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Hidden Hazards in the Nursery

Hidden Hazards **in the Nursery**

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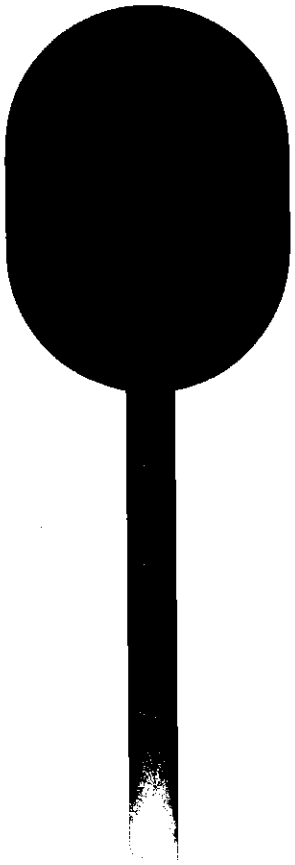


Hidden Hazards in the Nursery

Executive Summary

Parents expect the products they buy for their babies to be safe. But new testing of 20 baby and children's products, including bassinet pads, nursing pillows, changing pads, and car seats, has found toxic flame retardants in 85% of the items.

Washington Toxics Coalition and Safer States tested newly purchased baby and children's items from major retailers including Babies R Us, Sears, Walmart, and Target. Products were purchased in Connecticut, Maryland, Massachusetts, Michigan, New York, and Washington State. All of the products tested contained polyurethane foam, which is commonly treated with flame retardants in many types of products.

Analysis of the foam found toxic flame retardants present in 17 of the 20 items tested. Sixteen of the items with flame retardants contained "Tris" flame retardants. The most frequently detected Tris flame retardant was a chemical known as chlorinated Tris, or TDCPP. Chlorinated Tris became well known for its removal from children's pajamas in the 1970s after laboratory studies found it could cause mutations, making it potentially cancer-causing. It has received increased attention as it has come into widespread use to replace the phased out PBDEs as flame retardants in foam, and the State of California listed chlorinated Tris as a carcinogen in October of 2011. Another Tris flame retardant, TCEP, has also been designated a carcinogen.

Flame retardants were present at high concentrations. The 17 products that tested positive for the additives contained an average level of 3.9% flame retardants by weight in the foam. Because these flame retardants are not chemically bound to the foam, they can escape from it and contaminate home environments.

Children are likely to have both more exposure to flame retardants and greater vulnerability to their effects. Children spend more time on or near the floor, and have more hand-to-mouth contact than adults, increasing their exposure to chemicals found in household dust. Because they are still developing, children are also more susceptible to the harmful effects of toxic chemicals.

Legislatures in several states are considering restrictions on Tris flame retardants. Environmental health organizations across the country are calling for swift action to stop the use of chlorinated Tris in baby and children's products, as well as policy changes to stop companies from replacing one toxic chemical with another.

Washington State Legislatures should ban toxic Tris flame retardants in consumer products, particularly the carcinogens TCEP and TDCPP. States were the first to take action on PBDE flame retardants, and can take swift action to address this new threat. New York banned TCEP in early 2011, and a number of state legislatures will consider bans on Tris flame retardants in 2012.

Washington State should require companies to make safer products and switch to the safest chemicals and manufacturing methods. For too long, many companies have gone from one toxic chemical to another, never making health and safety a priority. To get off the toxic treadmill, companies need to find safer materials, processes, and chemicals to replace toxic chemicals in products. States should adopt policies requiring companies that use toxic chemicals to conduct thorough assessments and identify safer materials, processes, and chemicals.

Introduction

Flame retardant chemicals have a long history of toxic troubles. In 1973, Michigan farm families had high levels of flame retardant exposure when the flame retardants PBBs were accidentally mixed into cattle feed, contaminating the food supply in that state. PCBs, used as coolants in electrical installations around the world, were banned in the United States in 1979 when they were discovered to cause cancer.

