REPORT TO TWENTY-FIFTH LEGISLATURE
STATE OF HAWAII
2009

DECABROMODIPHENYLETHER
AND FEASIBLE FLAME RETARDANT ALTERNATIVES

PURSUANT TO H.C.R. NO. 84, 2006
REQUESTING THE DEPARTMENT OF HEALTH
TO REVIEW THE AVAILABLE SCIENTIFIC RESEARCH ON
DECABROMODIPHENYL ETHER AND ASSESS THE
AVAILABILITY OF SAFER, EFFECTIVE, AND TECHNICALLY
FEASIBLE FLAME RETARDANTS THAT CAN BE USED IN ITS
PLACE

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Introduction

House Concurrent Resolution No. 84 requests that the Department of Health review the available scientific research on decabromodiphenyl ether (Deca-BDE) and assess the availability of safer, effective, and technically feasible flame retardants that can be used in place of Deca-BDE. This report summarizes information prepared by other agencies and advocacy organizations. Chief among those is a report from the Minnesota Pollution Control Agency (2008) for health effects and reports from Illinois, Washington, and Clean Production Action on Deca-BDE alternatives.

Flame retardants are chemicals added to materials and products to slow ignition or prevent the spread of fire. The bromine-containing flame retardants are a significant portion of the flame retardant market because of their effectiveness and relatively low cost. The polybrominated diphenylethers (PBDEs) are one of the main classes of brominated flame retardants. They are of concern because of their widespread usage, persistence in the environment and bioaccumulation properties. The levels in human tissue have been increasing since the 1960s. PBDEs have been found in wildlife, in food that people eat, sediments, and house dust and sewage sludge. Because of these concerns, many states, including Hawaii have banned two of the three technical formulations.

Uses of Deca-BDE

The major end use for Deca-BDE is in electronic products, in particular televisions where it is combined with high-impact polystyrene (HIPs) polymers. In the U.S., television manufacturers constitute 45–80% of all Deca-BDE use (Washington, 2006). According to the Clean Production Action (2006), manufacturers of other electronic equipment, including manufacturers of personal computers (PCs) have largely eliminated their use of Deca-BDE.

According to the Lowell Center, between 10 and 20% of Deca-BDE use is in textiles, primarily office furniture and drapery (cited in MPCA, 2008). It is not used in children's clothing or residential upholstered furniture. Volume wise smaller than TV enclosures and textiles, Deca-BDE is also used in wiring in automobiles, communications cable for telephone and internet services, wiring in heating and air conditioning and security system controls (MPCA, 2008).

Summary of Health Concerns about PBDEs

MCPA (2008) has conducted a literature review of the toxicity of Deca-BDE and summarized findings from other states. Polybrominated diphenylethers (PBDEs) are ubiquitous in the environment and their concentrations are increasing in some environmental media. The concentrations of Deca-BDE in human tissue are much lower than the other PBDEs. The main ways that people are believed to be getting exposed to Deca-BDE is through diet and house dust. Nursing babies and young children have the highest intake of PBDEs including Deca-BDE.

Studies have shown that Deca-BDE breaks down chemically once released to the environment and forms more toxic, lower brominated congeners. The magnitude and extent of breakdown of Deca-BDE is not currently known.

Toxicity information on the human health effects of PBDEs is based mainly on laboratory animal studies. The studies indicate that Deca-BDE is less toxic than the lower brominated congeners such as those found in Penta and Octa BDE formulations. The concern with Deca-BDE is the potential for it to degrade or be metabolized to the lower brominated congeners

Deca-BDE is a large molecule and researchers thought that it would be poorly absorbed. However several recent studies have found Deca-BDE in human tissues. In addition, laboratory animal studies show that Deca-BDE can be absorbed by the oral route of exposure and does not accumulate in tissues.

