Introduction to Brominated Flame Retardants: Commercially Products, Applications, and Physicochemical Properties

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Abstract In order to meet fire safety regulations, flame retardants (FRs) are applied to combustible materials such as polymers, plastics, wood, paper, and textiles. Approximately, 25% of all FRs contain bromine as the active ingredient. More than 80 different aliphatic, cyclo-aliphatic, aromatic, and polymeric compounds are used as brominated flame retardants (BFRs). BFRs, such as polibrominated biphenyls (PBBs), polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane (HBCD), and tetrabromobisphenol A (TBBPA), have been used in different consumer products in large quantities and consequently they were detected in the environment. In this chapter, an overview of the production, application, and properties of most commonly used BFRs is presented.

Keywords Brominated flame retardants, Hexabromocyclododecane, Polybrominated biphenyls, Polybrominated diphenyl ethers, Production, Tetrabromobisphenol A

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Abbreviations and Symbols

ABS	Acrylonitryle butadiene styrene
ATE	2,4,6-Tribromophenyl allyl ether
BEP	Brominated epoxy oligomers
BFR	Brominated flame retardant
BPS	Brominated polystyrene
BSEF	Bromine Science and Environmental Forum
BTBPE	1,2-Bis(2,4,6-tribromophenoxy)ethane
CERCLA	Comprehensive Environmental Response, Compensation and Liability Act
DBDPE	Decabromodiphenyl ethane
DPTE	2,3-Dibromopropyl-2,4,6-tribromophenyl ether
EBFRIP	European BFR Industry Panel
EPA	Environmental Protection Agency
EPCRA	Emergency Planning and Community Right-to-Know
EPS	Polystyrene foams
FIFRA	Federal Insecticide, Fungicide and Rodenticide Act
FR	Flame retardant
HBBz	Hexabromobenzene
HBCD	Hexabromocyclododecane
HIPS	High impact polystyrene
K_{OW}	Octanol–water partition coefficient
OSHA	Occupational Safety and Health Administration
PBB	Polybrominated biphenyl
PBDE	Polybrominated diphenyl ether
PBEB	Pentabromoethylbenzene
PBT	Pentabromotuelene
POP	Persistent organic pollutant
PVC	Polyvinyl chloride
REACH	Registration, Evaluation, Authorization and Registration of Chemicals

TBBPA	Tetrabromobisphenol-A
TBBPA-DAE	TBBPA diallylether
TBECH	1,2-Dibromo-4-(1,2-dibromoethyl)cyclohexane
TBP	2,4,6-Tribromophenol
TBPA	Tetrabromophthalic anhydride
USA	United States of America
XPS	Extructed polystyrene foams

1 Introduction

Fire is a major source of damage to properties, loss of life, and public expenses. For example, in the United States, in 2007 over 1.5 million fires are reported, which result in 17,675 injuries, 3,430 deaths, and direct losses of over $14 billion [1]. The need to protect materials against fire has been a scientific undertaking for a very long time. In fact, Egyptians used alum to reduce the flammability of wood (450 BC), and about 200 BC Romans used a mixture of alum and vinegar to reduce the combustibility of wood [2]. Today in order to meet fire safety regulations such as California TB 116 and 117, flame retardants (FRs) are applied to combustible materials such as plastics, woods, paper, and textiles. FRs are chemicals that are added to or reacted with combustible materials to increase their fire resistance [3]. Recent advances in technology have resulted in an increase in use of synthetic polymers in household and office products such as computers and electronic equipment, which has drastically contributed to potential fire hazard in our commercial and residential buildings; consequently, over the past decades, the use of FRs has drastically increased. To protect ourselves from fire damage, various types of FRs have been developed based on diverse inorganic compounds such as aluminum and magnesium hydroxides and organic derivatives of nitrogen, phosphorous, chlorine, and bromine as active ingredients.

It should be noted that flame or fire retardant is not the same as flame or fire proof; in the first case, the starting material is flammable, and the application of FR will slowdown the burning process, hence increasing the possibility of escaping from a burning room/house. However, flame or fire proof material does not catch fire at all [4]. Currently, the market demand for FRs is estimated to be valued about US$2.3 billion, corresponding to be in excess of 1,200,000 metric tons of which about 36% of the value is based on brominated flame retardants (BFRs) [5]. To understand the mode of actions of FRs, it is essential to become familiar with the combustion process. Combustion is a gas phase reaction involving a fuel source and oxygen. There are four steps involved in the combustion process, which are preheating, volatilization/decomposition, combustion, and propagation (Fig. 1) [6]. Thus, a FR should inhibit or suppress the combustion in a particular stage of this process [7]. Depending on their mode of action, FRs can act chemically and/or physically in the solid, liquid, or gas phase. It is important to note that the flammability of a material is not an intrinsic property but depends on the fire conditions. Thus, changing the material composition, for example with the addition of a FR, will also change its reaction to fire behavior [4].

