

# THE APPROPRIATE FIRE RETARDANT FOR APPLICATION IN EXPANDED POLYSTYRENE

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## Abstract

*This article deals with the fire retardants that are used in the expanded polystyrene, especially with the most frequently used brominated hydrocarbons. It describes the mechanism of decomposition and subsequent retardation effect of the fire retardants. An increased emphasis is laid on hexabromocyclododecane that is the most frequently used fire retardant nowadays. However, this substance will be soon forbidden. Therefore, alternative substances with a potential to replace HBCD are described at the end of the article.*

## Key words

*expanded polystyrene, fire retardation mechanism, hexabromocyclododecane*

## Introduction

The expanded polystyrene has a wide range of utilisation, but it is applied mainly in the construction industry as thermal and acoustic insulation component, as protection against vibrations and mechanical damage and recently even in the aesthetic area of architecture as an economically advantageous alternative for production of interior decorations. Similarly as the other polymer hydrocarbons, the expanded polystyrene is also flammable. In order to improve its fire-technical properties, fire retardants are used, similarly as in the case of many other materials.

## Retardants used in expanded polystyrene

The fire retardant treatment of the expanded polystyrene primarily uses the additive fire retardants. These are substances that are bonded physically in the polymer, what means that chemical bonds are not created between the fire retardant and the polymer chain. Besides indisputable advantages, such as relatively low price and simple preparation, the mentioned method brings also complications with the achievement of necessary homogeneity or with possible migration of particles of the fire retardant from the material. Furthermore, it is necessary to use the fire retardants, which achieve a satisfactory effect at the lowest possible concentrations, whereas the additives added to the polymers in higher quantities significantly aggravate their use properties.

The major fire retardants, which are used in the polystyrene, are hexabromocyclododecane (HBCD) and tetrabromobisfenol-A-diallylether, because these additives have a high efficiency in considerably small quantities (1 - 2 %). This amount can even be lowered (<1 %) in bead foam by addition of radical initiators such as organic peroxides. The organic peroxides such as dikumyl peroxide or compounds such as oligomeric of diisopropylbenzene are used as synergistic radical initiators (TROITZSCH, 2004).

Other substances that utilised as the fire retardants in the polystyrene are tetrabromocyclooctane, dibromoethyldibromocyclohexane (MOROSE, 2006), brominated polystyrene (MASAŘÍK, 2003), triphenyl phosphine oxide, triphenyl phosphate, triphenylphosphine sulphide and sulfur. (BEACH et al., 2008) Tetrabromobisphenol A (MUNN et al., 2006), eventually decabromodiphenyl oxide or octabromodiphenyl oxide (MASAŘÍK, 2003) are added into high-impact polystyrene and acrylonitrile-butadiene-styrene. In case of the extruded polystyrene, expanded graphite can also be used as a fire retardant (BASF Aktiengesellschaft, 2002).

Hilado states that following compounds are utilised as the fire retardants for foam polystyrene: tetrabromobisphenol-A-diallylether, tribromophenol allylether, hexabromocyclododecane, stabilized hexabromocyclododecane and halogenated phosphates (HILADO, 1998).

As we can see, the fire retardants, which are used in case of the expanded polystyrene, rank mostly among compounds that contain bromine. The quantities of bromine in the particular brominated fire retardants are shown in Table 1.

THE CONTENT OF BROMINE IN MOLECULES OF THE BROMINATED FIRE RETARDANTS

Table 1

Fire retardant	CAS number	Bromine content [% hm.]
hexabromocyclododecane	3194-55-6	74,71
tetrabromobisfenol-A-diallylether	25327-89-3	51,22
tetrabromocyklooctane	31454-48-5	74,71
Dibromoethyldibromocyclohexane	30262-02-3	74,71
Tetrabromobisphenol A	79-94-7	58,77
Octabromodiphenyl oxide	32536-52-0	79,77
Decabromo diphenyloxyde	1163-19-5	83,31
Allyl tribromophenyl ether	3278-89-5	64,64

### Retardation mechanism of bromine compounds

During thermal decomposition of substances that contain brominated fire retardant, gaseous hydrogen bromide is released. This process may occur in two ways:

1. Hydrogen bromide is broken away from the molecule of the fire retardant by dehydrohalogenation.
2. The cleavage of bonds between bromine and carbon leads to creation of bromide radical. The radical subsequently reacts with hydrogen from simpler molecules, which arise during the thermal degradation of base substance.