So perhaps we shouldn't have been so surprised in 2003 to learn that PBDEs, which had become one of the most commonly used flame retardants in the United States, were contaminating U.S. women's breastmilk at levels far greater than in other countries[1]. Like PCBs, the PBDE flame retardants were able to build up in people and wildlife and concentrate in breastmilk. By the late 1990s and early 2000s, scientists were discovering frighteningly fast increases in PBDE levels in wildlife such as harbor seals and orcas[2-4]. And researchers were discovering in laboratory studies that a single dose of PBDEs at a critical point in development could have lifelong impacts on learning and memory[5].

By dominating the market for both polyurethane foam and certain plastics, PBDEs had made their way into major products in our homes: our televisions, couches, and other foam-containing items such as nursing pillows. They were escaping from these products and building up in house dust, exposing adults and children right in their homes.

Once information about the hazards of PBDEs became widely known, state legislatures took action. Washington, California, and Maine were the first to act, banning the flame retardants. Eventually, the chemical manufacturers came to an agreement with the U.S. Environmental Protection Agency (EPA) to stop producing all forms of PBDEs.

But instead of ending the legacy of toxic flame retardants, chemical companies and product manufacturers ignored what policymakers and consumers really wanted—safer products. Most companies failed to fully evaluate the replacement options for health and safety. Instead, they reached for the easiest substitutes, flame retardants that have their own toxic troubles.

Companies are not required to report what flame retardant they're using or label their products accordingly, so consumers have no way of knowing what chemicals their couch, changing pad, or nursing pillow contains. Scientists have attempted to fill in the information gap with testing, and the most recent information indicates that for baby products like changing pads and car seats, companies have chosen a chemical with a long history of problems: chlorinated Tris (TDCPP), used in children's pajamas in the 1970s and quickly removed when it was found to be mutagenic, making it potentially cancer-causing[6].

For most of the products we tested, no standard actually requires that they contain flame retardants. We only see flame retardants in many types of children's products because of an outdated flammability standard set by the state of California, known as TB117. These types of products are not required to contain flame retardants when they are sold in other states. Even in California, strollers, infant carriers, and nursing

pillows are exempt from flammability requirements. Car seats, however, are required to meet a national flammability standard under motor vehicle safety standards.

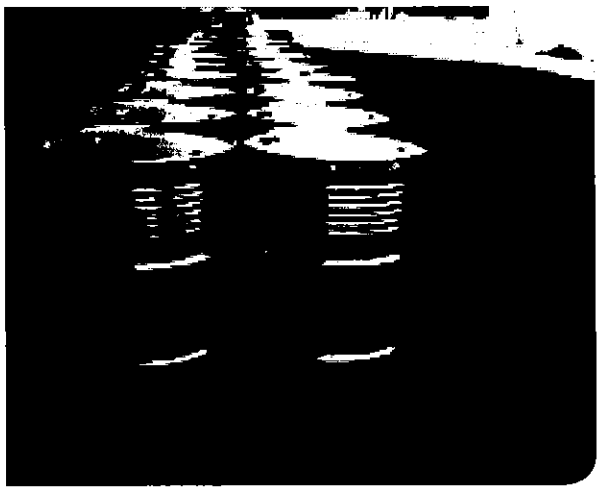
This study provides up-to-date information on what chemicals are being used in an array of baby products containing polyurethane foam. Washington Toxics Coalition and Safer States tested foam from changing pads, bassinet pads, nursing pillows, a walker, and a sleep positioner. We purchased 20 new products in Connecticut, Maryland, Massachusetts, Michigan, New York, and Washington State in September 2011. Pieces of the foam were removed from each item, labeled with a sample ID code, and shipped to Duke University for chemical analysis. Detailed information on the methods can be found in Appendix 2.

Toxic Cast of Characters

Chlorinated Tris, or TDCPP

TDCPP, or Tris (1,3-dichloro-2-propyl) phosphate, had its 15 minutes of fame in the late 1970s, when it was used in children's pajamas, then removed when it was discovered to be mutagenic[7]. The chemical faded out of the spotlight until the 2000s, when a replacement was needed for the persistent toxic flame retardant penta-BDE. TDCPP is now one of the leading chemicals used to treat polyurethane foam for flame resistance, and by 2006 between 10 and 50 million pounds were produced or imported into the United States on a yearly basis[8].

Sadly, the switch to TDCPP appears to have been more "out of the frying pan, into the fire" than a move from a toxic to safer chemical. TDCPP has not been thoroughly tested for health and safety, but the tests that have been conducted indicate that it is carcinogenic, may disrupt hormone levels, and may even be toxic to the nervous system.



