

REPLACEMENTS FOR PENTABDE FLAME RETARDANT: IS THERE AN IMPROVEMENT IN FIRE SAFETY OR HEALTH IMPACTS?

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Introduction

In 2005, the widely used furniture flame retardant (FR) pentabrominated diphenyl ether (pentaBDE) was phased out due to its toxicity, persistence, and bioaccumulation potential. This paper will discuss whether the commonly used replacements, TDCPP or chlorinated tris and Firemaster 550[®], are an improvement from a health, environmental, and fire safety perspective. These organohalogen flame retardants are used in furniture and baby product foam in California to comply with a state furniture flammability standard called Technical Bulletin 117 (TB117) which requires polyurethane foam used in upholstered furniture and juvenile products to resist ignition from exposure to a small open flame for at least 12 seconds¹. No other state has such a standard, yet most home and office furniture as well as juvenile and other products containing foam across all of the U.S. and Canada comply with TB117. In general, FR chemicals (most commonly organohalogens or phosphates) are semi-volatile organic compounds (SVOCs) and continuously escape from products into air and dust and making their way into humans and animals. We will evaluate the use of flame retardant in current use in foam for potential health, environmental and fire safety impacts. This evaluation is important for public health as a variety of home products contain retardants at levels up to 12 % of the weight of foam in these products. Exposure to such flame retardants may be contributing to neurological, reproductive, and endocrine problems as well as cancer in human, pets, and wild animals.

Materials and Methods

We carried out a review of the toxicological literature regarding flame retardants commonly used in foam in upholstered furniture. We also reviewed the fire science literature regarding foams that comply with TB117 ("TB117 foams") compared to untreated foams with respect to their effectiveness in preventing ignition, slowing flame spread, reducing peak heat release, and fire toxicity.

Results: Fire Safety Evaluation

The use of materials with the FR additives does not appreciably prevent ignitions from small flame sources. TB117 foam compared to non-TB117 foam, covered in identical fabrics, made no significant, consistent improvement in the ability of furniture to resist small-flame ignition. Also, no significant differences were observed between identically-constructed furniture using non-TB117 foam and furniture made with TB117 foam with regard to peak heat release rate and fire development establishing the severity of a fire.² Studies of pentaBDE and TDCPP led to similar results; however, there was an increase in fire toxicity. Laboratory studies on foams alone indicated that the addition of halogenated flame retardants to foam provided a small delay in ignition time (2-3 seconds) and a small decrease in the heat release rate, but generated additional smoke, carbon monoxide, and soot.³

Results: Toxicological Evaluation

PentaBDE. From the 1980s until it was phased out in 2004 TB117 was primarily met with pentabrominated diphenyl ether (pentaBDE) commonly used at levels of 3 to 5% of the weight of the foam⁴. In 1999 and 2001, 98% and 95% respectively, of the usage of pentaBDE, was in North America, primarily in foam for TB117 compliance⁵. Flame retardants migrate out of products⁷ into air and dust⁸. Inhalation and ingestion of contaminated dust is considered the major route of human exposure⁹. Biomonitoring studies have detected pentaBDE congeners in the body fluids of virtually all Americans tested, with the highest levels in Californians. In California, the serum pentaBDE levels in children are 2.5 times higher than in similar-aged children across the U.S., 2-10 times higher than in U.S. adults, and 10-100 times higher than those in similar aged children in Europe and Mexico¹⁰. Adverse reproductive, endocrine, and neurodevelopmental impacts of pentaBDE have been documented in animal^{11 12} and humans studies^{13 14 15 16 17}.

Despite restrictions on pentaBDE, large amounts of upholstered furniture, carpet padding, and automobiles containing the chemical are still in use in the U.S. and Canada and will need to be disposed of after their lifetimes. The legacy of products treated with pentaBDE has been called an environmental “time bomb,” as the toxic retardant continues to migrate from indoor reservoirs into the environment¹⁸.

