Use of Flame Retardant Chemicals in Furniture: What are the Risks?

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Outline

1. **Introduction and Background**
   a. What is a flame retardant (FR) and how do they work?
   b. What regulations govern the use of FRs in products?
   c. What type of products contain FRs?
   d. What type of FRs are used in consumer products?

2. **Exposure to the Flame Retardants PBDEs During Early Development**

3. **Identification of PBDE Replacement Chemicals in Furniture**
   a. In Baby Products
   b. In Residential Furniture

4. **What do we know about Exposure and Effects of PBDE Replacements: Are they Better or Worse?????**

5. **Conclusions/ Discussion**

Definition:

"A substance added or a treatment applied to a material in order to suppress, significantly reduce or delay the combustion of the material" *EHC:192, WHO 1997*

Regulations That Govern the Use of FRs

U.S. Residential Furniture:

- California Technical Bulletin 117

Electronics:

- Underwriters Laboratory Certifications for Insurance purposes (e.g. UL 746 and -94 V-2 – E&E)

Textiles:

- Children's Sleepwear (CPSC)
- Seats and Drapes in Public Buildings (NFPA 701, CA TB 133)

What Type of Products are Treated with Flame Retardants in Your Home?

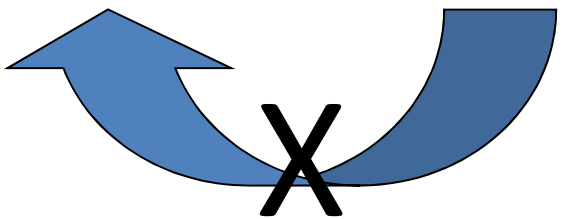
Sleep Positioners

Nursing Pillow

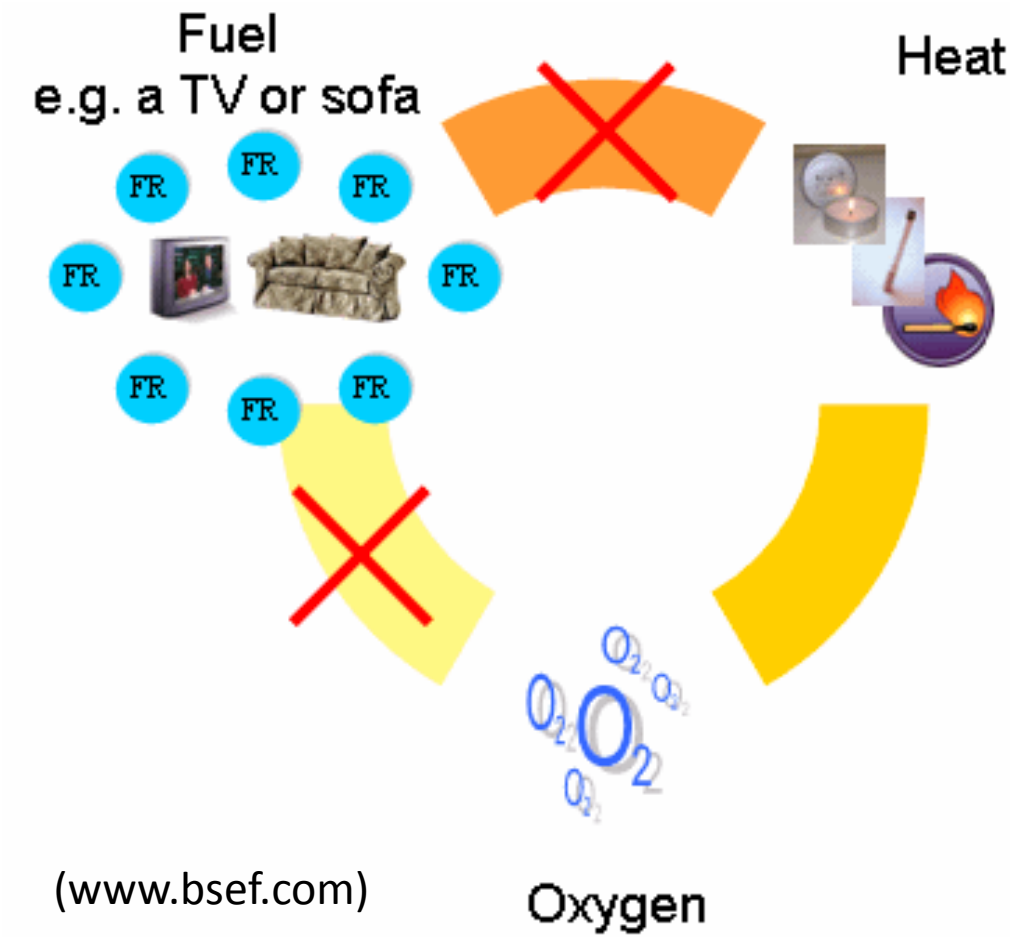
How Do They Work?

