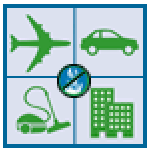
United States
Environmental Protection
Agency

An Alternatives Assessment for the Flame Retardant Decabromodiphenyl Ether (DecaBDE)

Chapter 3

Background on Flame Retardants



FINAL REPORT

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3 Background on Flame Retardants

This chapter begins with background information on flame retardants, including their classification (Section 3.1). Section 3.2 presents the flame retardants included in this assessment and Section 3.3 discusses those which were considered but excluded from the assessment. Section 3.4 presents the mechanisms by which flame retardants reduce or prevent combustion.

3.1 General Information on Flame Retardants

Flame retardants decrease the ignitability of materials and inhibit the combustion process, limiting the amount of heat released. The simplest way, in theory, of preventing polymer combustion is to design the polymer so that it is thermally stable. Thermally stable polymers are less likely to decompose into combustible gases under heat stress, which prevents combustion from initiating. Because thermally stable polymers are often difficult and expensive to process and may have performance limitations, manufacturers use other means, such as flame-retardant chemicals, to impart flame-retardant properties to polymers.

Flame retardants decrease the likelihood of a fire occurring and/or decrease a range of undesirable consequences of a fire (Lyons 1970; Cullis and Hirschler 1981). However, in other instances the incomplete combustion resulting from the use of flame retardants, where oxidation and/or thermal transfer are inhibited, can produce negative by-products. Carbon monoxide (CO), a by-product of incomplete combustion, acts as an asphyxiant in poorly-ventilated fire scenarios and can lead to CO poisoning and death (Nelson 1998; Peck 2011). These by-products are in addition to the production of other toxic chemicals (e.g., halogenated dioxins and furans) generated during combustion of materials containing flame retardants.

Fire occurs in three stages: (1) thermal decomposition, where the solid, or condensed phase, breaks down into gaseous decomposition products as a result of heat; (2) combustion chain reactions in the gas phase, where thermal decomposition products react with an oxidant (usually air) and generate more combustion products, which can then propagate the fire and release heat; and (3) transfer of the heat generated from the combustion process back to the condensed phase to continue the thermal decomposition process (Hirschler 1992; Beyler and Hirschler 2002).

The basic mechanisms of flame retardancy will vary depending on the flame retardant and polymer system. Flame retardants can be classified based on the phase (solid or gas) in which they act to reduce or prevent propagation of flame. Other flame retardants may form protective barriers over a polymer which may insulate the flammable polymer from heat or reduce the amount of polymer that is available to burn as fuel. In either state, gaseous or condensed, flame retardants will act to decrease the release rate of heat (Hirschler 1994), thus reducing the burning rate, flame spread, and/or smoke generation (Morose 2006). These mechanisms are discussed further in Section 3.4.

Typically, flame retardants contain one or more of the following elements: chlorine, bromine, aluminum, boron, nitrogen, phosphorus, or silicon (Lyons 1970; Cullis and Hirschler 1981). There are a number of alternatives and synergists that are also effective. Some elements, such as zinc (often used as zinc borate or zinc stannate) and molybdenum (often used as ammonium molybdates), are effective primarily as smoke suppressants in mixtures of flame retardants. In addition, antimony trioxide can serve as an effective synergist in combination with halogenated flame retardants.

The amount of flame retardant needed to pass a given flammability standard varies due to a number of factors. In general, the lowest levels of flame retardants are required with bromine-based chemistries, and higher levels are required when using mineral-type compounds. Ranges of typical "loading levels" (how much of a flame retardant is added to a material) for common flame retardants are shown in Table 3-1. Loading levels also depend on the polymers in which the flame retardant is used. For example, bromine-based flame retardants are used in a wide variety of products (e.g., polyolefins, styrene, polyamides (PAs), polyesters, polycarbonates (PCs) and textiles) and thus have a wide range of loading levels[9]. This is demonstrated by the fact that when used in polyesters, bromine-based flame retardants have a loading level of about 8 percent, whereas when bromine-based flame retardants are used in textiles, they are usually at about a 17 percent loading. On the other hand, the flame retardants that are not used in such a wide variety of products have much smaller loading ranges. For example, chlorophosphates have a 9 percent loading in epoxy resins and a 10 percent loading in polyurethane and are not reportedly used with other polymers (Weil and Levchik 2009).

Table 3-1: Typical Loading Levels[8] of Common Flame Retardants

Type of Flame Retardant	Loading (wt %)
Bromine-based	2 to 25%[1]
Aluminum Hydroxide	13 to 60%
Magnesium Hydroxide	53 to 60%
Chlorophosphates	9 to 10%
Organophosphorus	5 to 30%

[1] Polyethylene (PE) can require up to 31% of a bromine based flame retardant and 7-8 % antimony trioxide. However, this is rarely practiced in the market thus the upper limit displayed above is 25%.
Source: Weil and Levchik 2009

Flame-Retardant Classification

Flame retardants can be classified into four main categories according to chemical composition:

- *Inorganic*: This category includes flame retardants and synergists such as silicon dioxide, metal hydroxides (e.g., aluminum hydroxide and magnesium hydroxide), antimony compounds (e.g., antimony trioxide), boron compounds (e.g., zinc borate – which is often used as a synergist for both halogenated and non-halogenated flame retardants), and other metal compounds (molybdenum trioxide). As a group, these flame retardants represent the largest fraction of total flame retardants in use (Norwegian Pollution Control Agency 2009).

- *Halogenated*: These flame retardants are primarily based on bromine and chlorine. Typical halogenated flame retardants are halogenated paraffins, halogenated aliphatic and

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[9] These loading levels can be measured in percent by weight (i.e., percent in relation to the total weight of the components or final product) or in parts per hundred resin (phr) (i.e., all phrs will be over 100). Information in Table 3-1 is presented as a percentage of the weight of the final product.

aromatic compounds, and halogenated polymeric materials. Some halogenated flame retardants also contain other elements, such as phosphorus or nitrogen. The effectiveness of halogenated additives, as discussed below in Section 3.4, is due to their interference with volatile substances which are created in the combustion process, decreasing their combustibility. Brominated compounds represent approximately 18 to 21 percent (by volume) of the global flame-retardant production (Hirschler 1998).

- *Phosphorus-based*: This category represents about 20 percent (by volume) of the global production of flame retardants and includes organic and inorganic phosphates, phosphonates, and phosphinates as well as red phosphorus, covering a wide range of phosphorus compounds with different oxidation states. There are also halogenated phosphate esters, often used as flame retardants for polyurethane foams or as flame-retardant plasticizers, but not commonly used in electronics applications (Hirschler 1998; Green 2000; Weil and Levchik 2004).

- *Nitrogen-based*: These flame retardants include melamine and melamine derivatives (e.g., melamine cyanurate, melamine polyphosphate). Nitrogen-containing flame retardants are often used in combination with phosphorus-based flame retardants, with both elements in the same molecule (Morose 2006).

Halogenated flame retardants are commonly blended with a synergist, such as antimony trioxide. A synergist multiplicatively enhances the flame retardant effect. Many flame-retardant synergists do not have significant flame-retardant properties by themselves; their addition increases the overall effectiveness of the flame-retardant system. It should also be noted that the synergists may be very system specific; they are not universal. For example, antimony trioxide only shows flame retardant synergism with halogenated flame retardants and has no effect when combined with inorganic, phosphorus, or nitrogen-based flame retardants.

Flame retardants also can be classified by how they are incorporated into a polymer – additively or reactively. No reactive-type flame retardants were identified as alternatives to decabromodiphenyl ether (decaBDE) in this assessment.

- *Additive:* Additive flame retardants are incorporated into polymers via physical mixing, and are not chemically bound to the polymer. Flame-retardant compounds are mixed with existing polymers without undergoing any chemical reactions. As a result, the polymer/additive mixture is less susceptible to combustion than the polymer alone. Since additive flame retardants can be incorporated into the product up until the final stages of manufacturing, it is usually easier for manufacturers to use additive flame retardants than reactive flame retardants.

- *Reactive:* Reactive flame retardants are incorporated into polymers via chemical reactions and must be incorporated at an early stage of manufacturing. Once introduced, they become a permanent part of the polymer structure – i.e., the chemically-bound reactive flame-retardant chemicals cease to exist as separate chemical entities. As a result, reactive flame retardants have a greater effect on the chemical and physical properties of the polymer into which they are incorporated than do additive flame retardants. For examples of reactive flame retardants, refer to the Flame Retardants in Printed Circuit Boards Draft Report (U.S. EPA 2008).

Flame retardants can also be coated on the external surface of the polymer to form a protective barrier or to improve their compatibility with the polymeric matrix.

Both reactive and additive flame retardants can significantly change the properties of the polymers into which they are incorporated. Each flame retardant polymer combination is unique. For example, they may change the viscosity, flexibility, density, electrical properties, tensile strength, and flexural strength; and may also increase the susceptibility of the polymers to photochemical and thermal degradation.

