TECHNICAL BULLETIN

Chemical Insights
An Institute of Underwriters Laboratories Inc.

Organic Flame Retardant Exposure

Introduction

Chemical flame retardants based on organic composition have been added to consumer products including furniture, children's products, and electronics since the 1970s in response to concerns over structure fires as outlined in Technical Bulletin: Residential Fire Statistics. Halogenated flame retardants disrupt the production of free radicals in the vapor phase of a fire, which leads to reducing/suppressing flammable gas. Phosphate-based flame retardants act in the condensed phase, enhancing charring and ultimately inhibiting the flame from reaching to more fuel sources underneath the char layer. There are other types of flame retardants such as those with inorganics (ex. aluminum or magnesium hydroxides) and nitrogen based flame retardants (ex. melamine). The use of flame retardants have evolved over time; as more evidence on the health impacts of one class of flame retardant is found, the demand for another class of flame retardants arise. Most organic based flame retardants detected in products can be classified into three categories: brominated flame retardant, other halogenated flame retardant, and organophosphate flame retardant. Some flame retardants can be classified into more than one category. Newer flame retardants based on reactive chemistries are becoming available that offer reduced exposure potentials. Concerns over consumer exposure to flame retardant and health impacts date back to the 1970s.[1]

Exposure and Health Impacts of Flame Retardants

- Flame retardants can leach out of products and be found in air and settled dust in the surrounding environment. [2,3]
- Many are persistent in the environment, wildlife, as well as in human bodies.[4,5]

Polybronimated Diphenyl Ethers (PBDEs)

- Health effects from PBDEs exposure include thyroid hormone activity, liver effect, developmental neurotoxicity, and skin irritation.[5]
- PBDEs and their metabolites are biopersistent in humans. DecaBDE, with an apparent half-time of 15 days, is eliminated from human body faster than lower-brominated PBDEs, with apparent half-times as high as 94 days. Lower brominated PBDEs can stay in human body for many years, stored mainly in body fat. PBDEs and their metabolites can be excreted mainly in the feces and a very small amount in urine.[5]
- PBDEs have been found in placenta and breast milk. Infants and toddlers have the highest body burden via breast milk and household dust. Pre and post-natal exposure causes long term behavioral alterations.[5]
- Babies' elevated exposure to PBDEs is linked to high levels of PBDEs in breast milk accounting for infants' large daily dose (141 ng/kg/day). Ingestion of contaminated dust is the chief source of exposure for all other ages, descending with age; 47.2 ng/kg/day for 1-5 year old and 7.1 ng/kg/day for adults.[6]

Other Halogenated Flame Retardants

- As of May 2020, 48% of polyurethane products submitted to Duke University's Foam Project (which started in 2014) contained flame retardant(s), including the most commonly detected ones, tris (1,3-dichloro-2-propyl) phosphate (TDCPP), Firemaster® 550, and tris (1-chloro-2-propyl) phosphate (TCPP).[8]
- Halogenated flame retardant compounds have structures that are similar to thyroid hormones. Some of these compounds may cause health problems by acting like thyroid hormones and interfering with the normal activity of those hormones.[9]
- TDCPP (ex. Fryrol FR-2) was used as a flame retardant in children's pajamas in the 1970s. Animal studies suggest that TDCPP is mutagenic (likely to cause cancer),[10] increases incidence of tumors, neurotoxic, and is an endocrine disruptor.[11] Urinary metabolites of TDCPP are detected in more than 90% of the US population, and the levels are significantly higher in children relative to adults.[12]
- The use of TDCPP appears to be decreasing since 2014, coinciding with the addition of TDCPP to California Proposition 65 list.[7]
- Firemaster® 550 gained market share with the phase-out of pentaBDE.[1] Human exposure to Firemaster® 550 is widespread,[13] and components of Firemaster® 550 have been demonstrated to be potentially adipogenic, endocrine disrupting, neuro and developmentally toxic.[14]
- TCPP is structurally similar to TDCPP. Exposure to TCPP has shown delayed development and disruption of thyroid endpoints in an animal study.[15] Urinary metabolites of TCPP were detected in all samples tested by Butt et al.[16]

a 2211 Newmarket Parkway, Suite 106, Marietta, Georgia 30067 w chemicalinsights.org e chemicalinsights@ul.org