- **Most common method for retarding fire is to quench the radical species formed in the fire reaction**

$$\text{Fuel} + O_2 \longrightarrow \text{Heat} + CO_2 + H_2O$$



***Stop the formation of radical species**



(www.bsef.com)

Flame Retardants are Classified According to Use:

REACTIVE FRs:

- Chemically bound to the product they are flame retarding….less likely to leach out into the environment

ADDITIVE FRs:

-Mixed in with the resin during extrusion process…..more likely to leach out of products over time

Examples: **PentaBDE**
OctaBDE
DecaBDE

} Commercial Mixture Names

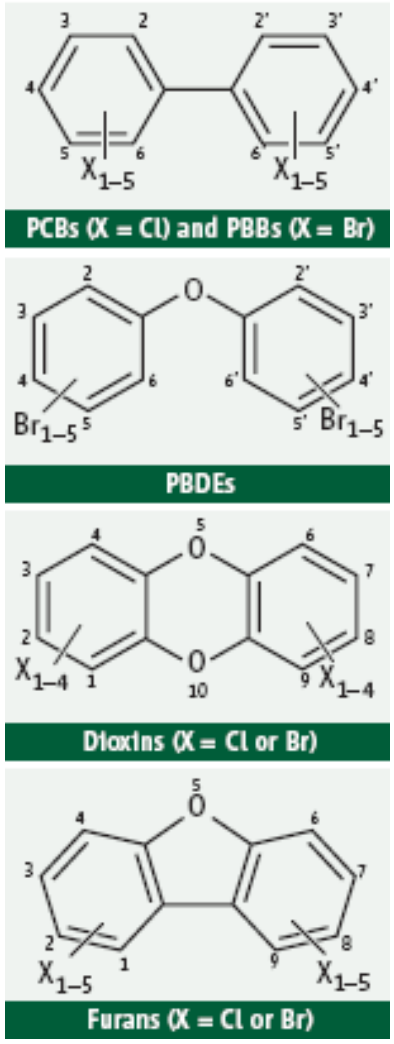
PBDE Commercial Mixtures

Congener (# of Br atoms)	% of Mixture
PentaBDE Commercial Mixture (DE-71; Phased out 2004)	
BDE 47 (4)	38.2
BDE 85 (5)	2.96
BDE 99 (5)	48.6
BDE 100 (5)	13.1
BDE 153 (6)	5.44
BDE 154 (6)	4.54
OctaBDE Commercial Mixture (DE-79; Phased out 2004)	
BDE 153 (6)	8.66
BDE 154 (6)	2.68
BDE 183 (7)	42.0
BDE 196 (8)	10.5
BDE 197 (8)	22.2
BDE 207 (9)	11.5
DecaBDE Commercial Mixture (Saytex 102E)	
BDE 206 (9)	2.19
BDE 207 (9)	0.24
BDE 208 (9)	0.06
BDE 209 (10)	96.8

Product Applications

(La Guardia et al 2006)

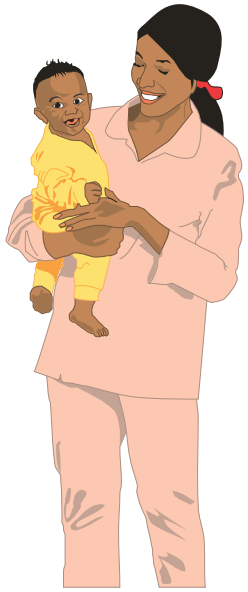
History of PBDEs and their Phase Out



- Polybrominated diphenyl ethers (PBDEs) have chemical structures which are very similar to known cancer causing and toxic compounds: **PCBs, dioxins, furans, etc**.
- Animal and Human studies have demonstrates that PBDEs are significantly associated with changes in thyroid hormone levels (Birnbaum and Staskal, 2003; Chevrier et al. 2010; Stapleton et al. 2011)
- Human health studies have found significant associations between PBDEs in blood at birth and deficits in cognitive function and behavior (Herbstman et al 2010; Eskenazi et al 2012)
- Phased out in European Union (2002); voluntary phase out in the US (Penta- and OctaBDE- 2005; Deca-2013)

How Are We Exposed to Flame Retardants?