3.2 Flame Retardants Included in this Assessment

With the assistance of the partnership, the U.S. Environmental Protection Agency (EPA) identified 29 alternatives to decaBDE which fit the scope of this project: to identify potentially functional, viable alternatives for use in the identified polyolefins, styrenics, engineering thermoplastics, thermosets, elastomers or waterborne emulsions and coatings (see Chapter 1). The impetus behind this alternatives assessment is the potential for adverse human health and environmental effects through decaBDE exposure. DecaBDE can break down into other polybrominated diphenyl ether congeners, which may be persistent, bioaccumulative, and toxic to both humans and the environment (U.S. EPA 2009). It is important to stress that these alternatives were not chosen based on environmental preferability but based on their functionality and viability. These alternatives were identified through the following process:

1) EPA developed an initial list of alternatives based on a review of the literature (Posner and Boras 2005; Danish Ministry of the Environment 2007; European Chemicals Bureau 2007; Washington State Department of Health 2008; Pure Strategies Inc. for Maine Department of Environmental Protection 2010) and consultation with industry experts.

2) This list was presented to the partnership, and through multiple discussions EPA confirmed which chemicals were potentially viable alternatives and identified any additional alternatives which were not found through the literature review process.

3) Chemicals that were initially included as potential alternatives (identified through the literature review) but were not deemed viable by the experts on the partnership were excluded from the assessment (see Section 3.3).

Chemical Alternatives and the Toxic Substances Control Act

EPA's Design for the Environment (DfE) program is administered by the Office of Pollution Prevention and Toxics (OPPT), which is charged with the implementation of the Toxic Substances Control Act (TSCA) and the Pollution Prevention Act (PPA).

Central to the administration of TSCA is the management of the TSCA Inventory. Section 8 (b) of TSCA requires EPA to compile, keep current, and publish a list of each chemical substance that is manufactured or processed in the United States. Companies are required to verify the TSCA status of any substance they wish to manufacture or import for a TSCA-related purpose. For more information, please refer to the TSCA Chemical Substance Inventory website: http://www.epa.gov/opptintr/existingchemicals/pubs/tscainventory/basic.html.

TSCA and DfE Alternatives Assessments

Substances selected for evaluation in a DfE Alternatives Assessment generally fall under the TSCA regulations and therefore must be listed on the TSCA inventory, or be exempt or excluded from reporting before being manufactured in or imported to, or otherwise introduced in commerce in, the United States. For more information see http://www.epa.gov/oppt/newchems/pubs/whofiles.htm.

To be as inclusive as possible, DfE Alternatives Assessments may consider substances that may not have been reviewed under TSCA, and therefore may not be listed on the TSCA inventory. DfE has worked with stakeholders to identify and include chemicals that are of interest and likely to be functional alternatives**,** ***regardless of their TSCA status***. Chemical identities are gathered from the scientific literature and from stakeholders and, for non-confidential substances, appropriate TSCA identities are provided.

Persons are advised that substances, including DfE-identified functional alternatives, may not be introduced into U.S. commerce unless they are in compliance with TSCA. Introducing such substances without adhering to the TSCA provisions may be a violation of applicable law. Those who are considering using a substance discussed in this report should check with the manufacturer or importer about the substance's TSCA status. If you have questions about reportability of substances under TSCA, please contact the OPPT Industrial Chemistry Branch at 202-564-8740.

Table 3-2 presents the potentially viable flame retardant alternatives included in this assessment, along with a summary of the polymers in which they are most often used, and end-use products into which the polymers are incorporated. The chemicals in Table 3-2 are additive flame retardants unless otherwise noted. Their modes of flame-retardant action are also given in Table 3-2 and discussed in Section 3.4. These modes of action include:

- CA - C: Chemical action in condensed phase,
- CA - G: Chemical action in gas phase,
- HS: Heat sink,
- CF: Char former,
- I: Intumescent[10], and
- D: Dilution effect

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[10] Intumescence is when a compound swells as a result of heat exposure, thus increasing in volume, and decreasing in density.

Table 3-2: Summary of Chemicals for Assessment with Polymer and End-Use Application

Flame Retardant Chemicals for Assessment[1]	Chemical Abstracts Service Registry Number (CASRN)	Polymer Applications[2]	End-Use Applications[3]									Mode of Action[4]
			Electronics	Wire and Cable	Public Buildings	Construction Materials	Automotive	Aviation	Storage and Distribution Products	Textiles	Waterborne emulsions & coatings	
Decabromodiphenyl ether, decaBDE	1163-19-5	Chlorinated polyethylene (CPE)	✓	✓								CA - G + CA - C (with metal hydroxide [HS])
		Elastomers	✓	✓	✓	✓	✓	✓				
		Emulsions								✓	✓	
		Engineering Thermoplastic	✓				✓				✓	
		High-impact polystyrene (HIPS)	✓									
		Polyethylene (PE)	✓	✓	✓	✓	✓	✓	✓			
		Polypropylene (PP)	✓	✓			✓		✓			
		Thermosets	✓		✓	✓						
Aluminum diethylphosphinate	225789-38-8	Elastomers	✓	✓			✓	✓				CF + I +HS
		Epoxy resins	✓				✓	✓				
		PA	✓				✓	✓		✓		
		Polybutylene terephthalate (PBT)	✓				✓	✓				
		Polyethylene terephthalate (PET)	✓				✓	✓		✓		
		Thermoplastic polyurethane (TPU)		✓								

[1] For full chemical name and relevant trade names see the synonym section of the individual profiles in Section 4.8.

[2] If a polymer is not listed for any specific flame retardant, then the flame retardant is not functional in that material application

[3] All categories may include military uses

[4] CA - C: Chemical action in condensed phase, CA - G: Chemical action in gas phase. Physical action can be HS: Heat sink, CF: Char former, I: Intumescent, or D: Dilution effect.

Flame Retardant Chemicals for Assessment[1]	Chemical Abstracts Service Registry Number (CASRN)	Polymer Applications[2]	End-Use Applications[3]									Mode of Action[4]
			Electronics	Wire and Cable	Public Buildings	Construction Materials	Automotive	Aviation	Storage and Distribution Products	Textiles	Waterborne emulsions & coatings	
Aluminum hydroxide	21645-51-2; 8064-00-4	Elastomers		✓	✓	✓	✓	✓				HS + I
		Emulsions								✓		
		Ethylene vinyl acetate (EVA)		✓	✓	✓	✓	✓				
		PE		✓	✓	✓	✓	✓				
		Thermosets	✓		✓	✓	✓	✓			✓	
Ammonium polyphosphate	68333-79-9; 14728-39-3	Elastomers		✓								CA - C + I
		Emulsions								✓	✓	
		PE		✓	✓	✓			✓			
		PP	✓	✓	✓	✓	✓		✓			
		Thermosets			✓	✓		✓	✓			
Antimony trioxide (Used as a synergist only)	1309-64-4	Elastomers	✓	✓	✓	✓	✓	✓	✓		✓	CA - G (synergists)
		Emulsions							✓		✓	
		Engineering Thermoplastic	✓	✓	✓	✓	✓	✓				
		HIPS	✓	✓	✓	✓	✓	✓	✓			
		PE	✓	✓	✓	✓	✓	✓	✓			
		PP	✓	✓	✓	✓	✓	✓	✓			
		Polyvinyl chloride (PVC)	✓	✓	✓	✓	✓			✓		
		Thermosets	✓		✓	✓						

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[3] All categories may include military use

[4] CA - C: Chemical action in condensed phase, CA - G: Chemical action in gas phase. Physical action can be HS: Heat sink, CF: Char former, I: Intumescent, or D: Dilution effect.

Flame Retardant Chemicals for Assessment[1]	Chemical Abstracts Service Registry Number (CASRN)	Polymer Applications[2]	End-Use Applications[3]									Mode of Action[4]
			Electronics	Wire and Cable	Public Buildings	Construction Materials	Automotive	Aviation	Storage and Distribution Products	Textiles	Waterborne emulsions & coatings	
Bis (hexachlorocyclopentadieno) cyclooctane	13560-89-9	CPE	✓	✓							✓	CA - G + CF; CA - G + CA - C (with metal hydroxide oxide [HS])
		Elastomers	✓	✓	✓	✓						
		Engineering Thermoplastic	✓									
		HIPS	✓									
		PE	✓	✓	✓	✓						
		PP	✓	✓								
		Thermosets	✓		✓	✓					✓	
Bisphenol A bis-(diphenyl phosphate)	5945-33-5; 181028-79-5 (reaction products)	Polyphenylene ether – high-impact polystyrene (PPE-HIPS)	✓									CA - C + CF; (synergist)
		PC	✓									
		Polycarbonate-acrylonitrile butadiene styrene (PC-ABS)	✓									
Brominated Epoxy Polymer(s)	Confidential	Acrylonitrile butadiene styrene (ABS)	✓									CA - G
		HIPS	✓									
		PE							✓			