MCPA (2008) concludes that animal studies provide evidence of toxic effects associated with exposure to Deca-BDE, but that they occur at concentrations above what is found in the environment. EPA (2008) has provided an overview of health effects linked to Deca-BDE. Health effects seen in laboratory animals include liver, thyroid, reproductive/developmental and neurobehavioral changes. Behavioral differences in lab animals exposed to Deca-BDE raise concern about possible neurotoxicity in children (EPA, 2008).

In summary, there is increasing evidence that Deca-BDE has the ability to break down into more toxic PBDE congeners. Research in animals indicates that exposure to Deca-BDE is associated with liver, thyroid, reproductive, developmental and neurological effects. Whether these health effects occur in humans is unknown.

Deca-BDE Alternatives

Several groups have recently reviewed Deca-BDE alternatives for electronics (Syracuse Research Corp. 2006; Maine DEP and Maine CDC, 2007; Illinois EPA, 2007; Danish EPA, 2007; Clean Production Action, 2007; MPCA, 2008; and Washington DOH, 2008). Alternatives to Deca-BDE for textiles are not addressed here because alternatives to chemical flame retardants are widely employed in the marketplace already. MCPA has prepared a summary table of commonly cited flame retardant alternatives to Deca-BDE (Attachment 1).

There appear to be alternatives to Deca-BDE that are available and affordable. However, the alternatives have not been studied as thoroughly as Deca-BDE and there are significant data gaps. There are two types of alternative chemical flame retardants that may be substituted for Deca-BDE: 1) non- halogenated; and 2) halogenated. The halogenated compounds contain bromine and chlorine. Two states, Illinois and Maine, have concerns about the toxicity of halogenated flame retardants. The non-halogenated compounds show the most promise and are the focus of this review.

Use of the non-halogenated alternatives cannot directly substitute for Deca-BDE in high impact polystyrene (HIPs) because the product will not meet flammability standards (Lowell, 2005 as cited in MCPA, 2008). Other types of plastics are compatible with the non-halogenated flame retardants and will meet flammability standards. One of the plastics, HIPs with polyphenylene ether (HIPs/PPO) is commonly used in Europe in combination with the phosphorus based flame retardant, resorcinol bis diphenylphosphate (RDP) to construct enclosures for televisions.

The most commonly mentioned phosphorus based flame retardants are shown in Table 10 of Attachment 1 (MCPA, 2008). Studies have indicated that phosphorus based flame retardants pose fewer health and environmental concerns than Deca-BDE although toxicity data are very limited. RDP is the one non- halogenated flame retardant that is cited as a potential alternative by Clean Production Action, Washington, Illinois, Maine and the Syracuse Research Corp.

RDP currently meets performance criteria for use in the external plastic housing of televisions. Commerical RDP is a mixture of chemicals:

- 65-80% phosphoric acid, 1,3-phenylene tetraphenyl ester (CAS #57583-54-7),
- 15-30% phosphoric acid, bis[3-[(diphen-oxyphosphinyl)oxy]phenyl] phenyl ester (CAS #98165-92-5), and
- <5% triphenyl phosphate (CAS #115-86-6).

Acording to MCPA (2008) RDP is considered one of the more promising alternatives to Deca-BDE. Risk assessment by Syracuse Research Corporation concluded that the chemical has low persistence potential. It has low toxicity to lab animals and medium/high aquatic toxicity. There are no carcinogenicity studies on the chemical and no data on potential human exposure. More toxicity information is needed.

Safer alternatives to Deca-BDE are now available for TV enclosures. The cost of making these changes is considered minor (Ilinois, 2007). However, cost is a concern for medical devices and transportation, due to the highly regulated nature of these industries. Fortunately, there appears to be a voluntary shift away from the use of Deca-BDE in computers and televisions (Clean Production Action, 2006). Manufacturers are also considering product redesign to eliminate the need for chemical flame retardants.

Summary

Animal studies indicate that Deca-BDE exposure can result in adverse health effects. Whether they occur in humans is not known. Additional studies are warranted to determine whether humans are more or less sensitive to Deca-BDE than laboratory animals.