Work Environment



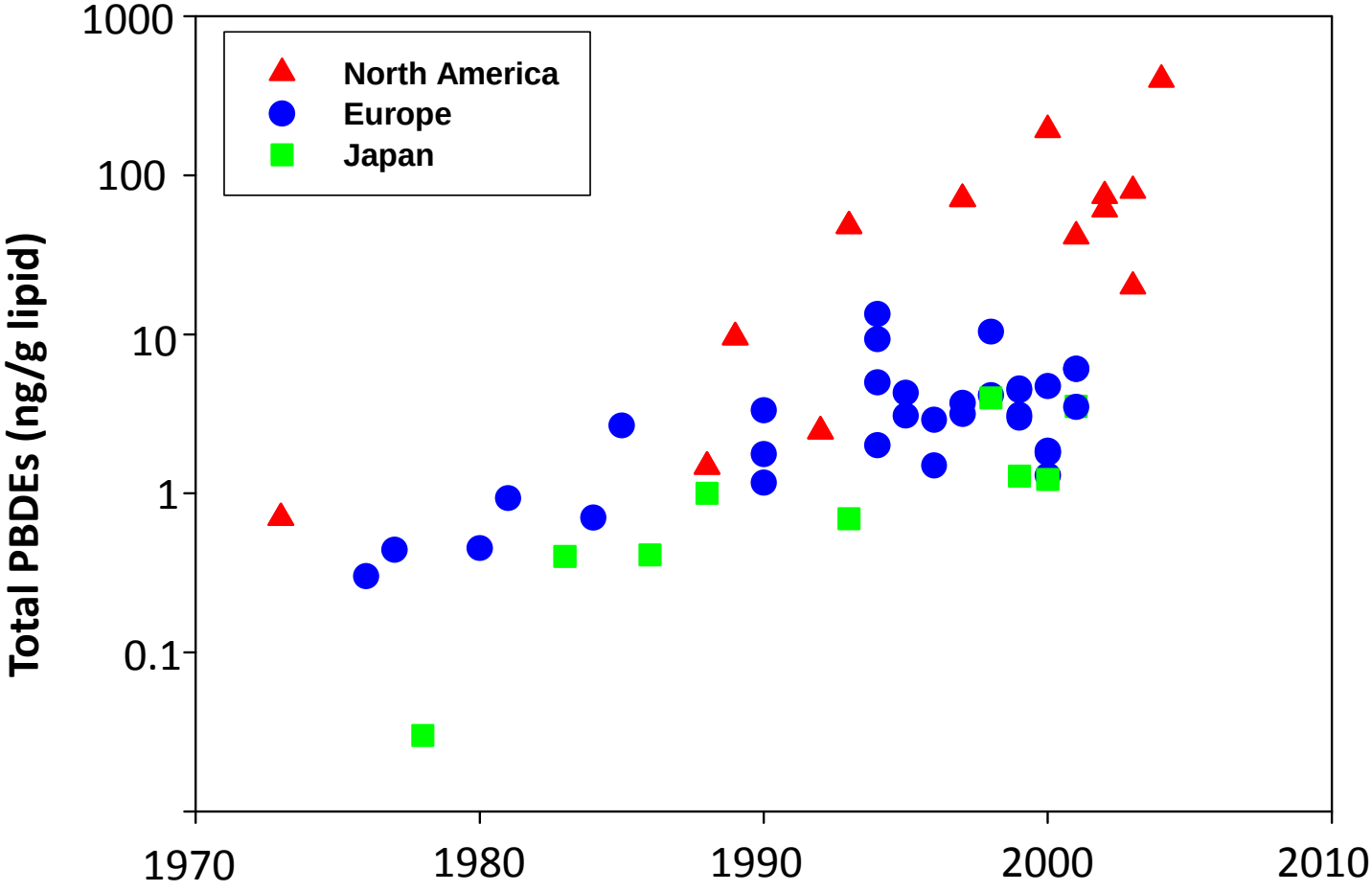
Our Home

House Dust

Diet

Vehicles

PBDEs in Human Samples From Around the World



From Hites et al., 2005

Human Exposure to PBDEs

- Exposure studies in US *adults* have observed significant associations with both diet (Wu et al., 2007; Fraser et al., 2010) and dust (Johnson et al., 2010)

- Exposure models suggested that *infants* would be receiving the highest exposure due to breast milk ingestion (Jones-Otazo et al., 2005; Schecter et al. 2003)

- However, recent studies suggest that toddlers have highest exposure among all age classes due to increased exposure to house dust:
  - Rose et al. (2010) reported levels in 2-5 year old children in California and found concentrations 2-50X higher than adults
  - Stapleton et al (2012) toddlers (ages 1-3) serum PBDE levels significantly associated with residues measured on hands, house dust, age, and race

- Several studies suggest exposure may be higher for individuals of lower SES
  - Quiros-Alcala et al. (2011) measured PBDEs in dust from low-income households; concentrations were among highest measured
  - Windham et al. (2010) measured PBDEs in 6 to 8 year old girls from California and Ohio; significantly higher concentrations in CA vs Ohio; higher in blacks compared to whites
  - Zota et al. (2010) wrote perspective article on PBDEs and socio-economic disparities

What Types of FRs are Being Used to Meet TB 117 Today?

- With the phase-out of PentaBDE, what type of chemical flame retardants would be most common in residential furniture?
- Will these new/alternate FRs accumulate in indoor dust and air- leading to human exposure?
- What is known about health effects for these new flame retardants?

