PBDES AND THEIR REPLACEMENTS: DOES THE BENEFIT JUSTIFY THE HARM?

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Introduction:

In the 1960s, naturally fire-resistant materials such as wood, cotton, wool, and leather were replaced with more flammable synthetic materials such as polyurethane and plastics. This decade also saw an increase in cigarette smoking which peaked in 1964 when more than 40% of all adult Americans smoked [1]. Together, these factors may have contributed to increases in home fire deaths and injuries during this same period [2]. In an attempt to reduce fire losses, flammability regulations were promulgated beginning in the 1970s for materials used in furniture, electronics, transportation, building, and other applications. Brominated and chlorinated flame retardant chemicals were found to be the most cost effective ways to meet the new flammability requirements. The potential adverse health and environmental impacts of these halogenated chemicals were not considered when the regulations leading to their use were implemented. Furthermore, when selecting flame retardants, manufacturers' primary criteria were cost and performance rather than human or environmental health considerations.

To meet flammability standards, five brominated flame retardants (BFRs) have been used extensively: tetrabromobisphenol A (TBBPA), hexabromocyclododecane (HBCD), and three commercial mixtures of polybrominated diphenyl ethers (PBDEs) – decabromodiphenyl ether (deca-BDE), octabromodiphenyl ether (octa-BDE), and pentabromodiphenyl ether (penta-BDE). Chlorinated flame retardants used include TDCPP or [tris (1,3-dichloro-2-propyl) phosphate] also known as chlorinated Tris; TCEP or tris(2-chloroethyl) phosphate; TCPP or tris(1-chloro-2-propyl) phosphate, Dechlorane Plus, and chlorinated paraffins.

In recent years most of these flame retardants have been recognized as persistent and/or global contaminants; several have been found to be associated with a wide range of adverse health effects in animals; and after three decades of use in homes, pentaBDE is being found to be associated with health problems in humans [3]. A few flame retardants, notably the PBDEs and TCEP have been banned or voluntarily phased out by manufacturers. These have been replaced by other organohalogens of similar structure and/or properties lacking adequate data on health effects. For example pentaBDE has been replaced by proprietary mixtures like Fire Master550 as well as chlorinated chemicals such as TDCPP which have been associated with adverse health impacts [4]. Replacements for the octa-BDE and deca-BDE include 1,2-*Bis*(2,4,6-tribromophenoxy)ethane (BTBPE; trade named FF-680) and decabromodiphenylethane (DBDPE), respectively, which are very similar in structure. Both BTBPE and DBDPE have been reported in air, water, sewage sludge, sediment, mussels, fish, and birds [5, 6, 7, 8] and in house dust from the U.S. [9]. Current concentrations of DBDPE in eggs of herring gulls from the Great Lakes are similar to or higher than those of BDE-209 and appear to be increasing after a comparatively short period of usage [6], suggesting that DBDPE may be more persistent and/or bioaccumulative than deca-BDE. High concentrations of DBDPE have also been reported in captive pandas [10] and waterbirds [11] from China's Pearl River Delta, where many e-waste recycling facilities are located.

Posing an additional concern, furniture and other products previously treated with banned flame retardants such as pentaBDE are still in use and continue to release these chemicals into homes and the environment. Although several organohalogen flame retardants have been withdrawn from the market, their overall production continues to increase [12]. Although the migration, persistence, bioaccumulation, and/or toxic effects of many halogenated flame retardants are well-documented, the health science community is relatively unfamiliar with evaluations of their fire safety benefits. Our research examines the effectiveness of organohalogen flame retardants in some consumer products in reducing fire hazard and suggests other means to maintain fire safety without potential toxicity.

Results and Discussion:

1. Organohalogen flame retardants can increase fire toxicity. Most fire deaths and most fire injuries result from inhalation of fire effluents such as carbon monoxide, irritant gases, and soot [13]. Although the incorporation of halogenated flame retardants can reduce the ignitability and heat release of a material, they also increase the yield of such toxic products when combustion occurs [14, 15].

Halogenated flame retardants act by replacing the most reactive H· and OH· free radicals in a flame with more stable Cl· or Br· free radicals. However, the OH· radical is required for the conversion of carbon monoxide to carbon dioxide.

$$CO + OH\cdot \rightarrow CO_2 + H\cdot$$

In the presence of brominated or chlorinated flame retardants this reaction is prevented, resulting in more carbon monoxide during the fire [16]. Thus the same flame retardant action which reduces heat release is also responsible for much higher yields of carbon monoxide. In addition, the flame quenching action of bromine and chlorine radicals prevents the oxidation of other hydrocarbons, irritant aldehydes, etc., to carbon dioxide and water, and significantly increases the smoke yield. These increased levels of acute toxic gases and soot will make escape more difficult.