Hydrogen bromide that arises by one of the mentioned ways enters the reaction with ·OH and ·H radicals in gaseous phase. Exactly these radicals play an important role in combustion.

Their extinction leads to deceleration or to complete interruption of the combustion process. The bromide radical reacts further with simpler, hydrogen containing substances, which arise during the thermal decomposition of the substance, to form hydrogen bromide. In this way hydrogen bromide is renewed. The amount of the fire retardant, which is needed to achieve the required effect, is therefore much lower and thereby also its influence on use properties of the material is reduced.

The stability of halogen compounds varies as follows:  $F > Cl > Br > I$ . Iodine compounds are not sufficiently stable in order to be used commercially, whereas compounds containing fluorine are too stable in order to be generally useful. Generally, most of the used halogen fire retardants are compounds of bromine and chlorine. The bromine compounds are more effective than the chlorine compounds, but are considerably more expensive (ZHANG, 2004).

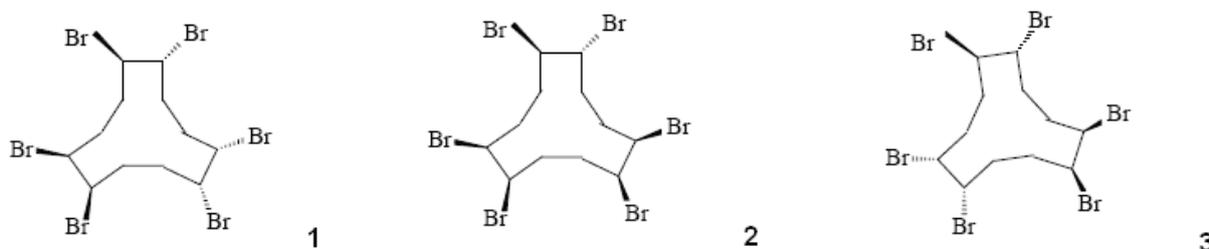
In practice, halogen fire retardants can be combined with other substances in order to achieve a synergistic effect. It means that the resulting effect of the applied fire retardants during thermal loading of the substance is higher than would be the sum of their individual retardation effects. In the case of polystyrene, for example, organic hydroxides can be applied as mentioned above. Properly selected combinations of the synergistic substances enable to minimize the amounts of the fire retardants, that are used and the final substance retains more markedly its original properties.

Besides chemical action, products of decomposition of the halogen fire retardants in gaseous phase have also physical effect. They create a partially inert atmosphere that makes the access of oxygen into the reaction zone of combustion difficult and the overall inhibitory effect is thereby boosted (MASAŘÍK, 2003).

### Hexabromocyclododecane

HBCD belongs to so-called brominated fire retardants and in English literature they can be found also under an abbreviation of BFR (Brominated Flame Retardants). It is a white powder with the initial decomposition temperature 210 °C. (MASAŘÍK, 2003) It has been used as the addition in EPS and XPS for more than 40 years (Building insulation: EPS...) and its production experiences a rapid growth since 1999 (KOVÁČIKOVÁ, 2002).

During the bromination of cyclododeca-1,5,9-triene, the way that the hexabromocyclododecane is produced, theoretically as many as 16 stereoisomers may arise. But practically, scientists managed to define only three stereoisomers, in technical mixtures of hexabromocyclododecane, labelled as alpha, beta and gamma (Fig. 1). (HEEB et al., 2005) Usually a mixture of these isomers of HBCD occurs at the market.



**Fig. 1** The main diastereoisomers in the technical HBCD (1  $\alpha$ HBCD, 2  $\beta$ HBCD, 3  $\gamma$ HBCD) (HEEB et al., 2005; modified by Rantuch)

Besides EPS and XPS, hexabromocyclododecane, as the fire retardant, is also added to fabrics that cover furniture, interior components of automobiles, glues and many polymer materials. It has high retardation effect already at very low quantities. It is supplied in the form of crystal powder. HBCD is soluble in organic solvents, mainly in alcohols, ketones and esters. If exposed to increased temperature as well as to ultraviolet radiation, it shows good stability. Hexabromocyclododecane is sold under a variety of names, for example HBCD, HBCDD or CD-75P. The most important producers of HBCD include the USA and Israel and Netherlands out of European countries. The consumption of HBCD in the European Union during 2003-2007 is listed in Table 2.

