, in large fires the fraction of burnt material converted into CO is fairly constant, at 20% [7-9] so that there is no significant effect of flame retarded materials in actual fires.

Halogenated materials (including ones with halogenated flame retardants) will contribute halogenated effluents, including acid gases, which will contribute to the acute toxicity of fire atmospheres, although it is normally overwhelmed, as discussed above, by the toxicity of CO. In some cases, the thermal decomposition or combustion of halogenated materials generates small amounts of polyhalogenated dioxins and furans as components of the associated smoke. The composition of emitted gases will depend not just on the material burnt but also on the presence of catalysts (including metals like copper) and the fire intensity. The concentrations of these gases are so small that they are not associated with acute smoke toxicity but with the chronic effects resulting from fires. In fact, the advances in analytical and detection techniques mean that scientists can now detect the presence of materials, or derivatives of materials, at levels so small as to not be meaningful. Thus, they may affect primarily those facing repeat exposures like firefighters.

Some of these halogenated dioxins and furans fall into the category of known human carcinogens, and thus research has analyzed smoke and soot residues to determine their concentrations during and after fires. A plethora of research has shown that all fire atmospheres contain large amounts of known carcinogens, especially polynuclear aromatic hydrocarbons (PAH), including benzo[a]pyrene [BAP], formed by all burning materials. In fact, BAP is the one combustion product with the highest level of toxic carcinogenicity. Therefore, work has been done comparing the toxic effects of dioxins and furans with those of PAHs. It was found that the concentrations of dioxins and furans in particulate residues were at levels 4,000 times lower than those of PAHs [16-19]. Moreover, analysis of pollutant data gathered from two well-documented German catastrophic fires found that PAH levels were thousands of times higher than those of polyhalogenated dioxins and furans [20]. Essentially, all reports to date indicate that dioxins and furans pose only a very minor exposure risk while the exposure risk to known human carcinogenic components, like PAHs, is extremely high and unaffected by the presence of halogenated compounds in a fire.





Inherent Toxicity Issues Associated with Individual Flame Retardants

The vast majority of flame retardants are not carcinogens, mutagens or reproductive toxins, and are neither bioaccumulative nor have acute toxicity. In 2000, the US National Research Council (Committee on Toxicology, Subcommittee on Flame-Retardant Chemicals, NRC) presented findings to the US Consumer Product Safety Commission (CPSC) and the US Congress [21-22]. The work analyzed the inherent toxic effects of individual flame retardants or flame retardant classes, both on their immediate effects (acute) and on their long-term effects (chronic), with primary focus on the latter. This was done by analyzing the toxicological and exposure data on 16 key flame retardant chemicals to assess potential health risks to consumers (primarily in residential furniture). The subcommittee was also asked to identify data gaps and make recommendations for future research. NRC made assessments to determine whether causal relationships existed between the dose of each chemical and each adverse health effect by reviewing human (epidemiological studies, clinical observations, and case reports) and laboratory animal data on neurotoxicity, immunotoxicity, reproductive and developmental toxicity, organ toxicity, dermal and pulmonary toxicity, carcinogenicity, and other local and systemic effects. NRC also reviewed in vitro data to determine the potential for genotoxicity as well as other toxic effects and to understand the mechanisms of toxic action. Toxicokinetic studies were also reviewed to understand the absorption, distribution, metabolism, and excretion of the FR chemicals. For some types of toxic effects, notably most cancers, the subcommittee conservatively assumed that no threshold for a dose-response relationship exists or that, if one does exist, it is very low and cannot be reliably identified. Therefore, the subcommittee's risk-estimation procedure for carcinogens was different from that for non-carcinogens: the relationship between the incidence of cancer and the dose of a chemical reported in an epidemiological study or an experimental animal study was extrapolated linearly to much lower doses at which humans might be exposed in order to overestimate conservatively the excess lifetime risk of cancer resulting from lifetime exposure to a chemical at a particular dose rate. This procedure does not provide a "safe" dose with an estimated risk of zero (except at zero dose), although at sufficiently low doses, the estimated risk becomes very low and is regarded to have no public-health significance. The actual risk is also highly likely to be lower than the upper bound, and it might be zero. In the final phase of the risk-assessment process, NRC integrated the data to determine the probability that individuals might experience adverse effects from a chemical under anticipated conditions of exposure, by calculating a hazard-index to judge whether a particular exposure would be likely to present a non-cancer toxicological risk.