Flame Retardants (FRs) Used to Meet California's TB 117

- Promulgated by California Bureau of Home Furnishing and Thermal Insulation, within the Department of Consumer Affairs

- Requires 12-second open flame testing for polyurethane inside furniture



PentaBDE Alternatives Assessment

Table 4-1 Screening Level Toxicology and Exposure Summary

L = Low hazard concern
M[4] = Moderate hazard concern
H = High hazard concern
N = No
Y = Yes
P = Yes for pure chemical
*Ongoing studies may result in a change in this endpoint
▲Persistent degradation products expected[5]
L, M[1], or *H* = Endpoint assigned using estimated values and professional judgment (Structure Activity Relationships)

Company	Chemical	% in Formulation[6]	Human Health Effects							Ecotoxicity		Environmental		Potential Routes of Exposure							Reactive or Additive?
														Worker			General Population				
			Cancer Hazard	Skin Sensitizer	Reproductive	Developmental	Neurological	Systemic	Genotoxicity	Acute	Chronic	Persistence	Bioaccumulation	Inhalation	Dermal	Ingestion	Inhalation	Dermal	Ingestion	Aquatic	
Albemarle	SAYTEX RZ-243																				
	Proprietary E Tetrabromophthalate diol diester		L	L	L*	L*	L	M*	L	L	H	L▲	L	N	Y	Y	N	N	Y	Y	Additive
	Proprietary B Aryl phosphate		L	L	M*	M*	M	M*	L	H	H	L	M	N	Y	Y	N	Y	N	N	Additive
	Triphenyl Phosphate CAS # 115-86-6		L	L	L	L	L	M	L	H	H	L	L	Y	Y	Y	Y	Y	Y	Y	Additive
Ameribrom	FR513																				
	Tribromoneopentyl Alcohol CAS # 36483-57-5		M	L	M	M	M	M	M	M	M	L	L	Y	Y	Y	N	N	Y	Y	Reactive
Great Lakes	Firemaster 550																				
	Proprietary F Halogenated aryl ester		L	L	M	M	L	M	L	H	H	L▲	L	N	Y	Y	N	Y	Y	Y	Additive
	Proprietary G Triaryl phosphate, isopropylated		L	L	M*	M*	M	M*	L	H	H	L	M	N	Y	Y	N	Y	N	N	Additive
	Triphenyl Phosphate CAS # 115-86-6		L	L	L	L	L	M	L	H	H	L	L	Y	Y	Y	Y	Y	Y	Y	Additive
	Proprietary H Halogenated aryl ester		L	L	M	M	L	M	L	H	H	L▲	L	N	Y	Y	N	Y	Y	Y	Additive
Great Lakes	Firemaster 552																				
	Proprietary F Halogenated aryl ester		L	L	M	M	L	M	L	H	H	L▲	L	N	Y	Y	N	Y	Y	Y	Additive
	Proprietary G Triaryl phosphate, isopropylated		L	L	M*	M*	M	M*	L	H	H	L	M	N	Y	Y	N	Y	N	N	Additive
	Triphenyl Phosphate CAS # 115-86-6		L	L	L	L	L	M	L	H	H	L	L	Y	Y	Y	Y	Y	Y	Y	Additive
	Proprietary H Halogenated aryl ester		L	L	M	M	L	M	L	H	H	L▲	L	N	Y	Y	N	Y	Y	Y	Additive

(Furniture Flame Retardancy Partnership V 1, EPA 2005)

Screening Consumer Products for FR Chemicals:

Project 1- Baby Products
Project 2- Residential Couches

Screening Consumer Products Meeting CA TB 117 :

Project 1- Baby Products

- car seats, nursing pillows, changing table pads, portable mattresses, sleep positioners, strollers, high chairs, etc