In addition, during accidental fires under uncontrolled conditions, products containing halogenated flame retardants can burn to form high levels of halogenated dibenzodioxins and dibenzofurans as combustion products [17, 18]. Firefighters can have elevated exposure to brominated and chlorinated dioxins and furans [19] while cleaning up after fires [20, 21]. Fire fighters are known to also have significantly elevated rates of four types of cancer that are potentially related to dioxin and furan exposure: multiple myeloma, non-Hodgkin's lymphoma, prostate, and testicular cancer [22, 20]. The question of whether the increase in cancer incidence in fire fighters can be related to exposure to combustion products of halogenated flame retardants warrants further investigation.

2. The health and environmental impacts as well as fire safety benefits of flammability standards should be considered.

Technical Bulletin 117 (TB117), a unique California flammability standard, requires the polyurethane foam in upholstered furniture and juvenile products to withstand exposure to a small open flame for twelve seconds [23]. According to the furniture industry, all furniture sold in California and about 30% of furniture sold in the U.S. outside California flame retardants complies with TB117. From its implementation in the early 1980s until 2004, TB117 was primarily met with pentaBDE, the most studied of the flame-retardants. PentaBDE and the other PBDEs are structurally similar to known human toxicants PBBs, PCBs, dioxins and furans. In addition to having similar mechanisms of toxicity in animal studies [24], PBDEs also persist and bioaccumulate in humans and animals [25]. In 1999 and 2001, 98% [26] and 95% [27], respectively, of the usage of pentaBDE, was in North America, in large part to meet TB117. PentaBDE was banned in California in 2003 due to its persistence and toxicity; eight other states and the European Union (EU) followed suit. In 2004, Chemtura (previously Great Lakes Chemical), the sole U.S. manufacturer, voluntarily ceased production, and in 2009 pentaBDE was listed as a persistent organic pollutant under the Stockholm Convention [28]. However pentaBDE-containing products will remain a reservoir for releases for many years to come. According to the furniture industry, the average lifetime for foam-containing household furniture is 30 years, suggesting that only a fraction of the total PBDEs used in furniture has reached the outdoor environment. The indoor reservoir of PBDEs has been termed an environmental "time bomb" [29]. It is predicted that the main exposure route for humans will eventually shift from the indoor environment to the food supply [29].

A major replacement for pentaBDE in furniture and juvenile product foam is Firemaster 550, also produced by Chemtura, a mixture of four flame retardant chemicals whose composition is a trade secret. In 2004, the EPA Design for the Environment predicted reproductive, neurological, and developmental toxicity and persistent degradation products for Firemaster 550 [30]. In 2005, Chemtura agreed to conduct reproductive and developmental toxicity and migration studies by January 2009. Data provided by Chemtura in November 2008 is currently being evaluated by the EPA. Firemaster 550 components include: (1) triphenyl phosphate (known to be eco-toxic); (2) Triaryl phosphate isopropylated (a probable reproductive toxin); (3) Bis (2-ethylhexyl) tetrabromophthalate; and (4) 2-ethylhexyl-2,3,4,5-tetrabromobenzoate [31]. Components of Firemaster 550 are found in dust [32] and sewage sludge, marine mammals, and seven species in the Arctic[33]. Firemaster 600, as described on the Chemtura website with a composition that is a trade secret, is beginning to replace Firemaster 550.

TDCPP or chlorinated tris is another widely used flame retardant for polyurethane foam. It is produced by ICL under the trade name Fyrol and by Albermarle under the trade name Antiblaze. TDCPP was removed from use in children's pajamas in 1978 due to its mutagenicity and has subsequently been found to be a probably human carcinogen by scientists at the U.S. Consumer Product Safety Commission (CPSC) [34]. A CPSC report estimates the lifetime cancer risk from tris-treated furniture foam is up to 300 cancer cases/million [34]. Their chronic hazard guidelines define a substance as hazardous if lifetime cancer risk exceeds one in a million.

An important question is whether adding pentaBDE and its replacements to furniture and juvenile product foam is effective in reducing fires injuries and deaths. Fires are complex and can vary enormously. A material's performance, as required to meet a flammability standard, will depend on the design of the standard, including the source of ignition, and the duration and location of a flame or heat source. A piece of furniture meeting a particular standard can behave in different ways under varied circumstances. For example, a flame impact a corner or a flat surface can have very different results. Once a standard test method is in place, manufacturers are likely to optimize their products to meet the criteria at the lowest cost. Standards that are designed to prevent a small open flame from igniting uncovered foam may not reflect the flammability of a complete upholstered chair [35]. Uncovered foam is most conveniently protected with the addition of halogenated flame retardants, while a fabric coated piece of foam can be protected using a greater range of strategies, including protective back coatings and interlayers.