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Flame Retardant Chemicals for Assessment[1]	**Chemical Abstracts Service Registry Number (CASRN)**	**Polymer Applications**[2]	**End-Use Applications**[3]									**Mode of Action**[4]
			Electronics	**Wire and Cable**	**Public Buildings**	**Construction Materials**	**Automotive**	**Aviation**	**Storage and Distribution Products**	**Textiles**	**Waterborne emulsions & coatings**	
Brominated Epoxy Polymers	68928-70-1	ABS	✓									CA - G + CA - C (with metal hydroxide [HS])
		HIPS	✓									
		Nylon	✓				✓					
		PBT	✓				✓					
		Unsaturated polyester (UPE)			✓	✓						
Mixture of Brominated Epoxy Polymer(s) and Bromobenzyl Acrylate	Confidential	ABS	✓									CA - G
		HIPS	✓									
		PE							✓			
Brominated epoxy resin end-capped with tribromophenol	135229-48-0	ABS	✓									CA - G + CA - C (with metal hydroxide [HS])
		HIPS	✓									
		Nylon	✓				✓					
		PBT	✓				✓					
		UPE			✓	✓						
Brominated polyacrylate	59447-57-3	PA	✓				✓					CA - G
		PBT	✓				✓					
		PP	✓				✓		✓			
		PE							✓			

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Flame Retardant Chemicals for Assessment[1]	Chemical Abstracts Service Registry Number (CASRN)	Polymer Applications[2]	End-Use Applications[3]									Mode of Action[4]
			Electronics	Wire and Cable	Public Buildings	Construction Materials	Automotive	Aviation	Storage and Distribution Products	Textiles	Waterborne emulsions & coatings	
Brominated poly(phenylether)	Confidential	CPE	✓	✓							✓	CA - G
		Elastomers	✓	✓	✓	✓	✓		✓			
		Emulsions								✓	✓	
		Engineering Thermoplastics	✓	✓			✓				✓	
		HIPS	✓									
		PE	✓	✓	✓	✓	✓		✓			
		PP	✓	✓			✓		✓		✓	
		Thermosets	✓		✓	✓						
Brominated polystyrene	88497-56-7	PA	✓				✓					CA - G
		PET	✓									
		PBT	✓									
		Thermoplastic polyester	✓									
		Thermoset polyester	✓									

[1] For full chemical name and relevant trade names see the synonym section of the individual profiles in Section 4.8.

[2] If a polymer is not listed for any specific flame retardant, then the flame retardant is not functional in that material application

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Flame Retardant Chemicals for Assessment[1]	Chemical Abstracts Service Registry Number (CASRN)	Polymer Applications[2]	End-Use Applications[3]									Mode of Action[4]
			Electronics	Wire and Cable	Public Buildings	Construction Materials	Automotive	Aviation	Storage and Distribution Products	Textiles	Waterborne emulsions & coatings	
Decabromodiphenyl ethane	84852-53-9	CPE	✓	✓							✓	CA - G + CA - C (with metal hydroxide [HS])
		Elastomers	✓	✓	✓	✓	✓		✓			
		Emulsions								✓	✓	
		Engineering Thermoplastics	✓	✓			✓				✓	
		HIPS	✓									
		PE	✓	✓	✓	✓	✓		✓			
		PP	✓	✓			✓		✓		✓	
		Thermosets	✓		✓	✓						
Ethylene bis-tetrabromophthalimide	32588-76-4	CPE		✓							✓	CA - G; CA - C (Increased thermal stability)
		Elastomers				✓						
		Engineering Thermoplastic	✓									
		HIPS	✓									
		PE	✓	✓	✓	✓	✓		✓			
		PP	✓	✓	✓	✓	✓		✓			
Magnesium hydroxide[5]	1309-42-8	Elastomers		✓	✓	✓	✓	✓				CF + HS
		EVA		✓	✓	✓	✓	✓				
		PA	✓									
		PE		✓	✓	✓	✓	✓	✓			
		PP		✓	✓	✓	✓	✓	✓		✓	

[1] For full chemical name and relevant trade names see the synonym section of the individual profiles in Section 4.8.

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[3] All categories may include military uses

[4] CA - C: Chemical action in condensed phase, CA - G: Chemical action in gas phase. Physical action can be HS: Heat sink, CF: Char former, I: Intumescent, or D: Dilution effect.

[5] Previously assessed by Design for the Environment (DfE) in other alternatives assessments (http://www.epa.gov/dfe/alternative_assessments.html)

Flame Retardant Chemicals for Assessment[1]	Chemical Abstracts Service Registry Number (CASRN)	Polymer Applications[2]	End-Use Applications[3]									Mode of Action[4]
			Electronics	Wire and Cable	Public Buildings	Construction Materials	Automotive	Aviation	Storage and Distribution Products	Textiles	Waterborne emulsions & coatings	
Melamine cyanurate	37640-57-6	PA	✓		✓	✓	✓	✓		✓	✓	HS + D
		PBT	✓		✓	✓	✓	✓		✓	✓	
		TPU	✓		✓	✓	✓	✓		✓	✓	
		UPE	✓		✓	✓	✓	✓		✓	✓	
Melamine polyphosphate[5,6]	15541-60-3	Epoxy resins	✓		✓	✓	✓	✓			✓	HS + D + CF
		PA	✓		✓	✓	✓	✓			✓	
		PBT	✓		✓	✓	✓	✓			✓	
		PE							✓			
		Phenolic based composites	✓		✓	✓	✓	✓			✓	
		PP							✓			
		TPU	✓		✓	✓	✓	✓			✓	
		UPE	✓		✓	✓	✓	✓			✓	
N-alkoxy hindered amine reaction products	191680-81-6	PE thin films				✓				✓		CA - G
		PP thin films and fibers				✓				✓		
Phosphonate oligomer[7]	68664-06-2	Thermosets	✓		✓	✓						CA - C; CF

[1] For full chemical name and relevant trade names see the synonym section of the individual profiles in Section 4.8.

[2] If a polymer is not listed for any specific flame retardant, then the flame retardant is not functional in that material application

[3] All categories may include military uses

[4] CA - C: Chemical action in condensed phase, CA - G: Chemical action in gas phase. Physical action can be HS: Heat sink, CF: Char former, I: Intumescent, or D: Dilution effect.

[5] Previously assessed by DfE in other alternatives assessments (http://www.epa.gov/dfe/alternative_assessments.html)

[6] This CASRN is specifically for Melamine Pyrophosphate. Please consult the Chemical Considerations section of this chemical's hazard profile for additional identity information on the closely related melamine phosphate salts that are anticipated to have similar hazard profiles.

[7] Also available as a reactive oligomer to react with the host polymer system

Flame Retardant Chemicals for Assessment[1]	Chemical Abstracts Service Registry Number (CASRN)	Polymer Applications[2]	End-Use Applications[3]									Mode of Action[4]
			Electronics	Wire and Cable	Public Buildings	Construction Materials	Automotive	Aviation	Storage and Distribution Products	Textiles	Waterborne emulsions & coatings	
Phosphoric acid, mixed esters with [1,1’-bisphenol-4,4’-diol] and phenol	1003300-73-9	PPE-HIPS	✓				✓	✓				CA – C + CF; (synergist)
		PC	✓				✓	✓				
		PC-ABS	✓				✓	✓				
Polyphosphonate	68664-06-2	Elastomers	✓	✓	✓	✓	✓	✓				CA - C; CF
		Engineering Thermoplastic	✓		✓	✓	✓	✓		✓		
Poly[phosphonate-co-carbonate]	77226-90-5	Elastomers	✓	✓	✓	✓	✓	✓				CA - C; CF
		Engineering Thermoplastic	✓		✓	✓	✓	✓				
Red phosphorus	7723-14-0	Elastomers		✓								CA - G + CA - C
		Emulsions					✓				✓	
		Epoxy resins	✓				✓	✓			✓	
		PA	✓	✓				✓				
		PA 66 GF	✓									
		PP	✓	✓								
Resorcinol bis-diphenylphosphate	125997-21-9; 57583-54-7	PPE-HIPS	✓									CA - C + CF; synergist
		PC-ABS	✓									

[1] For full chemical name and relevant trade names see the synonym section of the individual profiles in Section 4.8

[2] If a polymer is not listed for any specific flame retardant, then the flame retardant is not functional in that material application

[3] All categories may include military uses

[4] CA - C: Chemical action in condensed phase, CA - G: Chemical action in gas phase. Physical action can be HS: Heat sink, CF: Char former, I: Intumescent, or D: Dilution effect.