Without going into detail, for most of the most widely used flame retardants, NRC concluded that the hazard indices for noncarcinogenic effects are less than 1 for all routes of exposure for all flame retardants studied, meaning that they are not a concern. Carcinogenic risk assessments performed on the flame retardants that were found to be or likely to be carcinogenic indicate that some of the estimated excess cancer risks may be greater than 1×10–6. However, the NRC committee concluded that actual carcinogenic risk is likely to be much lower because of the extremely conservative (high) exposure estimates. Several of the flame retardants analyzed were actually chemical classes rather than single compounds.

In those cases one chemical was selected as a surrogate on the basis of representativeness and conclusions were based on the properties of the surrogate and the risk from other members of the class might be different from the risk from the surrogate. It is important to point out that this study (as opposed to many other studies) did not focus exclusively on halogenated flame retardants but discussed all types of chemistries.

NRC intentionally overestimated exposure levels as a precautionary approach to the protection of public health and concluded that the following flame retardants can be used on fabrics for residential furniture with minimal risk, even under worst-case assumptions:

- Hexabromocyclododecane,
- Decabromodiphenyl oxide,
- · Alumina trihydrate,
- Magnesium hydroxide,
- Zinc borate,
- Ammonium polyphosphates,
- Phosphonic acid (3-{[hydroxymethyl]amino}-3-oxopropyl)dimethyl ester,1
- Tetrakis hydroxymethyl phosphonium salts (chloride salt)

They also recommended that additional exposure studies be made on the following flame retardants to determine whether toxicity studies need to be conducted:

- Antimony trioxide,
- Antimony pentoxide and sodium antimonates,
- Calcium and zinc molybdates,

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- Organic phosphonates (dimethyl hydrogen phosphite),
- Tris (monochloropropyl) phosphates,
- Tris (1, 3-dichloropropyl-2) phosphate,
- Aromatic phosphate plasticizers (tricresyl phosphate), and
 Chlorinated paraffins.

In conclusion, the NRC committee found no significant risk concern with any of the flame retardants assessed, which covered a broad range of chemical compositions.

For some of these materials additional studies were performed after the NRC work, much of which was done for European Union risk analyses, and it filled in some of the gaps identified. Two brominated flame retardants, not directly studied by NRC, have been clearly associated with potential health issues and withdrawn from the market: pentabromobiphenyl oxide (pentaBDE) and octabromobiphenyl oxide (octaBDE). In the case of neither chemical have proven health effects (including carcinogenic effects) on humans been published but the fact that the chemicals are bioaccumulative and do have proven health effects on animals mean they should not be used. PentaBDE and octaBDE may enter the body by ingestion or inhalation and they are stored mainly in body fat. EPA studied pentaBDE in detail in 2008 [23]. Following a comprehensive risk assessment the European Union banned the use of both pentaBDE and octaBDE since 2004 [24]. In the US, as of 2005, "no new manufacture or import of" pentaBDE and octaBDE "can occur... without first being subject to EPA evaluation" and in May 2009, both were added to the Stockholm Convention on Persistent Organic Pollutants as it meets the criteria for the so-called persistent organic pollutants of persistence, bioaccumulation and toxicity.

In December 2009 all manufacturers voluntarily phased out production of a flame retardant in the same family as the last two, decabromobiphenyl oxide (decaBDE), in spite of the lack of proven health effects. The main reason for this action by the manufacturers is that many of the properties of decaBDE are similar to those of pentaBDE and octaBDE even if the health effects are not.

Much earlier, the first flame retardant found with negative health effects (carcinogenicity), and voluntarily withdrawn from the market (for children's sleepwear) in the 1970s, was brominated tris [tris (2,3-dibromopropyl) phosphate], which has not been commercially since. It is important to note that it is a different material from the chlorinated tris flame retardant used more cently for furniture, and which is being misidentified in the re press as the same material.

Hexabromocyclododecane (HBCD) has been found to have the potential for ecotoxicity but no demonstrated effects on humans have been reported. The Stockholm Convention recommended its inclusion in a list of persistent organic pollutants, an action not completed as of 2015. However, in 2014 manufacturers of HBCD, extensively used as a flame retardant for polystyrene thermal insulation, in conjunction with the manufacturers of the polystyrene foam itself, have decided to replace HBCD in the foam by a polymeric brominated flame retardant (polyFR) [25], which has very low bioavailability and intrinsic toxicity and is, thus, not bioaccumulative.

No other flame retardant has, at least until 2015, been demonstrated to have such an effect on risk to humans that it was deemed necessary to eliminate it from the market.