-donated by volunteers/families from in-use products

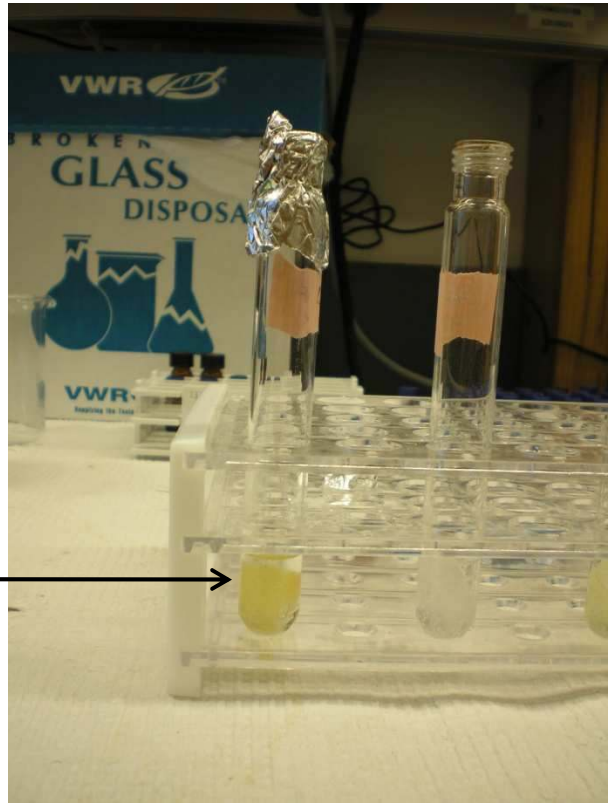
Project 2- Residential Couches

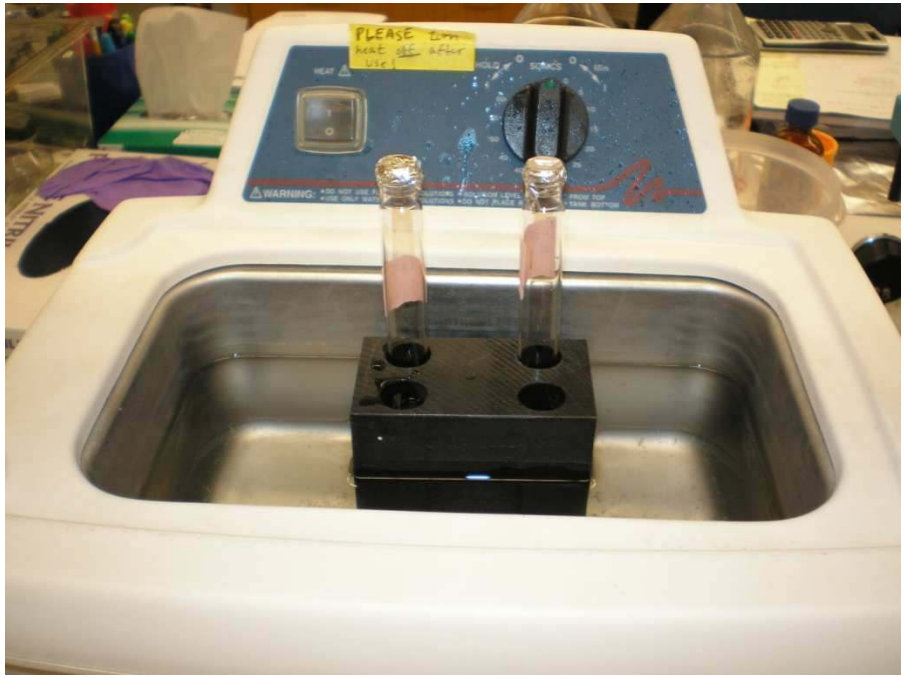
-only residential couches

- volunteers submitted samples had to know date and state of purchase

Analysis of the Foam Samples

Foam





Step 1. Place a small piece of foam into a test tube with dichloromethane

Step 2. Sonicate the test tube for 15 min.

Analysis of the Foam Samples

Step 3. Remove the dichloromethane, filter out the particles, and then inject the extract into a GC/MS*.

- Samples are run in full scan mode
- Signals detected are compared against a NIST mass spectral database
- For commonly known FRs we also now compare to authentic standards.

*Some sample extracts also run by LC/HRMS

Gas Chromatograph Mass Spectrometer (GC/MS)

Agilent Technologies Model 5975

Project 1: Flame Retardants in Children's Products

ENVIRONMENTAL Science & Technology

(2011)

Identification of Flame Retardants in Polyurethane Foam Collected from Baby Products

Sleep Positioners

Car Seats

Nursing Pillow

- **101 Baby products screened for flame retardant (FR) chemicals**
- **80% contained a FR**
- **TDCPP, Firemaster 550 (FM 550), and "V6" most common FRs identified**
- **PentaBDE found in 5 samples**
- **Identified two new chlorinated organophosphate flame retardant mixtures**
- **Risk/exposure assessments do not consider exposure from use of these products**
- **Now 3 infant/juvenile products exempted from TB 117**

Project 2: Flame Retardants in Couches

Environmental Science & Technology

Article

pubs.acs.org/est

(2012)

Novel and High Volume Use Flame Retardants in US Couches Reflective of the 2005 PentaBDE Phase Out

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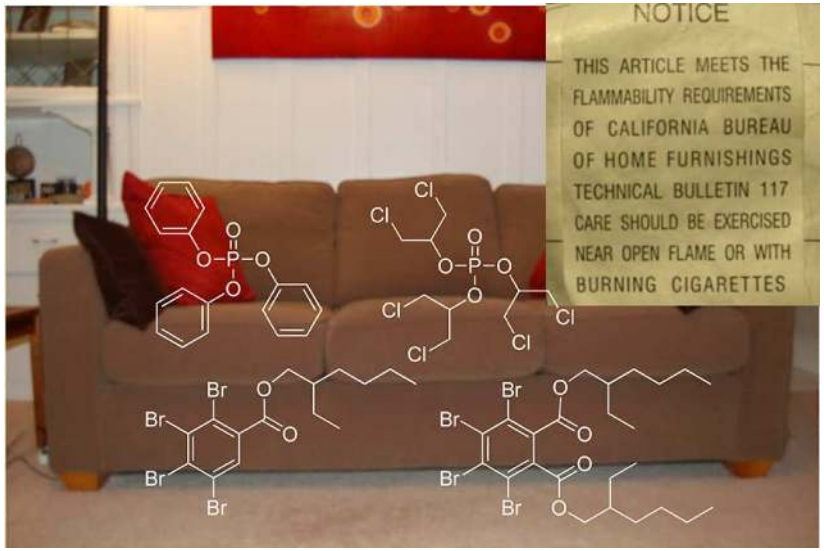
Supporting Information