THE GROWTH OF CONSUMPTION OF HBCD IN THE EUROPEAN UNION (ECHA, 2009)

Table 2

Year	The consumption of HBCD in the EU [t]
2003	9 600
2004	9 750
2005	11 000
2006	11 580
2007	11 000

Out of 11 580 tons of HBCD that were utilised in the European Union in 2006, the vast majority was used in the polystyrene foams (Fig. 2).

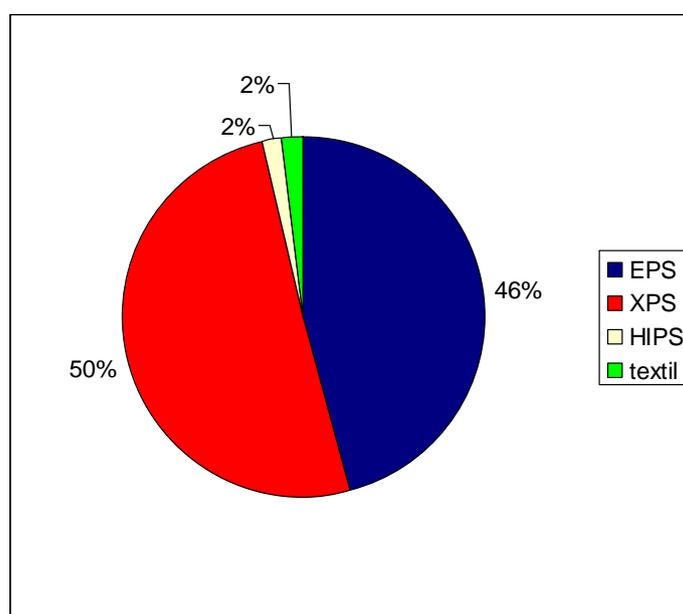
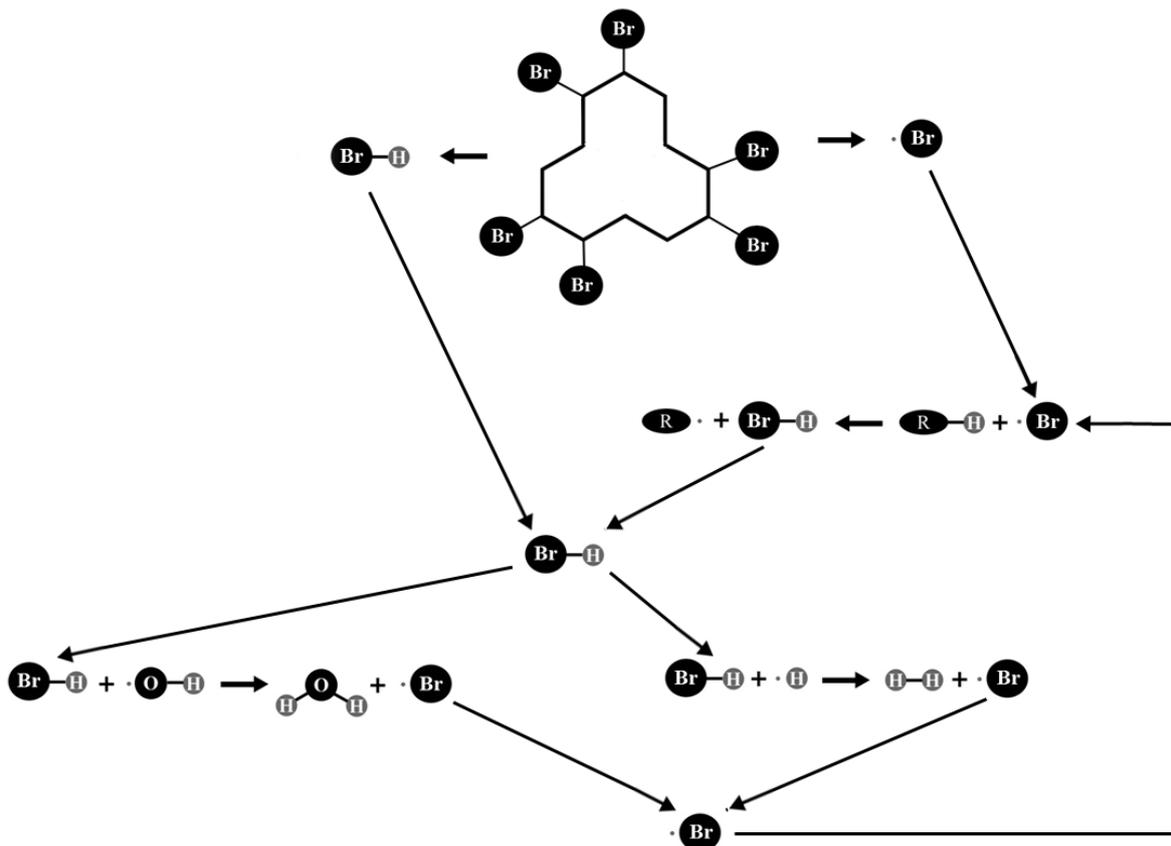