Health Effects of Flame Retardants in Actual Fires

Flame retardants, as discussed above, do not significantly contribute to acute toxicity in fires. Toxicologists comparing acute toxicities use a toxicity classification scale for inhalation that places LC50 (toxic potency) values of 10 to 100 in the highly toxic category and values of 10 or less in the extremely toxic category [26]. The smoke toxic potency values of flame retarded materials are so similar to those of the same materials without flame retardants that they are not statistically significantly different. Moreover, as properly flame retarded materials will generate lower masses of combustion products they will often cause fire atmospheres to be less toxic [15]. Thus, the use of flame retarded materials will not alter smoke toxicity in fire atmospheres.

With regard to the effects on the health of firefighters, it is undoubtedly true that firefighters should have special concerns because the rates of many chronic diseases, including cancers, are higher among firefighters than among the general population. These health effects on firefighters will be minimized by: (a) the continued use of self-contained breathing apparatus both during firefighting and during overhaul operations (after the fire has been brought under control) and (b) improvements in the effective treatments of firefighter protective clothing after each use. However, there is no evidence that this is associated with the use of flame retardants. In fact, there is significant evidence that the added effect of the combustion or thermal decomposition products of flame retardants have an insignificant added effect on toxicity concentrations of carcinogens in smoke and soot



PolyFlame 🌎

which polyhalogenated dioxins and furans (resulting from halogenated flame retardants) make relative to the extremely large contributions from PAH.

Conclusions

Flame retardants are based on many individual chemical components, including not just halogens. Some of them are also used in household applications unrelated to fire safety. Thus, any scientifically-based discussion of the toxicity and/or health effects flame retardants needs to address the specific material of potential concern and not a generic catch-all. While it is essential to ensure that materials with negative health effects not be used, this cannot be interpreted as a blanket attack on flame retardants in general or even on brominated and/or chlorinated flame retardants. Every flame retardant offered for commercial use should always be investigated and those materials proven to be toxic or harmful should be prohibited from use.

However, flame retardants are an important way to maintain robust fire safety in product and building designs. They are an essential first line of defense in terms of passive fire protection. Flame retardants are a broad class of materials with unique functionality, hazard characteristics, and impacts on fire events.

In conclusion, published data overwhelmingly shows that flame retardants do not contribute significantly contribute to either acute or chronic fire toxicity in real fires. While some flame retardants have been removed from the market in recent years the vast majority in commercial use do not present significant toxicological concerns.

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As the Editor-in-chief, I am often asked a common but a key question: why should researchers publish their work in JVAT, especially if it relates to flame retardancy or fire science? This is a fair question. We must not forget that flame retardancy does not come at the expense of other properties. FR additives are not used alone. To maintain or improve mechanical properties, stability, and, also for commercial viability, other non-FR additives are combined with the FR materials formulations. This is where JVAT distinguishes itself from specialized journals. Moreover, to increase readership and citation, JVAT provides researchers a unique opportunity to showcase their works to the broader science community. Instead of preaching to the choir, one needs to look at opportunities outside. Very recently, for example, Professor Baljinder Kandola of the University of Bolton reviewed flame retardants for epoxy resins in JVAT's February 2022 issue. Please visit the open access articles Journal of Vinyl and Additive Technology: Vol 28, No 1 (wiley.com).

The other question I am asked: is JVAT not a vinyl journal? Wait a minute! Vinyl is not limited to PVC, CPVC and PVDF. In fact, Vinyl or ethynyl (IUPAC) is a functional group derived from ethylene, that is, one hydrogen less than the ethylene molecule. Vinyl polymers and copolymers are diverse in nature. All successful polymeric materials contain an additive package.



Without additives, polymers just don't perform. That is why JVAT welcomes manuscripts on all aspects of fire science in matrices of thermoplastics and thermosets alike.

Prithu Mukhopadhyay

Editor-in-Chief

Journal of Vinyl & Additive Technology



New book :



Analysis of Flame Retardancy in Polymer Science

^{Edited} by Henri Vahabi, Mohammad Reza Saeb, Giulio Malucelli

Analysis of Flame Retardancy in Polymer Science helps students, early-career researchers, and junior engineers to understand the basic principles of fire characterization methods. This book is an indispensable resource for identifying the appropriate fire characterization methods to be utilized for research and development.

This book addresses issues such as how to evaluate flammability at different scales, how to compare the obtained results with previous or similar results in the literature, and how to compare the efficiency of a new flame retardant system with with previous or simil those of the literature.

- Key Features Includes background and advanced details about the techniques of characterization of fire and flame behavior Provides an overview of the major techniques of fire analysis Characterizes different types of materials at small, laboratory, and real-life scale Offers a comprehensive overview of fire behavior and testing and associated toxicity issues

About the Authors Henri Vahabi has been Associate Professor at the University of Lorraine since 2012. His research is focused on the thermal degradation, fire retardancy of thermoset and thermoplastics, and development of new biobased flame retardants He is a committee member of the "Fire group" of the Chemical Society of France.