Flame Retardant Chemicals for Assessment[1]	Chemical Abstracts Service Registry Number (CASRN)	Polymer Applications[2]	End-Use Applications[3]									Mode of Action[4]
			Electronics	Wire and Cable	Public Buildings	Construction Materials	Automotive	Aviation	Storage and Distribution Products	Textiles	Waterborne emulsions & coatings	
Substituted amine phosphate mixture	66034-17-1 and confidential	Elastomers	✓	✓	✓	✓	✓	✓	✓			CA - C; CF + I
		EVA		✓	✓	✓	✓	✓				
		PE	✓	✓	✓	✓	✓	✓	✓			
		PP	✓	✓	✓	✓	✓	✓	✓			
		TPU	✓	✓	✓	✓	✓	✓				
Tetrabromobisphenol A bis (2,3-dibromopropyl ether)	21850-44-2	Elastomers	✓		✓	✓	✓					CA - G + CA - C (with metal hydroxide [HS])
		PP	✓		✓	✓	✓					
Triphenyl phosphate[5]	115-86-6	PPE-HIPS	✓									CA - C + CF
		PC-ABS	✓									
Tris(tribromoneopentyl) phosphate	19186-97-1	PP	✓		✓	✓				✓		CA - G + CA - C + CF + I
Tris(tribromophenoxy) triazine	25713-60-4	ABS	✓									CA - G + CF + D
		HIPS	✓									
Zinc borate (Synergist for halogen and non-halogen)	138265-88-0; 1332-07-6	EVA	✓	✓	✓	✓	✓	✓			✓	HS + CF + CA - C
		PE	✓	✓	✓	✓	✓	✓	✓			
		PP	✓	✓	✓	✓	✓	✓	✓			

[1] For full chemical name and relevant trade names see the synonym section of the individual profiles in Section 4.8.

[2] If a polymer is not listed for any specific flame retardant, then the flame retardant is not functional in that material application

[3] All categories may include military uses

[4] CA - C: Chemical action in condensed phase, CA - G: Chemical action in gas phase. Physical action can be HS: Heat sink, CF: Char former, I: Intumescent, or D: Dilution effect.

[5] Previously assessed by DfE in other alternatives assessments (http://www.epa.gov/dfe/alternative_assessments.html)

Source: Personal communication with members of the partnership.

3.3 Flame Retardants Not Included in this Assessment

In addition to the chemicals listed in Table 3-2, the partnership considered other flame retardants for the assessment, including individual chemicals and materials. Section 3.3.1 describes chemicals that were identified as possible alternatives to decaBDE and the reasons they were excluded from the assessment. Sections 3.3.2 and 3.3.3 describe two general types of nanomaterials that were not assessed because EPA does not have sufficient experience to apply data from one form of a chemical substance (such as a bulk material) to a particular nanoform of that chemical.

3.3.1 Chemicals That Were Excluded from this Assessment

The chemicals listed in this section were identified as possible alternatives to decaBDE, but were not included in the alternatives assessment. Reasons for exclusion included:

- Not commercially available[11];
- The flame retardant is a blend of which a majority of the chemicals are included in the assessment;
- Compared to other chemicals being assessed, the flame retardant is used or has the potential to be used in only small quantities;
- Outside the scope of the project: not a flame retardant or not relevant to materials in the scope;
- The Hazard Evaluation Criteria (U.S. EPA 2011) cannot yet be applied to evaluation of nanomaterials;
- Regulatory action has been proposed or implemented making future use unlikely;
- Will be addressed qualitatively in this report;
- Limited use as a decaBDE replacement due to toxic byproducts or regulations; and
- Not functional in materials in which decaBDE has been used.

A summary of the chemicals which were discussed but not included in this assessment are listed in Table 3-3 with the reason for exclusion. Additionally, it is likely that the Partnership omitted some potential alternatives. For example, TBBPA carbonate oligomer (CASRN 94334-64-2; 71342-77-3) was mentioned but not identified as a high priority alternative and tetradecabromo-1,4-diphenoxybenzene (CASRN 58965-66-5) was not brought up during the survey of available alternatives. These chemicals and others not yet identified or currently under development may be included in future versions of this report.

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[11] Some flame retardants that are currently in the process of market commercialization are included in the list of flame retardants in Section 3.2.

Table 3-3: Chemicals Considered but Not Included in the Final Alternatives Assessment

Chemical Name	CASRN	Justification for Exclusion
1,2 - bis(pentabromophenoxy) ethane	61262-53-1	This chemical is no longer on the market. Neither is the similar but lower brominated 1,2 - bis(tribromophenoxy) ethane.
Ammonium polyphosphate + melamine + pentaerythritol		The flame retardant is a blend, of which the ammonium polyphosphate and melamine are included in the assessment.
Boehmite (Aluminum hydroxide oxide)	1318-23-6	Compared to other chemicals being assessed, it is used and/or has the potential to be only in small quantities. A similar but different compound to aluminum hydroxide.
Calcium molybdate (Powellite)	7789–82–4	This is more of a smoke suppressant than a stand-alone flame retardant and is for PVC.
Diphenyl cresyl phosphate (DPK)	26444-49-5	DPK is mostly used as plasticizer in PVC, and is not used as a decaBDE replacement.
Ethylenediamine-o-phosphate	14852-17-6	Compared to other chemicals being assessed, it is used and/or has the potential to be used in small quantities.
"Green Armor"	Confidential	The chemical is undergoing the Premanufacture Notice (PMN) review process at EPA.[1] The manufacturer prefers not to include this substance in the DfE process until PMN review is complete.
Huntite / hydromagnesite $Mg_3Ca(CO_3)(OH)_23H_2O$		Compared to other chemicals being assessed, it is used and/or has the potential to be used in small quantities.
KSS - Potassium 3-(phenylsulfonyl)benzenesulfonate	63316-43-8 (monosulfonate); 63316-33-6 (disulfonate)	KSS is mainly used in PCs, and not in PC blends.
Mesoporous silicate particles (MSPs)		The DfE Hazard Evaluation Criteria (U.S. EPA 2011) cannot yet be applied to evaluation of nanomaterials. EPA does not have sufficient experience to apply data from one form of a chemical substance (such as a bulk material) to a particular nanoform of that chemical. These materials are not assessed in this report but they are still of interest and are discussed in Section 3.3.3.

[1] Anyone who plans to manufacture or import a new chemical substance for a non-exempt commercial purpose is required by section 5 of TSCA to provide EPA with a PMN which must be submitted at least 90 days prior to the manufacture or import of the chemical.

Chemical Name	CASRN	Justification for Exclusion
Nanoclays		The DfE Hazard Evaluation Criteria (U.S. EPA 2011) cannot yet be applied to evaluation of nanomaterials. EPA does not have sufficient experience to apply data from one form of a chemical substance (such as a bulk material) to a particular nanoform of that chemical. These materials are not assessed in this report but they are still of interest and are discussed in Section 3.3.3.
Pentaerythritol	115-77-5	In contrast to melamine cyanurate and melamine polyphosphate, which are included in the assessment and can be used as flame retardants by themselves, pentaerythritol must be combined with melamine AND a phosphate to be effective and so is not included in this assessment as a stand-alone flame retardant
Phosphonic acid, (3-{[hydroxymethyl]amino}-3-oxopropyl)-dimethyl ester	20120–33–6	Limited use as a decaBDE replacement: this compound’s use in the United States is almost zero because it is used with compounds which can release formaldehyde.
Poly(aryl ether ketone) (PAEK – various suppliers – covers PEK, PEEK, PEKK, etc.)		Will be addressed qualitatively in the report: this is an inherently flame retardant (IFR) polymer (see Section 3.3.2).
Polyetherimde	61128-46-9	Will be addressed qualitatively in the report: this is an IFR polymer (see Section 3.3.2)
PET with built-in phosphorus on polyester backbone	25038-59-9	Not effective in most materials where decaBDE is currently used to meet required flammability standards. Therefore, the use of this chemical is limited and not a priority for assessment.
Short-Chain Chlorinated Paraffins (SCCPs) Medium-Chain Chlorinated Paraffins (MCCPs) Long-Chain Chlorinated Paraffins (LCCPs) very Long-Chain Chlorinated Paraffins (vLCCPs)	Chlorinated paraffins are categories of chemicals and defined as: $C_x H_{(2x-y+2)} Cl_y$ SCCPs: $10 \leq x \leq 13$, $3 \leq y \leq 12$ MCCPs: $14 \leq x \leq 17$, $3 \leq y \leq 15$ LCCPs: $18 \leq x \leq 20$, $5 \leq y \leq 17$ vLCCPs: $x \geq 21$, $y \geq 5$	EPA has entered into Consent Decrees with the major manufacturers of SCCPs that end manufacture and distribution of these substances in U.S. commerce. EPA has also proposed a Significant New Use Rule for any use of “alkanes, C12-13, chloro” (CASRN 71011-12-6). EPA is requiring all manufacturers of all CPs (which are not correctly listed on the TSCA Inventory) to submit TSCA section 5 premanufacture notices for these substances, where they will be evaluated for potential regulatory action. In addition, EPA is evaluating whether the manufacturing, processing, distribution in commerce, use and/or disposal of MCCPs and LCCPs should also be addressed under TSCA section 6(a).
Tetrabromobisphenol A	79-94-7	Was not identified as a prevalent alternative to decaBDE. Additionally, a full discussion of TBBPA manufacturing, process and hazard is provided in a previous DfE report (U.S. EPA 2008).
Tetrakis (hydroxymethyl) phosphonium, urea,	124–64–1	Not effective in most materials where decaBDE is currently used to meet required

Chemical Name	CASRN	Justification for Exclusion
chloride salts		flammability standards. Therefore, the use of this chemical is limited and not a priority for assessment.
Tricresyl phosphate	1330–78–5	Outside of the scope of this project: this is a plasticizer for PVC.
Tris (1,3-dichloropropyl-2) phosphate	13674–87–8	Previously assessed and limited use as a decaBDE replacement: this chemical is not used as a primary flame retardant in textile backcoatings and TDCPP was reviewed in DfE's Furniture Flame Retardancy Report (U.S. EPA 2005).
Tris (2-hydroxyethyl) isocyanurate	839-90-7	Not a flame retardant; part of a curing system for coatings.
Zinc molybdate	13767–32–3	Limited use as a decaBDE replacement: this is a potential alternative synergist to antimony trioxide when used in textiles. It is also a smoke suppressant. However, it is not a particularly viable alternative synergist because of cost and municipal water discharge restrictions.