Safer cost effective alternatives to Deca-BDE are now available for TV enclosures. Many manufacturers are voluntarily shifting away from the use of Deca-BDE in computers and televisions.

The Hawaii DOH will continue to work with other state agencies to encourage manufacturers to move away from using Deca-BDE in consumer products. In addition, DOH will continue to monitor new research on the toxicity of alternatives to Deca-BDE.

References

Clean Production Action (2006) Fact Sheet on Electronics Industry Phasing Out PBDE http://www.watoxics.org/files/cpatv

Clean Production Action (2007) The Green Screen for Safer Chemicals:Evaluating Flame Reatardants for TV Enclosures http://cleanproduction.org/library/Green%20Screen%20Report.pdf

Danish EPA (2007). Health and Environmental Assessment of Alternatives to Deca-BDE in Electrical and Electronic Equipment. http://www2.mst.dk/udgiv/publications/2007/978-87-7052-349-3/pdf/978-87-7052-350-9.pdf

EPA, 2008. Draft Toxicological Review of Decabromodiphenyl Ether (BDE-209). In Support of Summary Information on the Integrated Risk Information System (IRIS). http://www.epa.gov/IRIS/toxreviews/0035-tr.pdf

Illinois, EPA (2007) Report on Alternatives to the Flame Retardant DecaBDE: Evaluation of Toxicity, Availability, and Fire Safety Issues. http://www.epa.state.il.us/reports/decabde-study/decabde-alternatives.pdf

Lowell (2005) Decabromodiphenyl Ether: An Investigation of Non-Halogen Substitutes in Electronic Enclosures and Textile Applications, Lowell Center for Sustainable Production, University of Massachusetts:69 (cited in MCPA, 2008)

Maine DEP and Maine CDC (2007). Brominated Flame Retardants 3rd Annual Report to the Maine Legislature. http://maine.gov/dep/rwm/publications/legislativereports/pdf/finalrptjan07.pdf

Minnesota Pollution Control Agency (2008) Decabromodiphenylether (Deca-BDE) A report to the Minnesota Legislature. http://www.pca.state.mn.us/publications/reports/lrp-ei-2sy08.pdf

Syracuse Research Institute for the WA State Departments of Ecology and Health (2006). Flame Retardant Alternatives.
http://www.ecy.wa.gov/programs/swfa/pbt/docs/flameRetard.pdf

Washington State Department of Ecology and Department ofHealth. 2006. Washington State Polybrominated Diphenyl Ether(PBDE) Chemical Action Plan.
http://www.ecy.wa.gov/pubs/biblio/0507048.html

Washington State Department of Ecology and Department of Health. 2008. Alternatives to Deca-BDE in Electronic Enclosures and Residential Upholstered Furniture. Draft. September 1, 2008.

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ATTACHMENT 1

Alternatives to Deca-BDE from
Minnesota Pollution Control Agency (2008).

From:
Minnesota Pollution Control Agency (2008) Decabromodiphenylether (Deca-BDE) A report to the Minnesota Legislature. http://www.pca.state.mn.us/publications/reports/lrp-ei-2sy08.pdf

ALTERNATIVES TO DECA-BDE

Much of the concern surrounding a potential phase out of Deca-BDE centers on concern about the health risks posed by potential alternatives. Would a phase-out of Deca-BDE push manufacturers to use other types of chemical FRs that may be as harmful – or even more harmful- than Deca-BDE?

This is a realistic concern. There are a large number of potential alternatives for Deca-BDE, including other BFRs such as the high volume chemicals TBBPA and HBCD. Generally speaking, the brominated and chlorinated FRs have been found to be environmentally persistent, bioaccumulative and toxic to varying degrees. TBBPA and HBCD are currently being evaluated by the EU using the same risk assessment process applied to Deca-BDE.