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Giulio Malucelli is Professor at the Department of Applied Science and Technology of Politecnico di Torino, Italy. His research interests include the investigation of structure-property relationships, the fire behavior of textiles modified by surface-engineered systems, and the design and exploitation of bio-sourced products as effective flame retardants.



m/books-and-iournals







9.00 – 17.00 in MONS

WORKSHOP November 9 & 10, 2022

Recent developments in **flame retardant materials** by surface treatments

Materia Nova R&D & innovation center and "Degradation and fire behavior of organic materials" thematic group of the French chemical society are pleased to announce the organization of a workshop on "**Recent developments in flame-retardant materials by surface treatments**", in Mons (Belgium) on the 9th & 10th November 2022.



This workshop will gather international scientific and industrial experts to discuss and exchange their experiences in the field. Over the two days, the workshop will bring you insights into state of the art as well as the latest development of fundamental and applied research dealing with the development of Materials fire protection through surface treatment.

Contact: fouad.laoutid@materianova.be

Hôtel Van Der Valk de Mons

Workshop fees: 150 € including lunch & Coffee breaks

8h30-9h00	Registration
9h00-9h10	Openning
9h10-9h20	Bartosz WECLAWSKI (University of Bolton), 'Sustainable Flame Retardant Application to Nylon Textiles by Novel Atmospheric Plasma Surface Activation'
9h20-9h40	Thomas GODFROID (Materia Nova), 'Polymer surface functionalization by PECVD: application to fire retardancy'»
9h40-10h00	Mohammad Reza SAEB (Gdańsk University of Technology), 'Flammability and Sustainability: Monitoring the protection front from the bulk to the surface of polymers'
10h00 – 11h30	Coffee break
11h30-11h50	Abdelghani LAACHACHI (LIST), 'Intumescent coating of (polyallylamine-polyphosphates) deposited hemp fabric via layer-by-layer technique'
11h50-12h10	Massimo MARCIONI (Politecnico di Torino), Flame-retardant Lightweight materials from layer-by-layer coated cellulose fibers.
12h10-12h30	Rodolphe SONNIER (IMT Alès), 'Flame retardancy of natural fibers by radiografting of phosphorus- based FR'
12h30-14h00	Lunch
	Eulici
14h00-14h20	Séverine BELLAYER (Université de Lille - UMET), 'Transparent fire protective sol-gel coatings for wood panels'
14h00-14h20 14h20-14h40	Séverine BELLAYER (Université de Lille - UMET), 'Transparent fire protective sol-gel coatings for wood panels' Fouad LAOUTID (Materia Nova) « Flame retardant properties of PLA coated by Epoxy / aluminum hypophosphite nanoparticles»
14h00-14h20 14h20-14h40 14h40-15h00	Séverine BELLAYER (Université de Lille - UMET), 'Transparent fire protective sol-gel coatings for wood panels' Fouad LAOUTID (Materia Nova) « Flame retardant properties of PLA coated by Epoxy / aluminum hypophosphite nanoparticles» Industrial presentation : to be confirmed
14h00-14h20 14h20-14h40 14h40-15h00 15h00 – 15h30	Séverine BELLAYER (Université de Lille - UMET), 'Transparent fire protective sol-gel coatings for wood panels' Fouad LAOUTID (Materia Nova) « Flame retardant properties of PLA coated by Epoxy / aluminum hypophosphite nanoparticles» Industrial presentation : to be confirmed Coffee break
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14h00-14h20 14h20-14h40 14h40-15h00 15h00 – 15h30 15h30-15h50 15h50-16h10 16h10-17h10	Séverine BELLAYER (Université de Lille - UMET), 'Transparent fire protective sol-gel coatings for wood panels' Fouad LAOUTID (Materia Nova) « Flame retardant properties of PLA coated by Epoxy / aluminum hypophosphite nanoparticles» Industrial presentation : to be confirmed Industrial presentation : to be confirmed Industrial presentation : to be confirmed Round table: conclusions and perspectives
14h00-14h20 14h20-14h40 14h40-15h00 15h00 - 15h30 15h30-15h50 15h50-16h10 16h10-17h10 19h	Later Séverine BELLAYER (Université de Lille - UMET), 'Transparent fire protective sol-gel coatings for wood panels' Fouad LAOUTID (Materia Nova) « Flame retardant properties of PLA coated by Epoxy / aluminum hypophosphite nanoparticles» Industrial presentation : to be confirmed Longe break Industrial presentation : to be confirmed Industrial presentation : to be confirmed Round table: conclusions and perspectives Conference dinner (optional with registration) : 60 €