Fig. 2 The application of HBCD in various materials (according to: ECHA, 2009)

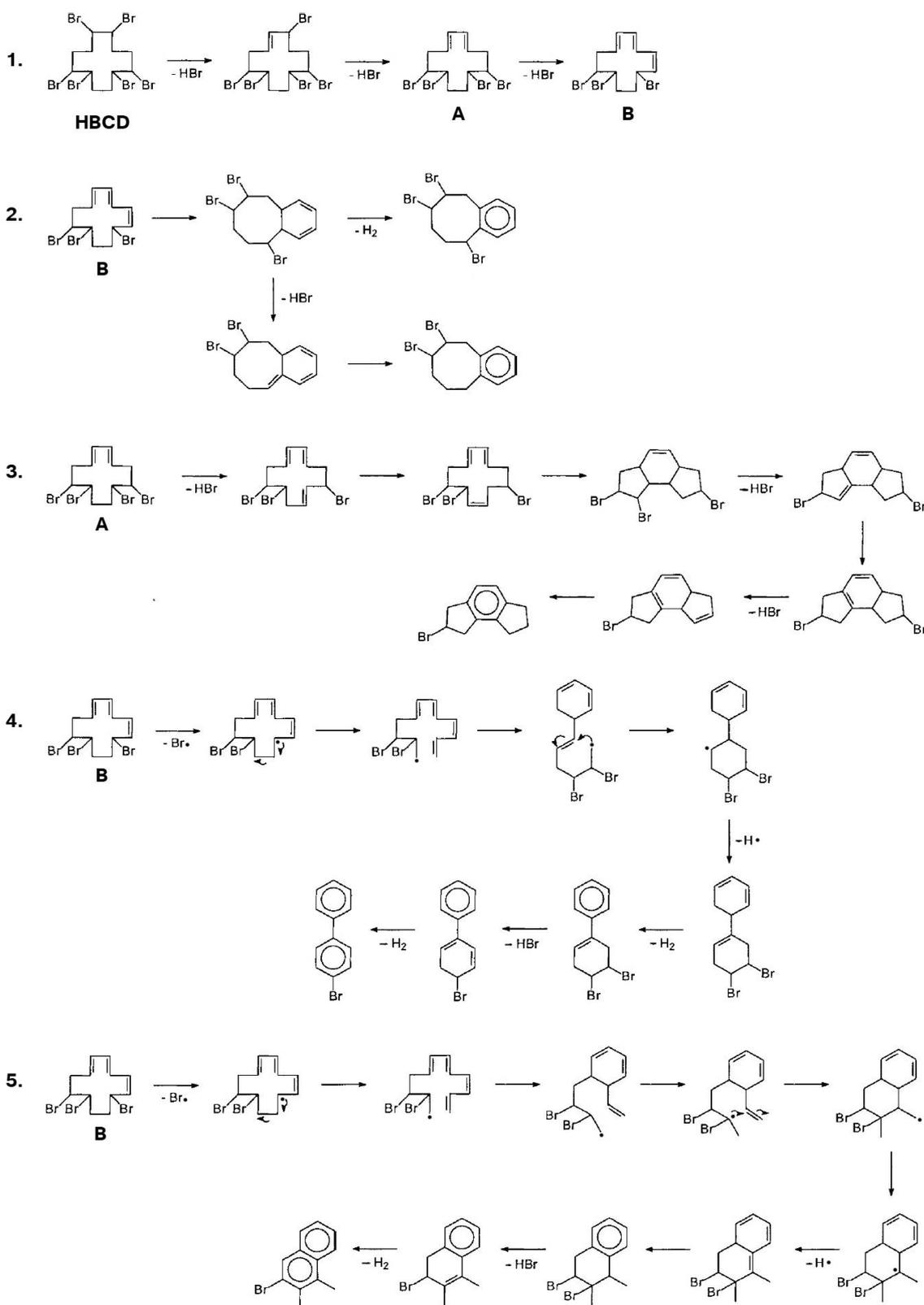
**The thermal decomposition of HBCD**

Equally as in all bominated fire retardants, it's the retardation effect of HBCD is based on the release of hydrogen bromide and bromine. The schematic illustration of the retardation effect of HBCD is shown in Fig. 3.



*Fig. 3 The diagram of the retardation effect of HBCD*

In their writings, Barontini, Cozzani, Cuzzola and Petarca dealt with the description of the thermal decomposition of HBCD. (BARONTINI et al., 2001) They define the decomposition products during thermal loading by means of gas chromatography-mass spectrometry. The schemes of the decomposition, that they proposed, are shown in Figure 4. But as the authors state further, Schemes 1 and 2 were designed by Larsen and Ecker in their writing that was published in 1986 (LARSEN, ECKER, 1986).



**Fig. 4** Proposed schemes of the thermal decomposition of HBCD (BARONTINI *et al.*, 2001; modified by Rantuch)

## **HBCD and human**

HBCD ranks among so-called bio accumulative substances. This means that it is cumulated in living organisms. It could be found for example in the bodies of birds, mammals, fish and other aquatic organisms. The human body absorbs it mainly through the digestive system and it accumulates in lipids (JANSSEN, 2005). During the tests, HBCD has been detected in the human body in the adipose tissue (JOHNSON-RESTREPO, ADAMS, KANNAN, 2008), blood (COVACI et al., 2006) or breast milk (COVACI et al., 2006; ABDALAH, HARRAD, 2011; Croes et al., 2012).

The 2008 report alleges that people could be exposed to HBCD that originates from several sources:

- working environment during the production of HBCD,
- industrial utilisation (HBCD is used as additive in the objects used in industry),
- use of consumer products,
- indirectly from the environment through food, soil, water and air.