3.3.2 Inherently Flame Retardant Materials

In addition to the use of flame retardant chemicals, flame retardancy can be achieved through the use of IFRs. IFR materials meet fire code standards without special processing or chemical additives. IFRs are not flammable, which means that the protection is built into the fiber and is less likely to be worn away or washed out (DuPont 2010). IFRs can be used in a multitude of materials, and are not limited to fibers. IFR technologies are used in textiles, electronics, aircraft, and ground transportation vehicles and may be used in place of decaBDE in some instances. Table 3-4 includes a few examples of IFRs, their attributes, and end-use products relevant to this assessment. Flame retardancy can also be achieved through the use of inherently flame retardant barriers that physically prevent fire spread to flammable materials. This report assessed flame retardant additives and did not assess polymers in which these additives are used nor these IFR materials for their own inherent hazard.

Table 3-4: Examples and Descriptions of Inherently Flame Retardant Materials

Inherently Flame Retardant Material	Description and Attributes	End Uses Relevant to this Assessment
Graphite impregnated foam	▪ Relatively new technology which is self-extinguishing and highly resistant to combustion. ▪ Can meet airline fire safety standards for the seats with a reduced dependency on flame-retarded fabric. (U.S. EPA 2005)	▪ Largely used in niche markets, e.g., general aircraft seating (U.S. EPA 2005)
Low heat release plastics (Nomex, Teflon)	▪ Characterized by lower heat release capacities. ▪ High melt temperature (if any), hard to process using conventional plastics processing methods. (Walters and Lyon 2003)	▪ Aircraft ▪ Firefighter apparel ▪ Soldier protection fabric ▪ Flame retardant tents (Nagarajan 2012)
Polyimides	▪ Linear polymers which contain a ring structure along the backbone. This backbone structure gives the polymer good high temperature properties. ▪ PIs have excellent physical properties and are used in applications where parts are exposed to harsh environments. ▪ Oxidative stability allows them to withstand continuous service in air at temps of 260°C. PIs will burn but they have a self-extinguishing property. (Modern Plastics and Charles A. Harper 1999)	▪ Wire enamel ▪ Bearings for appliances in aircrafts, seals and gaskets ▪ Flexible wiring and electrical motor insulation – used with film version of PI (Modern Plastics and Charles A. Harper 1999)
Polyketones	▪ Family of aromatic polyether ketones includes structures which vary in the location and number of ketonic and ether linkages on their repeat units including PEK, PEEK, PEEKK and other combinations. ▪ All have very high thermal properties due to their aromaticity of their back bones and are readily processed via injection molding. ▪ Toughness is high for such high-heat resistance materials. ▪ Low moisture absorption and good hydrolytic stability lend these materials to their applications. (Modern Plastics and Charles A. Harper 1999)	▪ Airplane and automobile engines (Modern Plastics and Charles A. Harper 1999)

Inherently Flame Retardant Material	Description and Attributes	End Uses Relevant to this Assessment
Geopolymers	▪ Polysialate family of inorganic matrices. ▪ Geopolymer is a two-part system consisting of an alumina liquid and a silica powder that cures at around 150°C. ▪ Low curing temperatures, high temperature resistance, and low cost. ▪ Compatible with carbon, glass, Kevlar, steel, cellulosics. (Nagarajan 2012)	▪ Items with high-use temperatures anticipated ▪ Engine exhaust system ▪ Aircrafts (Nagarajan 2012)
Liquid Crystal Polymer (LCP)	▪ Aromatic copolyesters - the presence of phenyl rings in the backbone gives chain rigidity, forming rod-like chain structures. ▪ Self-reinforcing with high mechanical properties. ▪ Known for high-temperature resistance, particularly heat-distortion temperature. ▪ Excellent mechanical properties, especially in flow direction. Good electrical insulation properties and low flammability. LCPs show little dimensional change when exposed to high temperatures and a low coefficient of thermal expansion. ▪ Can be high priced and often exhibit poor abrasion resistance. ▪ Can be injection molded on conventional equipment and regrind may be used. (Modern Plastics and Charles A. Harper 1999)	▪ Automotive ▪ Electrical chemical processing ▪ Household applications such as in ovens or microwave cookware (Modern Plastics and Charles A. Harper 1999)
Polyarylates	▪ Amorphous, aromatic polyesters prepared from dicarboxylic acids and bisphenols. ▪ Aromatic rings give the polymer good temperature resistance. ▪ Shows good toughness and ultraviolet resistance. ▪ Transparent and has good electrical properties. ▪ Abrasion resistance of polyarylates is superior to PC. ▪ Extreme rigidity of polymer chains (due to aromatic rings) leads to difficulty in processing. ▪ Polyarylates, while having low heat release, may not be IFR in all fire risk scenarios. (Modern Plastics and Charles A. Harper 1999)	▪ Automotive applications such as door handles, brackets, and headlamp and mirror housings ▪ Electrical applications for connectors and fuses (Modern Plastics and Charles A. Harper 1999)

3.3.3 Nanosilicates: Clays and Colloidal Solids

Nanosilicate clays and colloidal solids may be relevant considerations for alternative flame retardant formulations. The DfE Hazard Evaluation Criteria cannot yet be applied to evaluation of nanomaterials. EPA does not have sufficient experience to apply data from one form of a chemical substance (such as a bulk material) to a particular nanoform of that chemical. Nanomaterials are not assessed in this report but they are still of interest to the partnership and this section provides a brief overview, including applications and available hazard information on two relevant example materials: organoclays and mesoporous silicate particles (MSPs). The information in this section is not intended to be comprehensive but is rather a starting point to help the reader conduct further research. Additional books and peer-reviewed publication references on nanosilicate flame retardants are provided in Appendix A.

Organoclays

Organoclays were developed in the 1930s and 1940s (Theng 1974) and were originally used as rheological modifiers, additives used to thicken coating materials. They have since been modified and Cloisite organoclays are now designed for use in plastics and rubbers for applications including flame retardant synergists. The use of bentonite (Mehta and Weiss 1978) and organoclays (Jonas 1970; Breitenfellner and Kainmülle 1985; Shain 1987) as additives to flame retardant formulations is claimed in several older patents; just over ten years ago Gilman, Kashiwagi and Lichtenhan (1997) published a paper on “Nanocomposites as a revolutionary new flame retardant approach.” However, in the years that followed, it was discovered that adding organoclays to materials does not, by itself, enable materials to pass flame tests (Morgan 2006; Morgan and Wilke 2007). Organoclays improve flame retardant performance through synergistic actions, which has been documented for a variety of flame retardant additive types. When burned, organoclay particles in a nanocomposite move to the surface of the specimen increasing char strength and serving as a drip suppressant through formation of an insulating layer that can delay gasification. The typical loading amount varies between approximately three and six percent by weight (Gilman 1999; Gilman, Jackson et al. 2000).

Organoclays may pose a hazard to human health (minimal to moderate eye irritation, respiratory irritation observed in acute studies using high exposure levels, potential carcinogenicity) (US/International Council of Chemical Associations (ICCA) 2007), but the Organisation of Economic Cooperation and Development (OECD) has determined that organoclays are “of low priority for further work” (US/ICCA 2007).

Mesoporous silicate particles

MSPs can be thought of as holey silica ‘beads.’ Due to the large size of the pores, polymers interact with both the internal surfaces of the pores and the external surfaces of the particle, thereby forming a physically cross-linked polymer-particle network. The network created by the MSP, combined with their surface chemistry, improves the char barrier formed during combustion that reduces flame intensity while simultaneously improving the mechanical performance of the polymer into which they are compounded. (Some MSPs have surface areas in the range 200 to 1,200 m^2/g, uniform pores in the mesometric size range of 2 to 50 nm, and pore volumes between 0.20 and 2.0 cm^3/g (Pinnavaia, Roston et al.)). As with organoclays, MSPs on their own will not typically result in achieving flame retardancy, but by replacing a portion of the flame retardant loading with about 0.5 to 3 percent by weight MSPs, flame retardancy may be reached (Roston 2011).