CHALLENGES, CONTRAINTES ENVIRONNEMENTALES ET PERSPECTIVES **POLYMERS AND FIRE SAFETY:**

CHALLENGES. ENVIRONMENTAL CONSTRAINTS AND PERSPECTIVES



PLASTICS (POLYMERS



POLYMERES ET SÉCURITÉ INCENDIE OLYMERS AND FIRE SAFETY

La SFIP - Société Française des Ingénieurs des Plastiques - avec le soutien de Plastics Europe et Polym tiques – avec le soutien de Plastics Europe et Polymeris, organise les 25 et 26 janvier 2023, un congrès dédié aux polymères et à la sécurité incendie. Grâce à leurs multiples propriétés, les polymères sont au-jourd'hui très largement utilisés dans tous les domaines de la vie quotidienne et la sécurité incendie est une

exigence essentielle. Elle nécessite le développement d'une stratégie correspondant à chaque secteur en pre-nant en compte les réglementations et les contraintes environnementales.

Les principaux thèmes concernés sont :

» L'expression des justes besoins tels que l'inflammabilité, la propagation, la libération d'énergie et les effets collatéraux (fumées - toxicité et opacité, isolation électrique),

Jess innovations dans le domaine des ignifugeants, matières inturnescentes ou ablatives (céramisantes, vitriflantes...), composites, polyméres intrinsèquement ignifuges (cas des PVC, PPC). Jou aignifuges (PA, PAR, PBT, etc.), polymères réticulés, bioplastiques...

Les conséquences de cessolutions sur les performances et la mise en œuvre des matériaux,

 La compatibilité de ces solutions avec les contraintes environnementales et une démarche écoresponsable : tri des matières dans les centres de recyclage en liaison avec les ignifugeants utilisés (présence de brome, chlore et de phosphore), ACV...

» La conformité de ces solutions avec les réglementations actuelles et futures : GTR-EVS, REACh, POP.

»La caractérisation des performances par rapport aux besoins

L'analyse des composants,

Les futures demandes des grands donneurs d'ordre : bâtiment, automobile, ferroviaire, aéronautique, électrique/électronique..

Ce congrès s'adresse aux producteurs de matières premières, aux chercheurs industriels et académiques, aux concepteurs, aux transformateurs et fabricants de produits et aux prescripteurs/ donneurs d'ordre.

Si vous souhaitez proposer une communica-tion,merci de compléter le formulaire en pages 3 et 4 et de le renvoyer au plus tard le 30 septembre 022 à : ortes@sfip-plastic.org

SFIP - the French Society of Plastics Engineers - with the support of Plastics Europe and Polymeris, is organising a congress on 25 and 26 January 2023 dedicated to polymers and fire safety.

Thanks to their multiple properties, polymers are Thanks to their multiple properties, polymers are now widely used in all areas of daily life and fire safety is an essential requirement. It requires the development of a strategy corresponding to each sector, considering the regulations and environ-mental constraints.

The main themes concerned are

 The expression of the right needs such as flam-mability, propagation, energy release and collateral effects (smoke - taxicity and opacity, electrical insulation),

Innovations in the field of fire retardants, inturnescent or ablative materials (ceramics, vitri-fiers, etc.), composites, intrinsically fire-retardant polymers (PVC, PPS, etc.) or fire retarded (PA, PPA, PBT, etc.), cross-linked polymers, bioplastics, etc.

The consequences of these solutions on the performance and implementation of materials.

The compatibility of these solutions with environ mental constraints and an eco-responsible approach: sorting of materials in recorresponsible op-proach: sorting of materials in recycling centres in relation to the flame retardants used (presence of bromine, chlorine and phosphorus), LCA, etc.

Compliance of these solutions with current and future regulations: GTR-EVS, REACh, POP, etc.

> Characterisation of performance in relation to equirements.

Analysis of components.

 Future demands of major clients: building, autonotive, rall, aeronautics, electrical/ele etc

This congress is dedicated to raw material producers, industrial and academic researchers, designers, processors/converters and prescribers/ purc



POLYMERES ET SÉCURITÉ INCENDIE ND FIRE SAFET

COMITÉ SCIENTIFIQUE

Quentin BOULARD ADDIPLAST

Olivier GABUT

Laurent GERVAT Alain GIOCOSA

Frédéric GUILLAUME

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