An analysis of fire data from 1980 to 2005 by the U.S. National Fire Protection Association (NFPA) shows that the rate of reduction of fire deaths in California is similar to that of seven other states that lack California TB117's furniture flammability standards. One contributing factor might be that California Technical Bulletin 116 (TB116), the companion standard for fabric flammability, is a voluntary cigarette smoulder test and rarely used. Since fabric will ignite first in a furniture fire, the lack of an enforced fabric standard is one weakness of TB117. Laboratory research on TB117 supports this observed lack of measurable fire safety benefit. For example, small scale fire testing does not accurately predict large scale fire behavior. These researchers note that, "The component tests in TB117 did not satisfactorily predict composite ignition behavior. Fabrics and fillings that comply with TB117 often ignited when tested as finished chairs. TB117 would not, if federally mandated, ensure a substantial reduction in the risk of small open flame ignition of finished articles of furniture" [36].

In February 2008, the U.S. Consumer Product Safety Commission replaced a draft small open flame test standard for furniture foam similar to California's TB 117 with a draft "smolder test" or cigarette ignition resistance standard for furniture fabric. This draft standard can be met with smolder-resistant cover fabrics or interior fire-resistant barriers rather than leading to the addition of semi-volatile chemicals to foam. In a statement on the 2008 Notice of Proposed Rulemaking, then CPSC Commissioner Nancy Nord said the new standard would address furniture fires without requiring the use of fire retardant chemicals [37]. In an earlier statement on the proposal, CPSC Commissioner Thomas Moore stated, "No one wants to trade fire risks for chemical toxicity risks" [38]. This CPSC draft standard has been moving through the development process since 2008. If proposed and implemented, this standard, which regulates fabric flammability rather than foam, could preempt California TB117 and greatly reduce the use of halogenated flame retardants in furniture and baby products across North America.

3. Fire safe cigarettes, fire safe candles, child resistant lighters, sprinklers, and smoke detectors can prevent fires without the potential adverse effects of flame retardant chemicals.

The leading cause of fire fatalities in the U.S. is cigarettes [39]. A large majority of residential fire deaths in which upholstered furniture was the first item ignited are caused by cigarette ignition [40]. Between 1980 and 2005, smoking-related fire deaths in the U.S. have declined from 2,000 to 800 annually [41]. The most recent data show a continued decline to 720 deaths in 2007 [42]. The reduction of smoking, through a combination of education, taxation and location restriction policies, has proven the single most effective fire safety strategy.

Smoking rates in the United States had declined to 21% by 2004. The recent passage in all 50 states of legislation requiring the manufacture and sale of reduced ignition propensity (RIP) or "fire-safe", cigarettes [43], should further reduce fire deaths. The American Society for Testing and Materials (ASTM) E2187-09 test method for measuring ignition propensity of cigarettes is referenced in all 50 state laws. Many of these laws are just beginning to be implemented. Fire-safe cigarettes contain internal "speed bumps" of thicker paper that block the flow of oxygen to the rest of a lit cigarette that is no longer being smoked. If a cigarette is accidentally dropped on an ignitable surface (e.g., a couch or mattress), a fire-safe cigarette will normally extinguish itself in a few minutes when it reaches a speed bump, rather than smoldering for as long as 45 minutes and potentially starting a fire.

Early data suggests that a mandatory fire safety performance standard for cigarettes, recently in effect in all 50 U.S. states, will result in a large decline in the number of cigarette-caused fires and fire deaths, further reducing the potential benefit of retardants in furniture and other products.

4. After a fire safety hazard is demonstrated, safer alternatives to hazardous or untested flame retardant chemicals should be considered, including using less flammable materials, changing the design of products to minimize flammability, and using safer alternative flame retardants that have been evaluated for their hazard.

In the U.S., neither federal nor state environmental protection agencies have adequate authority to require manufacturers to ensure that flame retardants are safe for human health. Thus, a series of toxic or untested brominated and chlorinated flame retardant chemicals continue to be used in consumer products without adequate consideration of their impacts. PBBs, PCBs, brominated tris, Halon, asbestos, and PBDEs are all flame retardant materials which only after extensive use were found to have serious long-term negative effects on human health and/or environment. Moreover, many of the current replacements are proprietary mixtures, protected by confidential business information regulations, while others lack adequate toxicity information, making it difficult to accurately assess their potential hazards. Chemical producers should be required to disclose the identity of chemical additives in consumer products and provide health and toxicity data about flame retardants and replacement chemicals <u>before</u> they are marketed.

Flame-retardant chemicals can pose a potentially greater hazard to health and environment than the risk of the fires they are supposed to prevent. Based on the discussion above, the authors suggest that flammability requirements that are likely to be met with the addition of organohalogen flame retardants should be re-evaluated. The proven efficacy of standards such as California furniture standards TB117 for homes and TB133 for public places should be considered as well as their fire toxicity and potential adverse health and environmental impacts. Decision makers should use the best peer-reviewed science to evaluate fire safety benefits as well as health and environmental hazard prior to promulgating new requirements leading to the use of flame-retardant chemicals. Reducing the use of toxic and untested halogenated flame retardants can protect human and animal health and the global environment without adversely impacting fire safety.

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