In 2004, pentaBDE was withdrawn from commerce in the U.S. TDCPP and the commercial mixture Firemaster 550[®] have been the major replacements used to comply with TB117.^{19,20}

TDCPP, or Chlorinated Tris, or tris (1,3-dichloro-2-propyl) phosphate is used as an additive flame retardant in flexible polyurethane foams. This flame retardant was voluntarily removed from use in children’s pajamas in 1978 after it was shown to be a mutagen²¹. TDCPP has been measured in household and office dust, indoor air, and in streams, sewage influents, effluents, and sludge. In humans, TDCPP has been measured in adipose tissue, seminal plasma and breast milk. TDCPP has been tested for carcinogenicity in two-year rat studies where increases in the incidence of benign and malignant tumors were observed. It also induced mutations in salmonella and mouse lymphoma cells, induced chromosomal aberrations in mouse lymphoma and Chinese hamster fibroblast cells, and induced sister chromatid exchange (SCE) in mouse lymphoma cells. There is also evidence for DNA binding in mouse kidney, liver and muscle following in vivo exposure. TDCPP induced malignant cell transformation of Syrian hamster embryo cells in culture. TDCPP is metabolized to several chemicals identified as carcinogenic by IARC and listed under Proposition 65, namely 1,3-dichloro-2-propanol (1,3-DCP), 3- monochloropropane-1,2-diol (3-MCPD), epichlorohydrin and glycidol. TDCPP is structurally similar to two halogenated phosphate triester carcinogens identified under California’s Proposition 65, tris(2,3-dibromopropyl) phosphate (TDBPP or Tris) and tris(2-chloroethyl) phosphate (TCEP). Some of these metabolites and structurally similar compounds induce tumors at the same sites as TDCPP – liver, kidney, and testes.²² Also TDCPP has been shown to cause adverse neurological effects similar to chlorpyrifos, a known developmental neurotoxicant.²³

Last year TDCPP was listed as a California Proposition 65 carcinogen. Beginning October 18, 2012, stores selling products containing TDCPP will need to display a Proposition 65 warning label. Due to this, a majority of furniture, juvenile products and carpet cushion containing foam sold in California will require such a label.

Chemtura Corporation’s Firemaster 550[®], a mixture of brominated and phosphate flame retardants, is the other main chemical used in foam to comply with TB117. Based on the TDCPP being listed under Proposition 65, Firemaster 550[®] may become the primary chemical used to meet TB117. Chemtura developed Firemaster 550[®] in 2003, when its pentaBDE product was beginning to be phased out²⁴. The EPA expedited the approval of the mixture with no pre-market testing required and granted Chemtura’s request to protect the ingredients as Confidential Business Information (CBI). Testing by Chemtura showed that the components accumulated in fish and caused DNA damage²⁵. The EPA predicted reproductive, neurological, and developmental toxicity and persistent

degradation of products for the brominated components of Firemaster 550[®] and requested more information from Chemtura²⁶. In 2005, Chemtura agreed to conduct reproductive and developmental toxicity and migration studies by 2009. During the years the EPA was waiting for the studies to be submitted, Firemaster 550[®] was used in baby products, furniture, and foam in carpet cushions and automobiles, where it continues to be present today.

Analytical studies have since determined that 50% of Firemaster 550[®] is a mixture of the organohalogens 2,3,4,5-tetrabromo-ethylhexylbenzoate (TBB) and 2,3,4,5-tetrabromo-bis (2-ethylhexyl) phthalate (TBPH) and 50% is a mixture of tri mono-, di-, and tri-isopropylphenyl phosphates and triphenyl phosphate²⁷. One study found increases in DNA strand breaks in liver cells in fathead minnows when orally exposed to Firemaster 550[®]²⁸. Both TBB and TBPH were detected in tissues at approximately 1% of daily dosage along with brominated metabolites, suggesting the ability of Firemaster 550[®] to accumulate in fish.

The widespread use of chemicals such as Firemaster 550[®] in consumer products with high levels of human exposure without adequate toxicological information suggests the need for reform of the regulatory framework for chemicals.

CONCLUSION

We recommend that:

- Toxicological information should be required for all new chemicals before they are allowed to be used in consumer products. This information should be made publically available.
- Toxicological information should also be required for all existing chemicals with significant human exposure
- Both the fire safety benefit and potential for health and environmental harm of new flammability standards should be evaluated prior to their implementation.
- California should consider changing TB117 to the Consumer Product Safety Commission proposed rule 16 CFR 1634. This smolder standard for fabric which would provide additional fire safety without the use of potentially toxic flame retardants in foam.

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REFERENCES

- ¹ California Department of Consumer Affairs. Requirements, test procedure and apparatus for testing the flame retardance of resilient filling materials used in upholstered furniture. State of California, Department of Consumer Affairs, Bureau of Home Furnishings and Thermal Insulation (2000). <http://www.bhfti.ca.gov/industry/117/pdf>.
- ² Babrauskas, V., Blum, A., Daley, R., and Birnbaum, L. (2011) pp. 265-278 in *Fire Safety Science—Proc. 10th Intl. Symp.*, Intl. Assn. for Fire Safety Science, London.