The state reports on PBDEs have generally included risk evaluations of potential chemical FRs that could be used in place of Deca-BDE. In 2007, the State of Illinois prepared a report that focuses exclusively on the evaluation of potential alternatives to Deca-BDE.

Most of the state reports find that less is known about the environmental behavior and toxicology of alternative FRs than is known about Deca-BDE. Because of this, it is difficult to conclude that a potential alternative FR for Deca-BDE poses little or no risk and therefore is more safe for human health and the environment than Deca-BDE. However, Illinois' 2007 report concludes that some of the chemical alternatives do appear to be safer than Deca-BDE.

In this section, commonly mentioned alternatives to Deca-BDE are reviewed and discussed. However, other means are available than an alternative chemical flame retardant to meet flammability requirements. Reports indicate that many manufacturers are voluntarily looking for alternatives to Deca-BDE or are finding ways to redesign their products so that the use of chemical flame retardants is not necessary. These market and consumer driven changes will be discussed following the review of alternative chemical flame retardants.

Alternative Chemical Flame Retardants

The two types of alternative chemical FRs that may be substituted for Deca-BDE are discussed separately below: non-halogenated FRs and halogenated (i.e. brominated or chlorine-based) FRs.

Non-halogenated Alternatives

According to the Lowell (2005) report, non-halogenated alternatives cannot be used as direct substitutes for Deca-BDE in high impact polystyrene (HIPS) – the polymer where Deca-BDE has its primary use (80% of total volume). This is because HIPS that is flame-retarded with non-halogenated FRs cannot meet the required flammability standards.

However, other types of plastic, including high impact polystyrene/polyphenylene ether (HIPS/PPO) and polycarbonate/acrylonitrile-butadiene-styrene (PC/ABS) are compatible with non-halogenated FRs and can meet the required flammability standards. Most often, phosphorus-based FRs such as resourcinol bis diphenylphosphate (RDP) are used for this purpose (Lowell, 2005).

In Europe, HIPS/PPO with RDP is commonly used to construct enclosures for televisions, and the trend is to manufacture TV enclosures that meet European and the stricter U.S. flammability requirements so that the products can be sold in both markets (Maine 2007). Some manufacturers of LCD (Liquid Crystal Display) TVs are known to use PC/ABS resin with phosphorus based FRs to construct the enclosures. The cost of these flame-retarded plastic resin systems is about 1.5 to 2.5 times more expensive than Deca-BDE flame retarded HIPS (Lowell, 2005).

The most commonly mentioned phosphorus-based FRs used in combination with HIPS/PPO and PC/ABS are listed in Table 10. Of these, the first five are most frequently mentioned (numbers 1 through 5). Table 10 provides a summary of toxicity, persistence and bioaccumulation potential information for the listed alternatives, based on information provided in the various state PBDE reports (Washington, 2006; Maine, 2007; Illinois, 2007; Syracuse Research Corporation, 2006; Pakalin et al., 2007).

The state reports on PBDEs differ somewhat on the suitability of the non-halogenated alternatives. Only RDP, red phosphorus, and magnesium hydroxide were considered potential alternatives by at least one state and not also considered unsuitable by another state.

BAPP, one of the top five phosphorus-based FRs, breaks down to form bisphenol A (BPA). BPA is considered a potent endocrine disruptor and is accumulating in people; this chemical is receiving a great deal of scrutiny by organizations concerned about public health (e.g. Body Burden Work Group and Commonweal Bio-monitoring Resource Center, 2007).

However, the primary human exposure route for BPA is thought to be direct contact with consumer products that contain BPA, especially polycarbonate plastic products such as water bottles, baby bottles, and food storage and heating containers. The level of concern that may arise from BPA as a breakdown product of BAPP in the environment is less clear.