BARRELS OF TDCPP

Cancer: TDCPP was designated as a carcinogen by the State of California under Proposition 65 in October 2011 based on laboratory studies finding increases in kidney, liver, and testicular tumors as well as evidence of mutagenicity[9, 10]. Previously, a Consumer Product Safety Commission (CPSC) assessment designated the chemical as a probable carcinogen and estimated the number of excess cancers due to exposure at 300 cancers per million adults[11]. Since most regulations are designed to limit excess cancers to one per million, this assessment put TDCPP's cancer hazard at 300 times the level considered acceptable.

Mutagenicity: A number of studies have tested whether TDCPP can cause mutations, heritable changes in DNA that can lead to cancer and other problems. TDCPP caused several kinds of mutations in some but not all cell lines[7, 10].

Hormone disruption: A study published in 2010 found that men with greater exposure to TDCPP had lower levels of thyroid hormone and higher levels of prolactin, a hormone involved in a number of functions[12]. The study evaluated exposure by determining the level of the flame retardant in house dust, and hormones were measured in blood serum.

Nervous system harm: Researchers have begun to look at whether TDCPP, like other similar chemicals, can harm the nervous system. A 2011 study tested the chemical's effects on the development of brain cells and compared its effects to those of chlorpyrifos, a pesticide known to be toxic to the nervous system[13]. By some measures, TDCPP was even more toxic to the cells than chlorpyrifos, with effects on cell development, number, and DNA synthesis.

As a result of its widespread use, TDCPP has been detected in house dust, indoor air, breast milk, semen, urine, surface water, fish, food, and drinking water [10, 13-16]. A 2009 Boston study of 50 homes found it in house dust at levels that were comparable to those of PBDEs, an indication of the significance of its use in the home environment[17].

TCEP

Tris (2-chloroethyl) phosphate, or TCEP, is another "Tris" flame retardant found in polyurethane foam as well as in other products. TCEP has been used for several decades, with production in 2006 reported as between 500,000 and one million pounds. It has also been reported to be used as a plasticizer and in industrial processes[18].

TCEP has been widely detected in surface water, with the United States Geological Survey finding it in 58% of 139 streams sampled nationally[19]. Tests of indoor air have found the chemical in homes, offices, libraries, hospitals, and computer classrooms [20, 21].

Laboratory studies have indicated that TCEP causes cancer, harms the nervous system, and impairs fertility. Because of these concerns, the European Union has designated it as a Substance of Very High Concern, and it has been listed by the state of California as a carcinogen under Proposition 65.

Cancer: The National Institutes of Health conducted a two-year study of mice and rats exposed to TCEP in their food, and found increases in kidney tumors in rats[22]. Other studies have found increased rates of kidney tumors, leukemia, and thyroid cancer[23].

Nervous system harm: In laboratory studies, animals exposed to TCEP developed convulsions and striking damage to the brain including lesions and loss of neurons [23, 24]. The animals also had lasting damage to learning and memory.

Reproductive toxicity: TCEP appears to have the ability to broadly affect fertility. Mice exposed to the chemical had reduced sperm count, damaged sperm, and fewer pups per litter[25]. When researchers attempted to mate unexposed females with exposed males, the pairs did not exhibit normal mating behavior and only one female bore a litter.

TCPP

TCPP, or Tris (1-chloro-2-propyl) phosphate, is structurally similar to TCEP and TDCPP and apparently came into greater use in the 1960s as a replacement for TCEP[16]. It is produced in very large quantities, reported at between 10 and 50 million pounds in 2006, and used in both rigid and flexible polyurethane foams.