Some MSP materials have been tested in various thermosets (e.g., glassy epoxy and polyester), and thermoplastics (e.g., PP, PE, and nylon 6) to assess their effectiveness as both a flame retardant agent and mechanical reinforcing agent. Some particles have demonstrated the ability to reduce fire intensity while simultaneously increasing the strength of the composite (Pinnavaia, Roston et al.). Test results have also shown a reduction in dripping during fires (Pinnavaia, Roston et al.). Manufacturer brochures state that their MSPs are low-toxicity submicron inorganic compositions that can be easily dispersed in a polymer matrix without the use of organic surface modification (University of California, Los Angeles (UCLA) 2009).

Layer-by-layer technology

Layer-by-layer (LbL) coatings are nanocomposite structures assembled by an alternate deposition of anionic and cationic monolayers onto a substrate (Li, Schulz et al. 2009; Kim, Harris et al. 2012). The deposition of the anionic monolayer and the cationic monolayer (collectively known as a bilayer) is repeated until a coating with the desired properties is created (Li, Schulz et al. 2009). Electrostatic, van der Waals, covalent, and hydrogen bonds hold the monolayers together in LbL coatings (Kim, Harris et al. 2012; Carosio, Blasio et al. 2013). The LbL deposition technique was discovered in 1966, developed in the 1990s, and was reported in 2009 as being used for developing flame-retardant coatings (Li, Schulz et al. 2009; Li, Schulz et al. 2010; Apaydin, Laachachi et al. 2013). Flame-retardant LbL coatings are gaining attention beyond just the areas of academic research and development. Some industrial companies are now pursuing internal studies on the effectiveness of LbL coatings as flame retardants in commercial products including fabrics, foams, and films. Research has shown that LbL coatings can be effective flame retardants for a number of different substrates including cotton fabric (Li, Schulz et al. 2009; Laufer, Kirkland et al. 2012b), polyurethane foam (Kim, Harris et al. 2012; Laufer, Kirkland et al. 2012a), PC (Carosio, Blasio et al. 2013), nylon 6 (Apaydin, Laachachi et al. 2013), and PET (Carosio, Laufer et al. 2011). Specifically, some clay-based LbL coatings have been shown to effectively decrease the flammability of materials by generating a protective intumescent char layer when exposed to flames that limits heat and mass transfer (Li, Mannen et al. 2011; Kim, Harris et al. 2012; Laufer, Kirkland et al. 2012a; Apaydin, Laachachi et al. 2013). Montmorillonite clay (MMT) has proved to be compatible in the LbL process and effective as a flame retardant; the clay requires little processing prior to deposition because it is a naturally-occurring, inherently anionic material that is known to catalyze char formation (Bourbigot, Gilman et al. 2004; Kim, Harris et al. 2012; Apaydin, Laachachi et al. 2013). Recently, LbL flame retardant formulations formed solely from natural feedstocks (Chitosan and MMT) were used to provide flame retardancy for polyurethane foam with significant reductions in flame spread and heat release (Laufer, Kirkland et al. 2012a). Another system using strictly plant-based matter (Chitosan and phytic acid) was found to deliver localized intumescent protection for cotton fabrics from 100% renewable resources (Laufer, Kirkland et al. 2012b).

3.4 Flame Retardant Modes of Action

Polymer combustion is a complex process involving a number of interrelated and interdependent stages. It is possible to decrease the overall rate of polymer combustion by interfering with one or more of these stages. The basic mechanisms of flame retardancy will vary depending on the flame retardant and polymer system. Flame retardants can be classified based on the phase (solid or gas) in which they act to reduce or prevent propagation of flame. Other flame retardants may form protective barriers over a polymer which may insulate the flammable polymer from heat or reduce the amount of polymer that is available to burn as fuel.

3.4.1 Chemical Action in Condensed and Gas Phases

During fire, significant polymer degradation can occur due to heat in the condensed phase (1 mm from the flame/polymer interface), giving rise to volatile species that are liberated into the gas phase of the flame. Flame retardant compositions can either act on the condensed phase or the gas phase.

Radical Scavengers in the Gas Phase

Radical scavengers are also classified as chemical action flame retardant additives as they modify the radical process in the gas phase through chemical interaction with highly reactive species.

Halogenated Flame Retardants:

Halogenated flame retardants (e.g., decaBDE) mainly work through this mode of action by interfering with the gas phase of the combustion process (Troitzsch 1998). The mechanism of action of these types of flame retardants is shown in Figure 3-1. First, the flame retardant material breaks down and releases halogen radicals ($X^\bullet$) that react with the polymeric material (RH). The resulting reaction forms the corresponding halide (HX). The highly reactive radicals, hydrogen ($H^\bullet$) and hydroxyl ($OH^\bullet$), are responsible for degradation of volatile polymeric species into low molecular weight (MW) fragments. These radicals react with HX to produce less reactive (more stable) species, in some cases water, as shown in Figure 3-1. The addition of a catalytic amount of HX reduces the overall rate of combustion in this chain reaction (Hastie 1973). Consequently, the heat release rate and the heat transferred to the polymer are also reduced. When the gas phase is saturated with less reactive radicals or species, the conditions for limiting combustion can be reached, thus extinguishing the flame.

Figure 3-1: Mechanism of action of halogenated flame retardant

$$X^\bullet + RH \rightarrow R^\bullet + HX$$

$$HX + H^\bullet \rightarrow H_2 + X^\bullet$$

$$HX + OH^\bullet \rightarrow H_2O + X^\bullet$$

Source: Troitzsch 1998

Many aliphatic and aromatic halogenated flame retardants have been developed to meet specific compatibility requirements with commercial plastics. Brominated flame retardants are the preferred choice of halogenated flame retardants from a manufacturing standpoint due to their cost effectiveness, effectiveness at low loading levels for some applications, and ease of processing (minimal/no detrimental effect on polymer processing). This preferability does not consider hazard, risk, or performance.

Intumescents, Organic Char Forming Compounds and Radical Scavengers in the Condensed Phase

In the condensed phase, flame retardants can form protective barriers, which may be through intumescence or char formation, to prevent the propagation of flames. Phosphorous-based (e.g., ammonium polyphosphate, melamine polyphosphate) and nitrogen-based (e.g., melamine cyanurate) flame retardants both act in this way.

Some flame retardants cover the flammable polymer surface with a non-flammable protective coating. This helps insulate the polymer from the source of heat, reducing the formation of combustible breakdown products and release to the gas phase. The non-flammable coating may also prevent gaseous oxidants (e.g., oxygen from the air) from contacting the polymer surface. Intumescent compounds, which swell as a result of heat exposure, lead to the formation of a protective barrier in which the gaseous products of polymer decomposition are trapped.

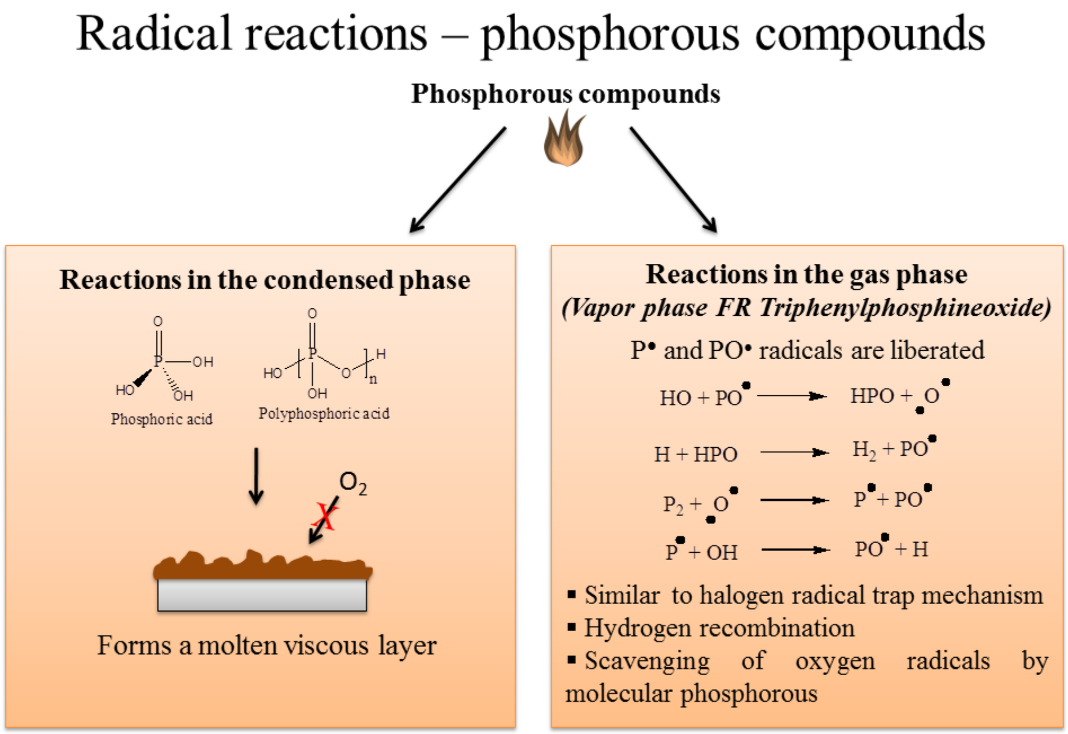
Alternatively, a non-flammable layer can be directly applied to the surface of the polymer to form a non-intumescent barrier coating. The formation of a thermally insulating char layer significantly influences subsequent degradation by serving as a protective coating layer preventing oxygen supply to the condensed phase. The properties of the char layer can further be bolstered by the presence of inorganic compounds. Many phosphorus-containing compounds form such non-intumescent surface chars. Char formation has several roles in flame retarding action. Char formation during combustion is an energy intensive process and occurs at the expense of other undesirable degradation reactions. There is dilution of the flame zone, and reduction in the amount of fuel available for further degradation (Kuryla 1979).