The Illinois 2006 Deca-BDE report suggests there is a potential for formation of toxic phosphine gas during combustion of products containing phosphorus-based flame retardants. This includes all of the non-halogenated alternatives in Table 10 except melamine cyanurate, magnesium hydroxide, and zinc borate. No data are available to evaluate this concern. However, there remains a possibility that if this is a significant issue, the toxicity of combustion-related gases from resin systems incorporating phosphorus-based FRs could be higher than is currently assumed.

Table 10. List of Commonly Cited Non-Halogenated Alternatives to Deca-BDE

	Chemical Name (Abbreviation) and CAS Number(s)	*Comments*	*Potential Alternative*	*Not Suitable as Alternative*
1	Resorcinol bis diphenylphosphate (RDP) 57583-54-7 and 125997-21-9	Low persistency; more toxicity info needed	WA, IL, ME, Syracuse 2006	
2	Bisphenol A diphosphate (BAPP, BPADP, BDP) 181028-79-5 and 5945-33-5	High persistency; more toxicity info needed; degrades to Bisphenol A.	IL, WA	ME
3	Diphenyl cresol phosphate (DCP) 26444-49-5	Persistent; moderate human and aquatic toxicity	WA	IL
4	Triphenyl phosphate (TTP) 115-86-6	Not persistent; more human toxicity info needed; high aquatic toxicity	WA	IL
5	Red phosphorus 7723-14-0	Inorganic (i.e. does not break down); low screening toxicity	ME	
6	Melamine cyanurate 37640-57-6	Biodegrades; little toxicity data		IL (insufficient data to make recommendation)
7	Magnesium hydroxide 1309-42-8	No known env. concerns; considered non-toxic.	IL, WA	
8	Zinc borate 1332-07-6	High human and aquatic toxicity	WA	IL
9	Ammonium polyphosphate 14728-39-9 and 68333-79-9	Biodegrades; little toxicity data	ME	IL (insufficient data to make recommendation)

CAS = Chemical Abstract Service

Halogenated Alternatives

Table 11 lists potential halogenated alternatives to Deca-BDE. Note that both HBCD and TBBPA are included on this list. These BFRs are both undergoing risk assessments by the EU. The descriptions of toxicity, persistence and bioaccumulation potential of the halogenated alternatives are based on review of other published evaluations (Washington 2006; Pakalin et al., 2007) and peer-reviewed studies of the alternatives (Birnbaum and Staska, 2004).

Note that the State of Illinois, in its 2007 report evaluating the availability of safer and affordable alternatives to Deca-BDE, decided not to evaluate bromine- and chlorine-based alternatives. This decision was based on concern about the generation of toxic byproducts such as dioxins and furans upon the burning or incineration of the resin systems containing these FRs. The State of Maine categorically ruled out consideration of other brominated FRs as potentially safer alternatives to Deca-BDE, since other brominated chemicals share the characteristics that make Deca-BDE problematic.

Table 11: Lists of Commonly Cited Halogenated Alternatives to Deca-BDE

	Chemical Name (Abbreviation) and CAS Number(s)	*Comments*	*Potential Alternative*	*Not Suitable as Alternative*
1	Bis(pentabromophenyl) ethane 84852-53-9	Limited toxicity & other information (indications of low toxicity, and bioaccumulation, expected to be very persistent)	WA	
2	1,2-bis (tetrabromophthalimido) ethane 32588-76-4	Limited toxicity & other information (indications of low toxicity, and bioaccumulation, expected to be very persistent)	WA	
3	Tetrabromobisphenol A epichlorohydrin polymer 40039-93-8	Limited toxicity & other information	WA	
4	Bis(tribromophenoxy) ethane 37853-59-1	Fairly limited toxicity & other information (indications of low toxicity, show tendency to persist and bioaccumulate)	WA	
5	Hexabromocyclo-dodecane (HBCD) 3194-55-6 and 25637-99-4	Concentrations in biota and environment are increasing; toxic (meets persistence, toxic and bioaccumulation criteria by EU, and WA		EU is conducting a risk assessment of HBCD, WA