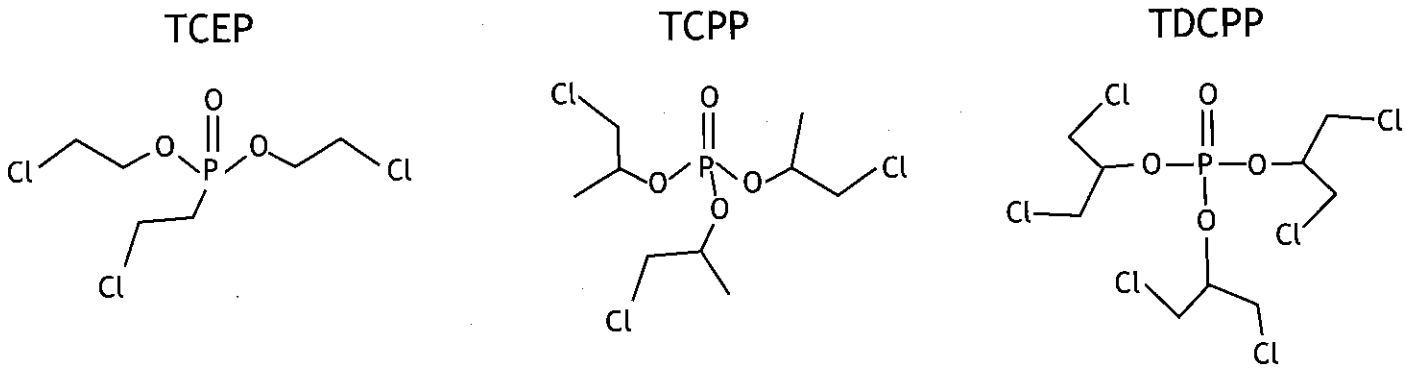
TCPP has been found in discharges from homes and industries[16]. It is known to leach out of foam into air, and has been found in air samples in cars, offices, and furniture stores[16, 26, 27]. Very little information is available on TCPP's toxicity. Basic laboratory testing shows that it has low to moderate acute toxicity and moderate to high aquatic toxicity. Full testing on reproductive and immune effects has not been conducted, but one study found that hens ceased egg production after treatment with TCPP[16]. The structural similarity of TCPP to the other Tris flame retardants raises suspicions that it will have similar toxicity.

Firemaster 550

Firemaster 550 is a mixture of four different compounds, introduced by Great Lakes Chemical Corporation in 2001 and used as a replacement for penta-BDE in foam. Firemaster 550 contains triphenyl phosphate (TPP), bis (2-ethylhexyl) tetrabromophthalate (TBPH), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (TBB), as well as a suite of triaryl phosphate isomers.

TBB and TBPH have been detected in house dust, and TBB has been found in biosolids at levels comparable to those of one of the PBDE forms, deca-BDE. Little is known about their toxic effects. TBPH is very similar, however, to the hormone-disrupting phthalate DEHP; it is essentially a brominated form of the chemical. Animals metabolize DEHP to the form MEHP, which in turn is similar to the Firemaster 550 component TBB[28].

A 2010 study tested whether Firemaster 550 could cause DNA damage in fathead minnows. Researchers found the fish can accumulate TBPH and TBB to some extent, and that exposed fish had damage to DNA[28]. The primary health and safety concern for TPP, the other component of Firemaster 550, is its toxicity to aquatic organisms[29].



THE SIMILAR CHEMICAL STRUCTURES OF TCEP, TCPP, AND TDCPP

Toxic Flame Retardants in Children's Products

Since companies don't disclose what flame retardants they are using in their products, scientists have been working since the phaseout of PBDEs to uncover their replacements. Since 2009, studies testing polyurethane foam in furniture and children's products have primarily identified the Tris flame retardants as well as the components of Firemaster 550.

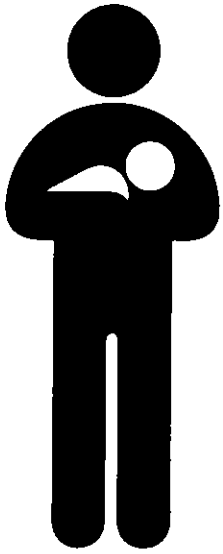
Earlier this year, a study of 101 baby products found chlorinated Tris in 36% of the products, TCEP in 14%, and Firemaster 550 in 17%. That study collected items currently in use, so it provided information on flame retardants in products already in homes, some in use since as early as 2002[6].

For this study, we purchased brand-new items to obtain up-to-date information on flame retardants in children's products currently for sale. We selected foam-containing baby and children's items from major retailers including Babies R Us, Target, Walmart, and Sears, in six states. We sent samples of the foam from each of these products to Dr. Heather Stapleton's research laboratory at Duke University for testing.