- **102 foam samples collected from residential couches in the US**
- **Information on year of purchase, state where couch purchased, and presence of TB 117 label recorded**
- **Samples purchased between 1985-2010**
- **87 of 102 samples contained a FR**
- **TDCPP, PentaBDE, and Firemaster 550 (FM 550) most common FRs identified**
- **Identified two new organophosphate flame retardant mixtures**

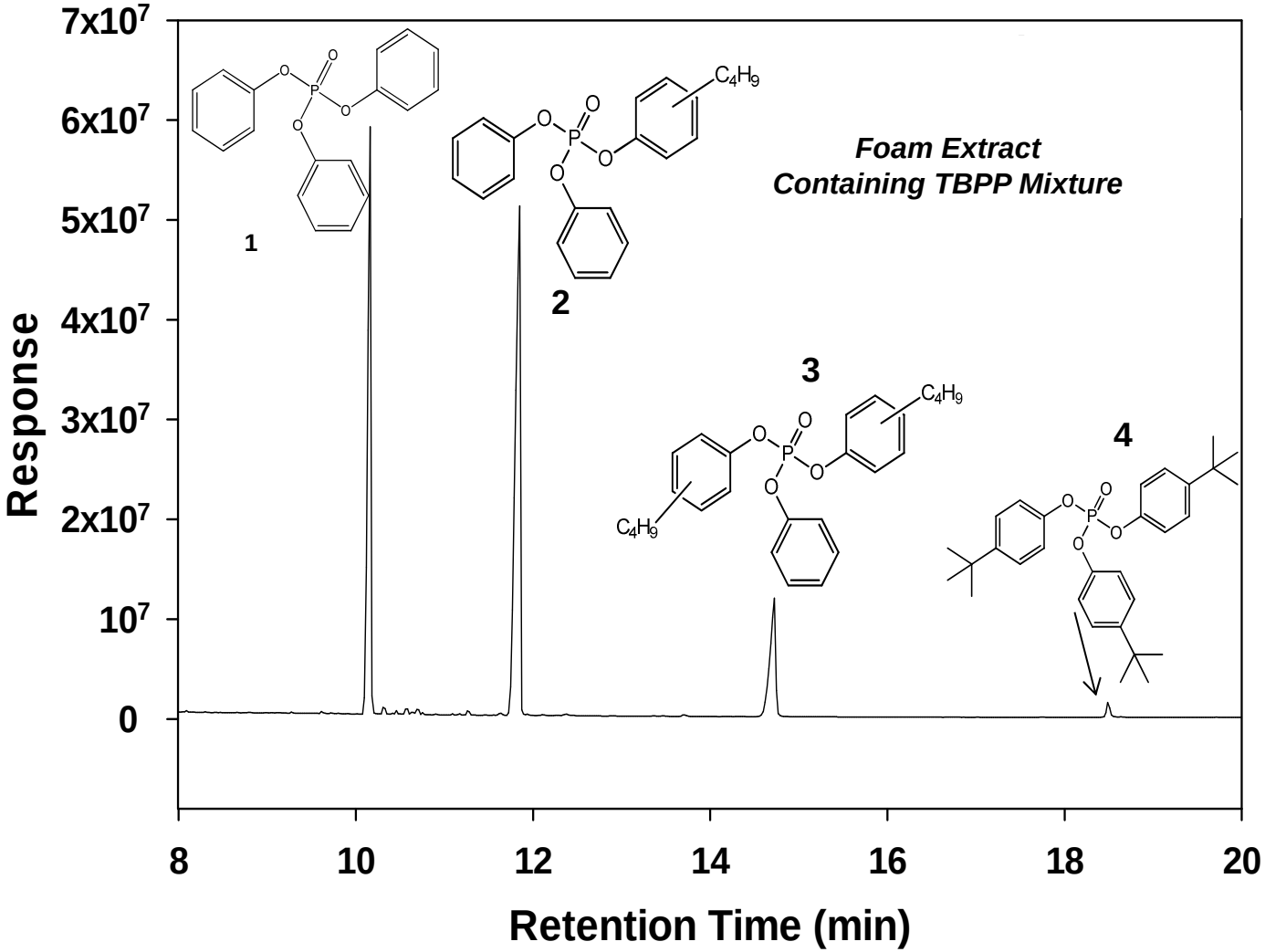
Flame Retardant Detection and Measurement:

Table 1. Flame Retardant (FR) Measurements and Descriptive Statistics of Polyurethane Foam Samples (n = 102). (Values in parenthesis represent percentage of the total number of samples for that specific column)

flame retardant	number of detects	average FR level (mg/g)	purchased prior to 2005[a]	purchased 2005 or later[a]	purchased in California[b]	purchased outside California[b]	yes TB 117[c]	no TB 117[c]
PentaBDE	17	20.23[d]	16 (39%)	1 (2%)[e]	7 (29%)	9 (12%)	9 (14%)	8 (24%)
TDCPP	42	44.87	10 (24%)	32 (52%)	10 (42%)	30 (41%)	33 (50%)	9 (26%)
FM 550	13	19.76[f]	2 (5%)	11 (18%)	3 (13%)	8 (11%)	12 (18%)	1 (3%)
V6/TCEP	1	41.77[g]	0	1 (2%)	1 (4%)	0	1 (2%)	0
TBPP mix	8	7.90[h]	0	8 (13%)	1 (4%)	7 (10%)	6 (9%)	1 (3%)
MPP mix	2	3.23[i]	0	2 (3%)	0	2 (3%)	1 (2%)	1 (3%)
TDCPP and PentaBDE	2	22.64	2 (5%)	0	1 (4%)	1 (1%)	1 (2%)	1 (3%)
TDCPP and FM 550	2	19.06	0	2 (3%)	0	2 (3%)	2 (3%)	0
FR < 0.2 mg/g	3[j]	0.11	1 (2%)	2 (3%)	0	3 (4%)	0	2 (6%)
none detected	12	-	10 (24%)	2 (3%)	1 (4%)	11 (15%)	1 (2%)	11 (32%)
totals	102		41	61	24	73	66	34

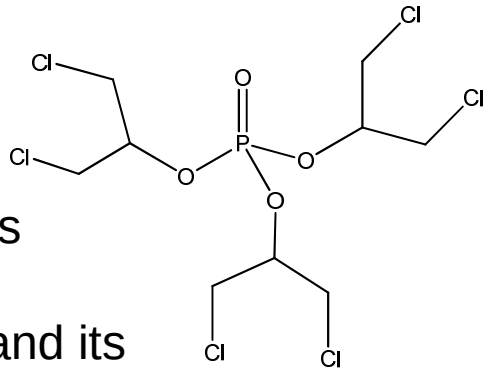
- Average Concentration in foam approximately 4-5% by weight of foam (40-50 mg/g)
- Significant increase in FR applications since 2005
- Significant increase in diversity of FR chemicals in furniture since 2005
- 62% of samples without a TB 117 label still contained FRs
- California TB 117 has become a *de facto* standard for the US

TBPP Flame Retardant Mix (n=8)



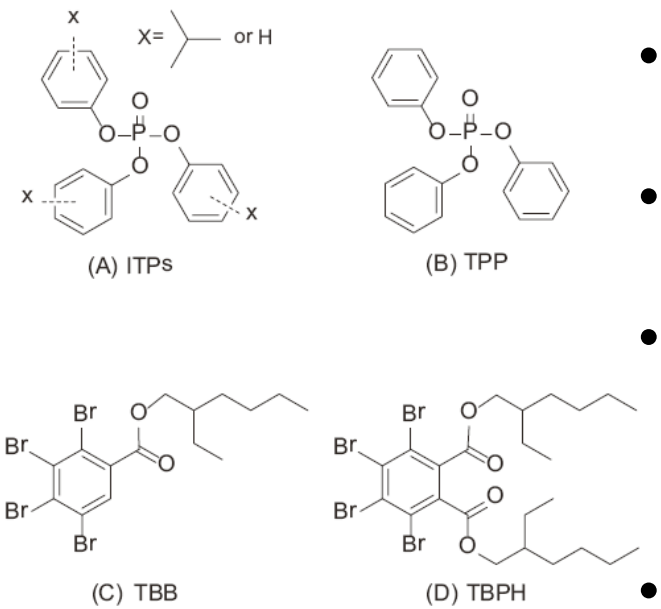
Are We Exposed to These Alternate Flame Retardants and What are the Health Risks?

TDCPP



- TDCPP was used as a FR in children's pajamas in the 1970s
- Studies conducted at UC Berkeley discovered that TDCPP and its brominated analogue were both mutagens (likely to cause cancer). (Gold et al 1978, Blum et al 1977)
- Studies conducted by the National Toxicology Program also found Increased Incidence of tumors in rats exposed to TDCPP over 2 years (NTP, 2000);
- CPSC issued a 2006 report estimating that exposure to TDCPP from residential furniture was greater than acceptable daily dose (Babich, 2006)
- TDCPP is ubiquitous in house dust with concentrations that are equal to or sometimes higher than PBDE levels (Stapleton et al 2009).
- Major urinary metabolite detected in more than 95% of population (ongoing)

Firemaster 550 (FM 550)



- Manufactured by Chemtura
- Advertised as replacement for PentaBDE
- EPA Issued Consent Order for More Testing in 2005, but only tested effects of two brominated components
- Before 2012, no studies on health effects of FM 550 in rodents/mammals
- TPP, TBB and TBPH ubiquitous in indoor dust, levels comparable to PBDEs (Stapleton et al. 2008; 2009)…..No human biomarker available yet…….