As mentioned above, both phosphorous- and nitrogen-based flame retardants work in the condensed phase. Below is a discussion on the modes of actions for these flame retardants.

Phosphorous Based Flame Retardants:

Phosphorous based flame retardants work efficiently in the condensed phase during combustion of a polymer. When heated, phosphorous reacts to produce phosphoric acid derivatives as shown in Figure 3-2. This acid is responsible for the formation of a glassy layer, which prevents flame propagation. Phosphorous-based flame retardants also generate intumescent char which acts as a two way barrier, namely hindering passage of combustible gas from the polymer to the flame and shielding the polymer layer from the flame. A range of phosphorous-based compounds including phosphines, phosphine oxides, phosphonium compounds, phosphonates, phosphinates, elemental red phosphorus, phosphites and phosphates are used as flame retardant additives. Phosphorus based flame retardants also include ammonium polyphosphate, melamine polyphosphate, and phosphate esters. Even though their predominant mode of action is through physical action (charring), there are certain proposed radical reactions that can take place during the combustion process as shown in Figure 3-2 (Carnaham, Haaf et al. 1979).

Figure 3-2: Mechanisms of flame retardant action in phosphorous based flame retardants



Source: Carnaham, Haaf et al. 1979

Inorganic phosphorus compounds are primarily used in PAs and phenolic resins, or as components in intumescent formulations. In the case of an intumescent material, a foamed char is developed on the surface upon combustion. In addition to char, intumescent materials can adhere to molten polymer, and help prevent dripping, which is necessary in fire quenching.

Nitrogen Based Flame Retardants:

Nitrogen-based compounds are often intumescent and were originally used in nitrogen-containing polymers such as polyurethanes and PAs. Melamine, melamine cyanurate, other melamine salts and guanidine compounds are currently the most used group of nitrogen-containing flame retardants. Melamine is used as a flame retardant additive for PP and PE. Melamine cyanurate is used as a flame retardant for PAs and polyesters (PET/PBT), epoxies and polyurethane resins. Melamine phosphate is also used in polyesters (PET/PBT).

3.4.2 Fillers / Diluents

Another mode of action is that exerted by inert solids incorporated into polymers. Such materials are known as fillers. Fillers include minerals like calcium carbonate or wollastonite. Sometimes the term filler gets used with magnesium and aluminum hydroxides due to their mineral structure. These mineral hydroxide fillers that impart flame retardant properties can be categorized as functional fillers. Metal hydroxides decompose with endothermicity when exposed to a fire and dilute the condensed phase of the burning polymer. These additives act as a heat sink, releasing water and/or carbon monoxide that interfere with combustion products in the vapor phase. As a result, fillers keep polymers cool and prevent them from thermally decomposing. Since fillers act predominantly via a physical rather than a chemical process, large loadings of fillers are needed to meet flammability standards.

3.4.3 Inorganic and Hydrated Compounds and Synergists

Metal hydroxides are the largest (by tonnage) class of all flame retardants used commercially and are employed alone or in combination with other flame retardants to achieve necessary improvements in flame retardancy. Metal hydroxides can function both in the condensed and gas phases of a fire by absorbing heat and decomposing to release their water. This process cools both the polymer and the flame and dilutes the flammable gas mixture. The high concentrations (typically 13 to 60 percent or greater by weight) required to impart flame retardants properties often adversely affect the mechanical properties of the polymer into which they are incorporated.

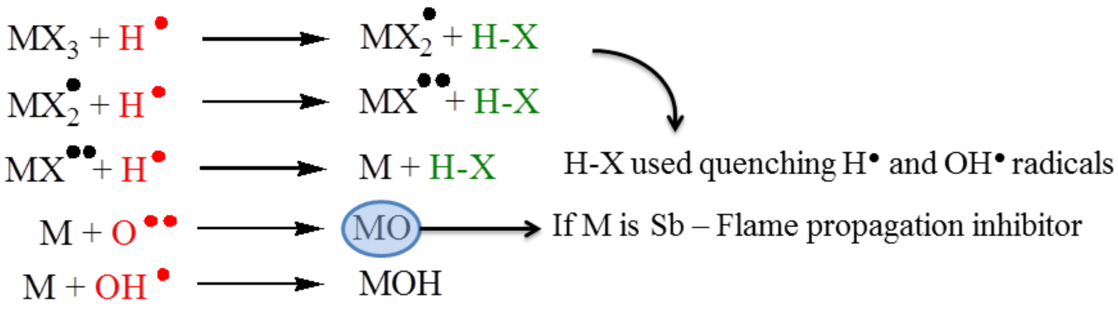
Aluminum hydroxide, also known as alumina trihydrate, is the largest volume flame retardant in use today. The low decomposition temperature (220-230°C), limits the polymers in which it can be incorporated. Magnesium hydroxide is stable to temperatures above 330-350°C and can be processed into several polymers.

Antimony trioxide may not be considered a flame retardant by itself but is often used as a synergist. It is used in plastics, rubbers, textiles, paper and paints with organochlorine and organobromine compounds to diminish the flammability of a wide range of plastics and textiles. Boron compounds display synergism with antimony oxide. Zinc borate can function as a flame retardant and smoke suppressant.

Antimony-based compounds are synergistic co-additives used in combination with halogenated flame retardants, facilitating the reduction in total amount of flame retardants required to achieve a desired level of flame retardancy. Antimony oxides and antimonates are converted to volatile species by halogen acids in the fire. The halogen acids react with the antimony-containing materials to form antimony trihalide and/or antimony halide oxide. The higher MWs of antimony halides in comparison to hydrogen halides, allow them to remain in the combustion zone longer, thus improving the efficiency of flame retardancy. This synergism only occurs in the presence of halogen flame retardants, as antimony does not react to form any other species in the presence of non-halogenated flame retardants.

Antimony oxychloride or trichloride reduces the rate at which the halogen leaves the flame zone, thus increasing the probability of reaction with the reactive species (i.e., hydroxyl radicals). The mechanism of action also involves radical scavenging as shown in Figure 3-3.

Figure 3-3: Synergistic Mechanism of Metal Halides Produced by a Combination of Halogen and Metal Oxides



Other Metal Based Compounds

Molybdenum compounds have been used as flame retardants in cellulosic materials and PVCs for many years and more recently with other polymers, mainly as smoke suppressants. Zinc compounds, such as zinc stannate and zinc hydroxy-stannate, are also used as synergists and as partial replacements for antimony trioxide.

3.4.4 Melting and Dripping

Some flame-retardant chemicals inhibit combustion by interfering with the transfer of heat from combustion back to the polymer (e.g., melamine cyanurate). Certain chemicals may promote depolymerization, which lowers the MW of the polymer and facilitates melting. As the burning melt drips away from the bulk of the polymer it carries with it a proportion of the heat that would otherwise contribute to polymer decomposition and volatilization. By reducing the release of volatile decomposition products into the gas phase, these flame retardants reduce the amount of gaseous decomposition products available to feed the flame. While enhanced melting should decrease flammability in theory, in practice droplets of burning molten polymer may help spread a fire to other combustible materials.

3.4.5 Smoldering (Non-Flaming) Combustion

Smoldering (non-flaming) combustion and the closely related phenomenon of glowing combustion (i.e., only embers are present) occur primarily with high-surface area polymeric materials that break down during combustion to form a residual carbonaceous char (typically cellulosic materials). In general, it is possible to inhibit non-flaming combustion either by retarding or preventing the initial breakdown of the polymer to form a char, or by interfering with the further combustion of this char. Boric acid and phosphates are the primary flame retardants used for preventing non-flaming combustion of organic polymers.

3.5 References

Apaydin, K., A. Laachachi, et al. (2013). "Polyallylamine-montmorillonite as super flame retardant coating assemblies by layer-by layer deposition on polyamide." Polymer Degradation and Stability **98**: 627-634.

Beyler, C. L. and M. M. Hirschler (2002). Thermal Decomposition of Polymers. In SFPE Handbook of Fire Protection Engineering, DiNenno, P.J.

Bourbigot, S., J. W. Gilman, et al. (2004). "Kinetic analysis of the thermal degradation of polystyrene-montmorillonite nanocomposite." Polymer Degradation and Stability **84**: 483-492.