Our tests indicate that chlorinated Tris is far and away the most prevalent flame retardant in children's products. TDCPP was present in 16 of the 20 products, an 80% detection rate. Products containing the chemical included a nursing pillow, a co-sleeper, changing pads, bassinet pads, car seats, booster seats, and an activity walker. Altogether, TDCPP made up 63% of the total flame retardants detected in the 20 products tested.

Flame retardants were present in the products at high levels. TDCPP was detected in the foam portion of the product at an average level of 2.6% by weight, and concentrations ranged up to 5%. Total flame retardant concentrations ranged from 1.5% to 5.5%, with an average of 3.9%.

TDCPP was nearly always paired with TCPP, although the latter was often present in smaller concentrations. In some cases, TCPP was present at higher concentrations than TDCPP. Only one product included TCEP, paired with several other flame retardants including one known as V6, which contains TCEP as an impurity. Firemaster 550 was present in only one product, an infant recliner made with dense foam. An as yet unidentified chlorinated organophosphate flame retardant (U-OPFR) was also detected in six products, and was observed in the previous study of baby products[6].



WE SELECTED FOAM-CONTAINING BABY AND CHILDREN'S ITEMS FROM MAJOR RETAILERS INCLUDING BABIES R US, TARGET, WALMART, AND SEARS, IN SIX STATES...FLAME RETARDANTS WERE PRESENT IN THE PRODUCTS AT HIGH LEVELS.

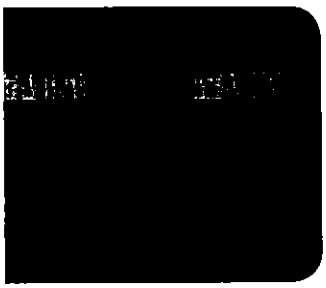


Table 1: Flame Retardants in Children's Products

Product	State Purchased	Flame Retardants*
My Brest Friend Deluxe Nursing Pillow	WA	TDCPP, TCPP
Balboa Baby Nursing Pillow	WA	none detected
Mini classic Co-sleeper by Arm's Reach	WA	V6, TCPP, TCEP, TDCPP, U-OPFR
Munchkin Contour Changing Pad	WA	TDCPP, TCPP
Summer Changing Pad	WA	TDCPP, TCPP, U-OPFR
Babies R Us Contoured Changing Pad	WA	TCPP, TDCPP, U-OPFR
Summer Bassinet Pad	WA	TDCPP, TCPP, U-OPFR
Graco Turbobooster Elite Booster Seat (for auto use)	WA	TDCPP, TCPP
Comfort Deluxe Booster Seat (for auto use)	WA	TDCPP, TCPP
Safety 1st Sounds 'n Lights Activity Walker	WA	TDCPP, TCPP
First Years Co-sleeper	MD	none detected
Dex Changing Pad	MD	TDCPP, TCPP
Nap Nanny Infant Recliner	MA	Firemaster 550
Cosco Scenera Convertible Car Seat	MA	TCPP, TDCPP, U-OPFR
Eddie Bauer Pop-up Booster Seat (non-auto use)	NY	none detected
Nod-a-way Bassinet	CT	TDCPP, TCPP
Babies R Us Bassinet Pad	CT	TCPP, TDCPP, U-OPFR
Graco Snugride Infant Car Seat	MI	TDCPP
Chicco Key Fit Infant Car Seat	MI	TDCPP, TCPP
Britax Roundabout 50 Convertible Car Seat	NY	TDCPP

** Flame retardant detected at highest concentration listed first.*

From Foam to People

In researching the now phased-out PBDE flame retardants, scientists learned that for some pollutants, ingestion of house dust can be the main source of exposure. Like PBDEs, the Tris flame retardants are additive, meaning they are not chemically bound to the materials they are used in, and are therefore likely to escape from those materials. Tris flame retardants are not yet as well studied as PBDEs, but studies so far indicate that they are building up in house dust as well as in indoor air.