- ³ Shaw S., A. Blum, R. Weber, K. Kanan, D. Rich, D. Lucas, C. Koshland, D. Dpbraca, S. Hanson, and L. Birnbaum. (2010) *Reviews on Environmental Health* 25 (4): 261-305.
- ⁴ Blum A (2007) *a. Science* 318:194-195.
- ⁵ Hale R.C., Alae M., Manchester-Neesvig J.B., Stapleton H.M., Ikonomou M.G. (2003). *Environ. Int.*, 29, 771-779.
- ⁶ Bromine Science and Environmental Forum (BSEF) (2003) Major brominated flame retardants volume estimates: Total market demand by region in 2001.
- ⁷ Hutzinger O., Thoma H. (1987) *Chemosphere*, 16, 1877-1880.
- ⁸ Jones-Otazo H., Clarke J.P., Diamond M.L., Archbold A.J., Ferguson G., Harner T., Richardson G.M., Ryan J.J., Wilford B. (2005) *Environ. Sci. Technol.*, 39, 5121–5130.
- ⁹ Johnson-Restrepo B., Kannan K. (2009) *Chemosphere*, 76, 542-548.
- ¹⁰ Rose M., Bennett D.H., Bergman Å., Fangstrom B.F., Pessah I.N., Hertz-Picciotto I. (2010) *Environ. Sci. Technol.*, 44, 2648–2653.
- ¹¹ Costa L.G., Giordano G., Tagliaferri S., Caglieri A., Mutti A. (2008); *Acta Biomed.*, 79,172-183.
- ¹² Shaw S.D., Kannan K. (2009). *Rev. Environ. Health*, 24,157-229.
- ¹³ Herbstman J.B., Sjödin A., Kurzon M., Lederman S.A., Jones R.S., Rauh V., Needham L.L., Tang D., Niedzwiecki M., Wang R.Y., Perera F. (2010) *Environ. Health Persp.*, 118, 712-719.
- ¹⁴ Chevrier J., Harley K.G., Bradman A., Gharbi M., Sjödin A., Eskenazi B. (2010) *Environ. Health Persp.*, 118, 1444-1449.
- ¹⁵ Meeker J.D., Stapleton H.M. (2010) *Environ. Health Persp.*, 118, 318-323.
- ¹⁶ Harley K.G., Marks A.R., Chevrier J., Bradman A., Sjödin A., Eskenazi B. (2010) *Environ. Health Persp.*, 118, 699-704.
- ¹⁷ Roze E., Meijer L., Bakker A., Van Braeckel K.N.J.A., Sauer P.J.J., Bos A.F. (2009) *Environ. Health Persp.*, 117,1953-1958.
- ¹⁸ Harrad S.J., Diamond M.L. (2006) *Atmos. Environ.*, 40,1187-1188.
- ¹⁹ Stapleton HM, Klosterhaus S, Blum A, Webster TF (2010); *Organohalogen Comp.* 72 (in press).
- ²⁰ Stapleton HM, Klosterhaus S, Eagle S, Fuh J, Meeker JD, Blum A, Webster TF (2009); *Environ Sci Technol.* 43(19):7490-7495
- ²¹ Gold MD, Blum A, Ames BN (1978). *Science* 200(4343): 785-7.
- ²² OEHHA (2011). Office of Environmental Health Hazard Assessment, California Environmental Protection Agency , Evidence on the Carcinogenicity of Tris(1,3-Dichloro-2-Propyl) Phosphate)
- ²³ Dishaw, Laura V., Powers, Christina M., Ryde, Ian T., et al. *Toxicology and Applied Pharmacology*. 1 Nov. 2011. Vol 256 Issue 3. 281-289
- ²⁴ Sissel K (2003) Great Lakes agrees to flame retardant phaseout. *Chemical Week* 165(41):13.
- ²⁵ Chemtura Corporation technical data sheet under the GreatLakes Solutions, a Chemtura business. <http://www.chemtura.com/bu/>
- ²⁶ EPA, Furniture Flame Retardancy Partnership: Environmental Profiles of Chemical Flame-Retardant Alternatives for Low-Density Polyurethane Foam (EPA 742-R-05-002A, September, 2005), pp. 4-2 to 4-5.
- ²⁷ Berr JS, Stapleton HM, Mitchelmore CL. Accumulation and DNA damage in fathead minnows (*Pimephales promelas*) exposed to 2 brominated flame-retardant mixtures, Firemaster (R) 550 and Firemaster (R) BZ-54. *Environ Toxicol Chem* 2010;29:722–9.