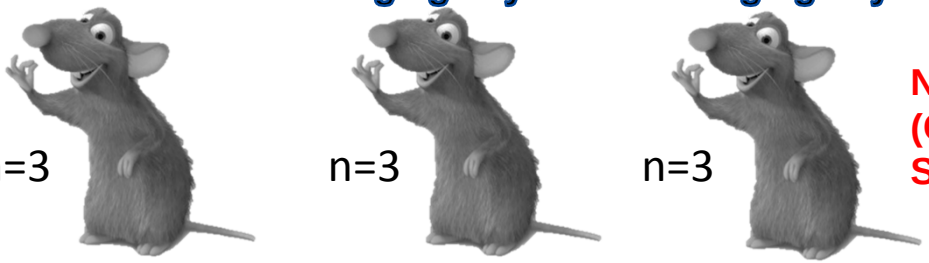
FM 550 Reproductive Study

(Patisaul et al 2012)

Pregnant rats exposed to FM 550 or control from Gestational Day 6 to Postnatal Day 21

Control | **Low Dose 0.3 mg/kg/day** | **High Dose 3.0 mg/kg/day**

Pregnant Dams



n=3 n=3 n=3

NOAEL = 50 mg/kg/day (Chemtura sponsored Study)

Dams: collected serum, liver, brain, fat, and muscle on PND 21

Pups

Pups: - Collected serum (limited), liver, brain, fat, and muscle from pups on PND 21, and 7 months of age

- Assessed reproductive development, behavior and growth

Effects Observed from FM 550 Exposure

(Patisaul et al 2012)

- Pregnant dams had significant increase in thyroid hormone levels
- Both pregnant dams and pups accumulated FM 550 components
- Female pups born to dams in the high dose group had early onset of puberty
- All pups born to dams in the high dose group became obese (male pups 32% heavier than controls and female pups 22% heavier than controls)
- Suggests FM 550 is an endocrine disruptor

Discussion Points

- PentaBDE exposure is chronic among the US population and children receive higher exposure than adults;
- Chronic exposure to flame retardants used as replacements for PentaBDE (e.g. TDCPP, FM 550) is occurring today;
- Exposure to TDCPP may be higher than acceptable daily doses, leading to increased risks of cancer;
- Many of these newer flame retardant chemicals have properties suggestive of toxic effects, yet no studies have been conducted to evaluate potential health impacts on humans;
- Questions have been raised about purported fire safety benefits of these flame retardants at levels found in furniture meeting TB 117 standards……



Flame Retardants Make National News

- Deceptive tactics used by chemical manufacturers to promote sales of their Products;
- Close ties between flame retardant manufacturers and tobacco companies;
- Highlights lack of proven fire safety benefits;
- Discusses issues with new flame retardants on the market

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TRIBUNE WATCHDOG

Playing with fire

A deceptive campaign by industry brought toxic flame retardants into our homes and into our bodies. And the chemicals don't even work as promised.

BY PATRICIA CALLAHAN AND SAM ROE
Tribune reporters

Dr. David Heimbach knows how to tell a story.

Before California lawmakers last year, the noted burn surgeon drew gasps from the crowd as he described a 7-week-old baby girl who was burned in a fire started by a candle while she lay on a pillow that lacked flame retardant chemicals.

"Now this is a tiny little person, no bigger than my Italian greyhound at home," said Heimbach, gesturing to approximate the baby's size. "Half of her body was severely burned. She ultimately died after about three weeks of pain and misery in the hospital."

Heimbach's passionate testimony about the baby's death made the long-term health concerns about flame retardants voiced by doctors, environmentalists and even firefighters sound abstract and petty.

But there was a problem with his testimony: It wasn't true. Records show there was no dangerous pillow or candle fire. The baby he described didn't exist.

Neither did the 9-week-old patient who Heimbach told California legislators died in a candle fire in 2009. Nor did the 6-week-old patient who he told Alaska lawmakers was fatally burned in her crib in 2010.

Heimbach is not just a prominent burn doctor. He is a star witness for the manufacturers of flame retardants.

His testimony, the Tribune found, is part of a decades-long campaign of deception that has loaded the furniture and electronics in American homes with pounds of toxic chemicals linked to cancer, neurological deficits, developmental problems and impaired fertility.

The tactics started with Big Tobacco, which wanted to shift focus away from cigarettes as the cause of fire deaths, and continued as chemical companies worked to preserve a lucrative market for their products, according to a Tribune review

stoked the public's fear of fire and helped organize and steer an association of top fire officials that spent more than a decade campaigning for their cause.

Today, scientists know that some flame retardants escape from household products and settle in dust. That's why toddlers, who play on the floor and put things in their mouths, generally have far higher levels of these chemicals in their bodies than their parents.

Blood levels of certain widely used flame retardants doubled in adults every two to five years between 1970 and 2004. More recent studies show levels haven't declined in the U.S. even though some of the chemicals have been pulled from the market. A typical American baby is born with the highest recorded concentrations of flame retardants among infants in the world

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NIEHS
National Institute of Environmental Health Sciences

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