Studies in Sweden conducted in the early 2000s found TDCPP and TCEP in dust collected from homes, a day care center, a hospital, offices, and other public locations. Concentrations ranged up to 94 ppm, with the highest level of TCEP found in a library and the highest TDCPP concentrations in an office. Researchers also tested air for the flame retardants, finding both compounds and concluding that both air and dust

are significant sources of exposure for children and adults. Because of their greater contact with the floor and higher hand-to-mouth contact, children were predicted to have much higher exposures than adults[30].

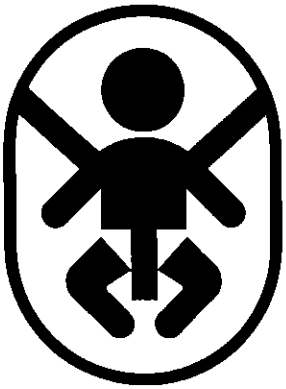
In the U.S., samples of dust from homes in the Boston area contained surprisingly high levels of TDCPP, with 96% of the samples containing the chemical. The mean level was 1,890 parts per billion (ppb), comparable to the levels of PBDEs found in the homes. Some homes had extremely high concentrations, however, leading researchers to conclude that approximately 5% of American homes could have very high levels of the compounds[17].

In a typical U.S. home, Tris flame retardants are most likely to be found in foam-containing items, including upholstered furniture and baby products. The products tested in this study are likely to contribute to contamination of indoor air and house dust with TDCPP and TCEP and thus contribute to human exposures. Infants may have particularly high exposures to the flame retardants from baby products because of their close proximity. Use in car seats is also likely to lead to air and dust exposures inside automobiles.

Table 2: Summary Chart of Flame Retardants Found in Children's Products

Flame Retardant	Number of Products	Types of Products
TDCPP (Chlorinated Tris)	16	Nursing Pillow, Co-sleeper, Changing Pads, Bassinet Pads, Car Seats, Booster Seats, Activity Walker
TCPP	14	Nursing Pillow, Co-sleeper, Changing Pads, Bassinet Pads, Booster Seats, Car Seats, Activity Walker
U-OPFR (unidentified chlorinated organophosphate flame retardant)	6	Co-sleeper, Changing Pads, Bassinet Pads, Car Seat
TCEP	1	Co-sleeper
V6	1	Co-sleeper
Firemaster 550 (TPP, TBB, TBPH)	1	Infant Recliner

Safer Choices



ORBIT BABY, A MANUFACTURER OF STROLLERS, BASSINETS, AND CAR SEATS, REPORTS THAT IT MEETS FLAMMABILITY STANDARDS WITHOUT THE USE OF BROMINATED OR CHLORINATED CHEMICALS.

Flame retardants are used in children's products such as changing pads primarily to meet a flammability standard set by the state of California. This standard applies to furniture and juvenile products only within California, but is widely adhered to by companies with national distribution for their products. Nursing pillows and baby carriers were recently specifically exempted from this standard, known as Technical Bulletin 117. For car seats, a flammability standard under the Federal Motor Vehicle Safety Standards applies.

While many companies use chemical flame retardants to meet these standards, others use alternative materials that do not involve chemical additives. For instance, manufacturers can replace plastic components with non-flammable materials such as metal, glass, or ceramics; polyester fill, such as that typically used in pillows, can replace foam for some uses, meeting standards without added flame retardants[31]. Even with polyurethane foam, barriers can be used and commonly are for mattresses.

When Washington State evaluated alternatives to deca-BDE for upholstered furniture, it concluded that inherently fire-resistant cover materials could be used, such as those made from synthetic fibers, as well as barrier materials[29].

Because of the widespread concern about toxicity of flame retardants containing bromine or chlorine, which describes most of the commonly used flame retardants on the market today, efforts are underway to generate additional safer alternatives. Options under development include a polymer based on a byproduct of cashew nut processing, a silicon-based polymer, nanoclay, and others[32-34]. Alumina trihydrate is also considered a safer, effective option[35].

Orbit Baby, a manufacturer of strollers, bassinets, and car seats, reports that it meets flammability standards without the use of brominated or chlorinated chemicals. Instead, its blend of cotton and wool meets the California standard for juvenile products as well as federal motor vehicle standards for car seats.