Breitenfellner, B. and T. Kainmülle (1985). Flame-retarding, reinforced molding material based on thermoplastic polyesters and the use thereof. U.S.

Carnaham, J., W. Haaf, et al. (1979). Proceedings of Fourth International Conference of Flammability Standards, San Francisco.

Carosio, F., A. D. Blasio, et al. (2013). "Layer by layer nanoarchitectures for the surface protection of polycarbonate." European Polymer Journal **49**: 397-404.

Carosio, F., G. Laufer, et al. (2011). "Layer-by-layer assembly of silica-based flame retardant thin film on PET fabric." Polymer Degradation and Stability **96**: 745-750.

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

Danish Ministry of the Environment (2007). Health and Environmental Assessment of Alternatives to Deca-BDE in Electrical and Electronic Equipment. Environmental Protection Agency.

DuPont. (2010). "DuPont Personal Protection NOMEX Frequently Asked Questions." Retrieved February 10, 2011, from http://www2.dupont.com/Personal_Protection/en_US/products/Nomex/nomexind/nomex_industrial_faq.html#5QD.

European Chemicals Bureau (2007). Review on production processes of decabromodiphenyl ether (decaBDE) used in polymeric application in electrical and electronic equipment, and assessment of the availability of potential alternatives to decaBDE. Institute on Health and Consumer Protection.

Gilman, J. W. (1999). "Flammability and thermal stability studies of polymer layered-silicate (clay) nanocomposities." Applied Clay Science **15**: 31-49.

Gilman, J. W., C. L. Jackson, et al. (2000). "Flammability Properties of Polymer-Layered Silicate Nanocomposites. Polypropylene and Polystyrene Nanocomposites." Chemical Matter **12**: 1866-1873.

Gilman, J. W., T. Kashiwagi, et al. (1997). Nanocomposites: A revolutionary new flame retardant approach. 42nd International SAMPE Symposium.

Green, J. (2000). Chapter 5: Phosphorus-containing flame retardants. Fire Retardancy of Polymeric Materials, Grand, A.F., Wilkie, C.A. New York, Marcel Dekker**:** 147.

Hastie, J. W. (1973). "Molecular basics of flame inhibition." Journal of Research of the National Bureau of Standards **1973**(77A): 733-754.

Hirschler, M. M. (1992). Fire hazard and fire risk assessment; ASTM STP 1150. Amer. Soc. Testing and Materials, Philadelphia, PA.

Hirschler, M. M. (1994). Fire Retardance, Smoke Toxicity and Fire Hazard. Proceedings of Flame Retardants '94, London, UK.

Hirschler, M. M. (1998). Fire Performance of Poly(Vinyl Chloride) - Update and Recent Developments. Proceedings of Flame Retardants '98, London, UK, Interscience Communications.

Jonas, D. M. (1970). Solid polymer compositions having flame retardant and drip resistant properties and additive compositions for imparting said properties thereto. U.S.

Kim, Y. S., R. Harris, et al. (2012). "Innovative Approach to Rapid Growth of Highly Clay-Filled Coatings on Porous Polyurethane Foam." ACS Macro Letters **1**: 820-524.

Kuryla, W. C. (1979). Flame retardancy of polymeric materials. New York, Marcel Dekker.

Laufer, G., C. Kirkland, et al. (2012a). "Clay-Chitosan Nanobrick Walls: Completely Renewable Gas Barrier and Flame-Retardant Nanocoatings." ACS Appl Mater Interfaces **4**(3): 1643-1649.

Laufer, G., C. Kirkland, et al. (2012b). "Intumescent Mulitlayer Nanocoating, Made with Renewable Polyelectrolytes, for Flame-Retardant Cotton." Biomacromolecules **13**(9): 2843-2848.

Li, Y.-C., S. Mannen, et al. (2011). "Intumescent All-Polymer Multilayer Nanocoating Capable of Extinguishing Flame on Fabric." Advanced Materials **23**(34): 3926-3931.

Li, Y.-C., J. Schulz, et al. (2009). "Polyelectrolyte/Nanosilicate Thin-Film Assemblies: Influence of pH on Growth, Mechnical Behavior, and Flammability." ACS Appl Mater Interfaces **1**(10): 2338-2347.

Li, Y.-C., J. Schulz, et al. (2010). "Flame Retardant Behavior of Polyelectrolyte-Clay Thin Film Assemblies on Cotton Fabric." ACS Nano **4**(6): 3325-3337.

Lyons, J. W. (1970). The Chemistry and Use of Fire Retardants. New York, Wiley.

Mehta, R. K. S. and P. Weiss (1978). Bentonite/halogen flame retarding additive. US.

Modern Plastics and Charles A. Harper (1999). Modern Plastics Handbook McGraw Hill

Morgan, A. and C. A. Wilke (2007). Flame Retardant Polymer Nanocomposites. NY, John Wiley & Sons.

Morgan, A. B. (2006). "Flame retarded polymer layered silicate nanocomposites: a review of commercial and open literature systems." Polymers for Advanced Technologies **17**: 206-217.

Morose, G. (2006). An Investigation of Alternatives to Tetrabromobisphenol A (TBBPA) and Hexabromocyclododecane (HBCD) Prepared for: The Jennifer Altman Foundation.

Nagarajan, R. (2012). Personal Communication - Inherently Flame Retardant Materials. L. B. Emma Lavoie.

Nelson, G. L. (1998). "Carbon Monoxide and Fire Toxicity: A Review and Analysis of Recent Work." Fire Techonology **34**(1): 39-58.

Norwegian Pollution Control Agency (2009). Emerging New Brominated Flame Retardants in Flame Retarded Products and the Environment.

Peck, M. D. (2011). "Structure Fires, Smoke Production, and Smoke Alarms." J Burn Care Res **32**(5): 511-518.

Pinnavaia, T. J., G. P. Roston, et al. (2011). Mesoporous silicate particle as fire retardants in plastics. 22nd Annual Conference on Recent Advances in Flame Retardancy of Polymeric Materials, Stamford, CT.

Posner, S. and L. Boras (2005). Survey and technical assessment of alternative to Decabromodiphenyl ether (decaBDE) in plastics. The Swedish Chemicals Inspectorate. Stockholm.

Pure Strategies Inc. for Maine Department of Environmental Protection (2010). "Decabromodiphenyl Ether Flame Retardant in Plastic Pallets: A Safer Alternatives Assessment."

Roston, G. P. (2011). Personal Communication. Loading Levels in Nanomaterials. E-mail to Emma Lavoie and Lauren Brown.

Shain, A. L. (1987). Low smoke generating, high char forming, flame retardant thermoplastic multi-block copolyesters. U.S.

Theng, B. K. G. (1974). Interactions with Positively Charged Organic Species. The Chemistry of Clay-Organic Reaction. NY, John Wiley & Sons.

Troitzsch, J. H. (1998). "Overview of flame retardants, fire and fire safety, markets and applications, mode of action and main familites, role in fire gases and residues." Chemistry Today **16**(1/2): 18.

U.S. EPA. (2005). "Furniture Flame Retardancy Partnership: Environmental Profiles of Chemical Flame-Retardant Alternatives for Low-Density Polyurethane Foam (EPA 742-R-05-002A)." Retrieved November 18, 2013, from http://www.epa.gov/dfe/pubs/flameret/ffr-alt.htm.

U.S. EPA. (2008). "Flame Retardants in Printed Circuit Boards (Review Draft)." Retrieved November 18, 2013, from http://www.epa.gov/dfe/pubs/projects/pcb/full_report_pcb_flame_retardants_report_draft_11_10_08_to_e.pdf.

U.S. EPA. (2009). "Polybrominated Diphenyl Ethers (PBDEs) Action Plan." Retrieved November 18, 2013, from http://www.epa.gov/opptintr/existingchemicals/pubs/actionplans/pbdes_ap_2009_1230_final.pdf.

U.S. EPA. (2011). "Design for the Environment Program Alternatives Assessment Criteria for Hazard Evaluation (version 2.0)." Retrieved November 18, 2013, from http://www.epa.gov/dfe/alternatives_assessment_criteria_for_hazard_eval.pdf.

UCLA. (2009). "UC TSR&TP Amorphous Silica Literature Review." Retrieved March 2011, from http://www.maa.org/pubs/Calc_articles/ma002.pdf.

US/ICCA (2007). SIDS Initial Assessment Profile: Organoclays Category.

Walters, R. N. and R. E. Lyon (2003). "Molar Group Contributions to Polymer Flammability." J. App. Polym. Sci **87**: 548-563.

Washington State Department of Health (2008). Alternatives to Deca-BDE in Televisions and Residential Upholstered Furniture. Department of Ecology. Olympia, WA.

Weil, E. D. and S. Levchik (2004). "A Review of Current Flame Retardant Systems for Epoxy Resins." Journal of Fire Science **22**: 25-40.

Weil, E. D. and S. V. Levchik (2009). Flame Retardants for Plastics and Textiles: Practical Applications, Hanser.