6	Tetrabromobisphenol A (TBBPA) 79-94-7	Very persistent; bisphenol A is a likely breakdown product (meets persistence, toxic and bioaccumulation criteria by WA)		EU is conducting a risk assessment of TBBPA, WA
7	Tetrabromobisphenol A bis (2,3-dibromopropyl ether) 21850-44-2	Fairly limited toxicity & other information		

CAS = Chemical Abstract Service

Voluntary Market Changes

Many manufacturers have already eliminated the use of Deca-BDE in their products. One of the first companies to do so was Ikea, the Swedish furniture manufacturer. Its products have been free of PBDEs since 2002 (Betts, 2007).

Computer and television manufacturers are also voluntarily moving away from the use of Deca-BDE. Clean Production Action, a nonprofit that helps organizations design greener products and manufacturing processes, documents manufacturer's progress in a fact sheet dated November 15, 2006. It states that manufacturers of personal computers have largely eliminated their use of Deca-BDE, and by 2010 four of the eight largest TV manufacturers selling in the U.S. will have eliminated Deca-BDE use, if they follow through on their plans to do so.

The list of manufacturers that are phasing out the use of Deca-BDE from some or all of their products include:

Apple	Cannon
Dell	Ericsson
HP Monitors	IBM
Intel	Toshiba
LG Electronics	Nokia
Panasonic	Samsung
Sony-Ericsson	Motorola

Source: Environmental Working Group (EWG), 2006

A news article in the journal *Environmental Science and Technology* reported on September 27, 2007 that FR formulators are acknowledging that many of their customers are steering them towards offering of non-halogenated products. Computer manufacturers such as Dell are also clearly stating that they are competing to be viewed as "green," and halogen-based flame retardants do not have a green image (Betts, 2007).

Product redesign, including the use of metal components to protect the power supply, removal of the power supply from inside electronic product enclosures, and use of inherently flame resistant fibers, are ways that the need for chemical FRs can be reduced or eliminated.

According to Maine's 2007 report, the textile industry has many choices in chemical flame retardants beside Deca-BDE. There are also many ways to modify fibers and fabrics to meet flammability standards without using chemical flame retardants. There is also the choice of using inherently flame resistant fibers and fabrics.

Mattress manufacturers needing to comply with the new national CPSC standard that went into effect in July 2007 have shunned the use of Deca-BDE, according to the Maine report (2007). The Maine report (2007) also reports that furniture industry sources suggest that in most cases, chemical flame retardants will not be needed to meet pending national standards for residential upholstered furniture.

Quoting directly from Maine's 2007 report:

> "Safer alternatives are available for TV cabinets and textiles, the applications that consume most decaBDE. In the case of textiles, alternatives that do not require the use of chemical flame retardants already are widely employed in the marketplace. In the case of TVs, the use of safer alternatives to decaBDE will require manufacturers to shift from using cabinets made of high impact polystyrene (HIPS) to other types of plastic that can be treated to meet flammability standards using phosphorous compounds such as resorcinol bis diphenylphosphate (RDP). RDP presents a significantly lower threat to the environment and human health than decaBDE."

The cost of making these changes in most cases is considered minor (Illinois, 2007). However, in the fields of medical devices and transportation, particularly the aircraft and aerospace industries, cost is a concern. This is primarily a result of the highly regulated nature of these industries and the extensive product testing that is required by both regulatory agencies and the manufacturers themselves to qualify their products.

In its 2007 report, the State of Maine recommended that a ban of televisions and other consumer electronics that are encased in plastic containing more than 0.1% Deca-BDE be delayed until 2012 to ensure that manufacturers have sufficient lead time to retool their production processes. The Maine report also underlines the fact that manufacturers of products that have many small electrical parts or extensive wiring, such as in automobiles, airplanes, and ships, may not be able to easily ascertain which components contain Deca-BDE. Several years may be needed to complete the process of identifying all instances of Deca-BDE usage in these products.