Getting Off the Toxic Treadmill

Thirty-five years after passage of what was supposed to be a landmark federal toxics law, most chemical companies and product manufacturers have never made health and safety a priority in their chemical choices. The law doesn't require them to. The Toxic Substances Control Act, passed by Congress in 1976, grandfathered in tens of thousands of chemicals, allowing their use without requiring them to undergo testing or be safe for people and wildlife. New chemicals today must undergo only a perfunctory approval lacking the kind of rigorous testing most Americans would expect.

Our testing of flame retardants in baby products shows that when companies abandoned PBDEs, neurotoxic flame retardants that were building up in people and wildlife, they failed to replace them with a safer option. Instead, most companies reached for a chemical previously removed from children's sleepwear because of safety concerns.

To get us off this toxic treadmill, we need laws that require testing of all chemicals for health and safety and end the use of chemicals that cause cancer, infertility, nervous system harm, and other serious health problems. The Safe Chemicals Act of 2011, introduced in Congress by Senator Frank Lautenberg, would move in this direction. At the state level, a number of states have taken action to ban toxic chemicals including bisphenol A (BPA) and toxic flame retardants. Some are also developing programs to move companies toward safer chemicals, materials, and processes in their products.

Recommendations

The Washington State Legislature should ban toxic Tris flame retardants in consumer products, particularly the carcinogens TCEP and TDCPP.

States were the first to take action on PBDEs, and can take swift action to address this new threat. New York banned TCEP in early 2011, and a number of states will consider bans on Tris flame retardants in 2012. States can't wait for Congress—they need to protect their residents from this immediate threat. At the same time, action at the state level will prompt Congress to act. States are proven laboratories for chemicals policy, showing what actions will succeed in protecting health and providing a model for federal action. State action also motivates industry to seek a federal solution, to avoid a patchwork of regulation across the country.

Washington State should require companies to replace toxic chemicals with safer solutions.

To get off the toxic treadmill, companies need to find safer materials, processes, and chemicals to replace toxic chemicals in products. Without legal requirements, however, only the most health- and safety-conscious companies will take this kind of action. To level the playing field and avoid costly and unproductive substitutions, states should pass legislation requiring companies that use toxic chemicals to conduct thorough assessments and identify safer materials, processes, and chemicals. Eleven states are already working together, as part of the Interstate Chemicals Clearinghouse, to create a common understanding of how companies should assess chemical hazards and identify safer options.

Appendices

						Firemaster 550		
	TCEP (mg/g)	TCPP (mg/g)	TDCPP (mg/g)	"V6" (mg/g)	U-OPFR (mg/g)	TPP (mg/g)	TBB (mg/g)	TE
/	< 0.04	2.04	30.50	ND	ND	<0.02	<0.02	
	< 0.04	<0.01	<0.08	ND	ND	<0.02	<0.02	
h	2.99	17.95	0.64	24.97	X	<0.02	<0.02	
	< 0.04	4.48	40.12	ND	ND	<0.02	<0.02	
	< 0.04	17.68	25.27	ND	X	<0.02	<0.02	
	< 0.04	37.65	17.20	ND	X	<0.02	<0.02	
	< 0.04	19.84	22.30	ND	X	<0.02	<0.02	
t	< 0.04	0.31	34.98	ND	ND	<0.02	<0.02	
o	< 0.04	16.83	24.10	ND	ND	<0.02	<0.02	
	< 0.04	1.86	24.78	ND	ND	<0.02	<0.02	
	< 0.04	<0.01	<0.08	ND	ND	<0.02	<0.02	
	< 0.04	0.76	23.55	ND	ND	<0.02	<0.02	
	< 0.04	<0.01	<0.08	ND	ND	15.85	20.20	
	< 0.04	15.34	0.05	ND	X	<0.02	<0.02	
	< 0.04	<0.01	<0.08	ND	ND	<0.02	<0.02	
	< 0.04	9.85	33.04	ND	ND	<0.02	<0.02	
	< 0.04	25.80	16.22	ND	X	<0.02	<0.02	
	< 0.04	<0.01	50.63	ND	ND	<0.02	<0.02	
	< 0.04	0.43	34.72	ND	ND	<0.02	<0.02	
r	< 0.04	<0.01	46.48	ND	ND	<0.02	<0.02	

LC/MSMS, but no standard was available for measurement or confirmation purposes

Appendix 2:

Detailed Methods

Children's products containing polyurethane foam were purchased in Connecticut, Maryland, Massachusetts, Michigan, New York, and Washington State from major retailers. In most cases, products outside of car seats bore the TB 117 label. An approximately one-inch cube of foam was cut from each product, packaged in aluminum foil and a ziploc bag, labeled with the sample ID, and sent to Duke University for analysis.