According to the authors of the mentioned study, the release of HBCD by means of diffusion from waste that contains this substance (HBCD) as well as during the waste disposal could be important from the long-term point of view (EC, 2008).

### **The alternative fire retardants suitable for the expanded polystyrene**

In 2008, HBCD was classified as a substance that is a candidate for authorisation, and subsequently in 2011 its use in the European Union from 2015 was forbidden. For the mentioned reasons of gradual toughening of HBCD monitoring until its prohibition, the pressure is put on finding of appropriate alternative. In terms of the retardation of polystyrene foams, HBCD is hardly replaceable. Already at low concentrations of HBCD, the fire-technical characteristics of material are significantly improved. Recently, several substances were discovered with a potential to replace HBCD. One of them is brominated copolymer of butadiene-styrene. It was developed by Dow Global Technologies LLC Company. Butadiene-styrene is a stable substance with high molecular mass that does not belong to PBT. (The Dow Chemical Company, 2011) Whereas the butadiene-styrene copolymer ensures a good miscibility with the polystyrene, the presence of bromine atoms is responsible for retardation properties of the substance. It is offered for example under the names of Emerald 3000 and FR122P (EPA, 2012).

Another alternative fire retardant is Benzene,1,1'-(1-methylethylidene)bis[3,5-dibromo-4-(2,3-dibromo-2-methylpropoxy) ]. It is also available under the trade name of Pyroguard SR-130. It is a white powder with characteristic odour and the bromine content at least 63.5% (Eurošarm, 2007).

In the first half of 2012, Albemarle Company announced its intention to start the production of ecological fire retardant. This additive, named GreenCrest, is the fire retardant based on a polymer with high molecular mass. Albemarle plans to commercialize the production until 2014 (Albemarle, 2012).

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