Organophosphate Flame Retardants (OPFRs)

- The halogenated flame retardants like tris (1,3-dichloro-2-propyl) phosphate (TDCPP), Firemaster® 550, and tris (1-chloro-2-propyl) phosphate (TCPP) discussed above are also organophosphate flame retardants. Some additional ones include isopropyl triphenyl phosphate (ITP) mix and methyl phenyl phosphate (MPP) mix.9
- Organophosphate esters are synthetic phosphoric acid derivatives used in a wide variety of applications including flame retardants and plasticizers.4
- Organophosphate esters production and usage have increased in recent years due to the phase-out of other flame retardant formulations (e.g., polybrominated diphenyl ethers, PBDEs),4,17 yet their toxicological hazards have yet to be well characterized.[17]
- Studies have demonstrated that both halogenated and non-halogenated OPFRs are associated with adverse reproductive health and birth outcomes, asthma and allergic disease, early growth and adiposity, affecting neurodevelopment, endocrine system, neurodevelopment, behavioral development, reproductive outcomes, preterm birth, respiratory outcomes, and allergic diseases.[18]
- Some organophosphates are prevalent and persistent in both indoor and outdoor environments.[19] Therefore, exposure to OPFRs is ubiquitous in people and in outdoor and indoor environments.[4,17]
- Both PBDEs and OPFRs are applied to polyurethane foam at roughly identical percentage range (3–7% by weight).[17]
- OPFRs are also heavily used in electronics.[17]
- OPFRs have higher vapor pressures compared to PBDEs, leading to increased off-gassing of OPFRs from treated products into indoor air.[17]
- OPFRs are often found at higher levels compared to PBDE peak exposure levels. Studies from North America and Europe conducted in the early to mid-2000s, when PBDE use and exposure were at their height, reported average ΣBDE indoor air concentrations in 100–600 picogram per cubic meter (pg/m^3). Recent studies report levels of OPFRs in an order of magnitude higher at least (nanogram per cubic meter, ng/m^3) than for PBDEs. Higher concentrations have been detected for OPFRs than for PBDEs in hand wipe and settled dust samples (micro to milligrams per gram of dust) as well.[17]
- A study on OPFR exposure from upholstered furniture estimated the average daily dose of OPFRs from a single lounge chair to be 20 ng/kg/day for adults, 36 ng/kg/day for toddlers, and 54 ng/kg/day for infants.[20] This is just from a single chair, the total daily dose is expected to be much greater.
- OPFRs showed comparable toxicity activity to brominated flame retardants in the assays tested.[21]
- OPFRs are found on human hands[12] and shown to metabolize in the human body,[16,22] implying that flame retardant exposure to humans occurs via inhalation, hand-to-mouth contact, and dermal absorption.[17,20]
- OPFRs have recently been detected in placental tissues, suggesting they may be transferred to the developing infant.[18]
- OPFRs and especially chlorinated OPFRs are more soluble and can persist in water, which makes it persistent mobile organic compounds.[17] Wildlife and fish species across North America, Europe, and Asia have been consistently found to contain quantifiable organophosphate ester concentrations.[4]
- OPFRs have also accumulated in Arctic sediments at concentrations 10–100 times greater than those of PBDEs.[17]

Reactive Flame Retardants

- Reactive flame retardants are copolymerized in polyurethane foam and bound in the foam during manufacturing. [7,20,23]
- Some reactive flame retardants, such as Clariant's Exolit® OP 560, were awarded the US Environmental Protection Agency (EPA) New Chemicals Program P2 Recognition Project Award for their low environmental impacts.[24]
- Flame retardant identification via current analytical screening processes cannot easily detect reactive flame retardants because of their proprietary status. Therefore, the screening process may not identify a flame retardant if its chemical composition is unknown.

a 2211 Newmarket Parkway, Suite 106, Marietta, Georgia 30067 w chemicalinsights.org e chemicalinsights@ul.org

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a 2211 Newmarket Parkway, Suite 106, Marietta, Georgia 30067 w chemicalinsights.org e chemicalinsights@ul.org