Analytical methods are as follows, courtesy of Heather Stapleton, Duke University.

Materials:

Internal standards were purchased from Chiron (Trondheim, Norway) and Wellington Laboratories (Guelph, Ontario). 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (TBB) and bis (2-ethylhexyl)-2,3,4,5-tetrabromophthalate (TBPH) were purchased from Wellington Laboratories. Tris (2-chloroethyl) phosphate (TCEP), tris (1-chloro-2-propyl) phosphate (TCPP) and tris (1,3-dichloroisopropyl) phosphate (TDCPP) were purchased from Sigma-Aldrich (St. Louis, MI), Pfaltz & Bauer (Waterbury, CT), and ChemService (West Chester, PA), respectively. Deuterated standards for TCEP and TDCPP were synthesized by Dr. Vladimir Belov (Goettingen, Germany). Deuterated TPP was purchased from Sigma Aldrich (St. Louis, MI). A commercial mixture of V6 was purchased from a flame retardant manufacturer in China (Hongming Auxiliaries CO., LTD, Jiande, Zhejiang Province, China). All solvents used throughout this study were HPLC grade.

Sample Analysis by Mass Spectrometry:

All foam samples were first screened for flame retardant additives. Briefly, small pieces of foam (approximately 0.05 grams) were sonicated with 1 mL of dichloromethane (DCM) in a test tube for 15 minutes. The DCM extract was syringe-filtered to remove particles and then transferred to an autosampler vial for analysis by gas chromatography mass spectrometry (GC/MS). All extracts were analyzed in full scan mode using both electron ionization (GC/EI-MS) and negative chemical ionization (GC/ECNI-MS). Pressurized temperature vaporization injection was employed in the GC. GC/MS method details can be found in [36]. All significant peaks observed in the total ion chromatograms were compared to a mass spectral database (NIST, 2005) and to authentic standards when available.

If a previously identified flame retardant chemical was detected during the initial screening, a second analysis of the foam sample, using a separate piece of the foam, was conducted for quantitation of detected flame retardants. Methods for extracting and measuring flame retardants in foam are reported in earlier publications[6, 17]. Briefly, approximately 100mg samples of foam were extracted with dichloromethane using accelerated solvent extraction. Extracts were reduced in volume to approximately 2-3 mLs and weighed. Aliquots (100-500 µL) were transferred to 100 mL volumetric flasks and diluted with dichloromethane. A final 1 mL aliquot was then transferred to a GC autosampler vial and the appropriate internal standards (dTCEP, dTDCPP, dTPP or F-BDE 69) were added. The brominated components of the Firemaster 550 mixture, TBB and TBPH, were quantified by GC/ECNI-MS by monitoring molecular fragments m/z 357/471 and 463/515, respectively. TCEP, TCPP, TDCPP, and TPP were quantified by GC/EI-MS by monitoring m/z 249/251, 277/201, 381/383, and 325/326, respectively. V6 was measured using liquid chromatography tandem mass spectrometry (LC/MS-MS) using multiple reaction monitoring (MRM) by integrating responses for the transition from m/z 582.7 to 234.8 and using dTCEP as an internal standard. A five point calibration curve was established for all analytes with concentrations ranging from 20 ng/mL to 2 µg/mL.

Appendix 3:

Glossary

Acronym	Full Chemical Name
DEHP	bis (2-ethylhexyl) phthalate
MEHP	mono (2-ethylhexyl) phthalate
PBB	polybrominated biphenyl
PBDE	polybrominated diphenyl ether
PCB	polychlorinated biphenyl
TBB	2-ethylhexyl-2,3,4,5-tetrabromobenzoate
TBPH	bis (2-ethylhexyl) tetrabromophthalate
TCEP	Tris (2-chloroethyl) phosphate
TCPP	Tris (1-chloro-2-propyl) phosphate
TDCPP	Tris (1,3-dichloro-2-propyl) phosphate
TPP	triphenyl phosphate

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