For example, free radicals (highly oxidizing agents) are produced during the combustion process; these are essential elements for the flame to propagate. Halogens are very effective in trapping free radicals, hence removing the capability of the flame to propagate. All four halogens are very effective in trapping free radicals, with trapping efficiency of I > Br > Cl > F [4]. Organohalogen compounds are good materials for storage and delivery of halogens in the polymers. However, not all of the organohalogen compounds are suitable FRs. Fluorinated compounds are very stable and decomposed at much higher temperature than the polymers burn. On the other hand, iodinated compounds are not very stable and decompose at slightly elevated temperatures. Consequently, only organochlorine and organobromine compounds are suitable as FRs. With higher trapping efficiency and lower decomposing temperature, organobromine compounds have became more popular FR than their organochlorine counterparts [5].

2 Bromine Industry and Applications

Bromine is a major ingredient in the production of BFRs. Therefore, it is important to dedicate a few lines to the industrial production and applications of bromine. Bromine is used in the production of BFRs, clear brines for the oil drilling industry,

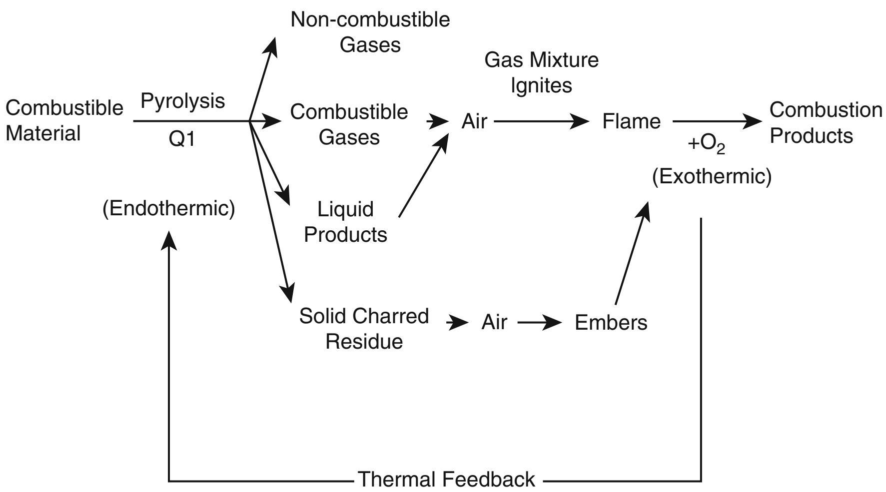

Fig. 1 Combustion process steps. Reproduced from [6]

soil and space fumigation products, and bromine-based biocides for water treatment. However, the main use of bromine is in the manufacturing of BFRs. For example, in the United States, between 40% and 50% of demand for bromine is for BFRs [8].

Bromine is a reactive element, consequently it is mostly found in the form of inorganic salts of the alkalis and alkaline earth metals mainly in seawater, saline lakes, brine, and earth crust. Currently, there are a limited number of brines around the world with high enough concentrations of bromine to make this process commercially viable. Arkansas brine wells with 2–5 g/L bromide are the main source of bromine in the United States [8]. Dead Sea with a concentration up to 12 g/L is the world's largest source of bromine [5].

The production of bromine begins with the oxidation of bromide with chlorine followed by an absorption and purification process. The global production of bromine in 2007 was 556,000 metric tons [8]. As shown in Fig. 2, United States was the largest producer of bromine followed by Israel. The global production of bromine has been fairly stable over the past decade. The emergence of Jordan as the third largest bromine producer is interesting; however, it was not unexpected based on the vast amounts of bromide present in the Dead Sea. China also has rich bromide sources, particularly in Laizhou Bay located in Shangong province [9]. In 2008, there was an increase in the price of bromine and brominated compounds, reflecting the expanding markets for bromine and major increases in energy costs, raw materials, regulatory compliance, and transportation [10]. In Table 1, the estimated world refinery production between 1997 and 2007 was summarized. Growth was expected to increase in demand for BFRs as the result of the Consumer Product Safety Commission approves fire safety standards for upholstered furniture in the United States and if more stringent flammability standards are voluntarily adopted for televisions in Europe. An increase in the global demand for bromine is expected as the use of BFRs in developing countries begin to use more modern materials and develop more stringent flammability standards [8].

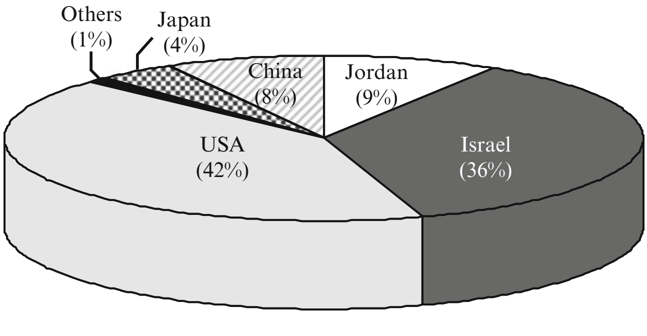

Fig. 2 Global production of bromine. Adapted from [8]

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