

Flame Retardant Chemicals: Uses in Consumer Products and Human Exposure Concerns

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Outline

- Background
 - What are Flame Retardants?
 - Why types of products contain flame retardants
- Human Exposure Pathways

Human Health Concerns





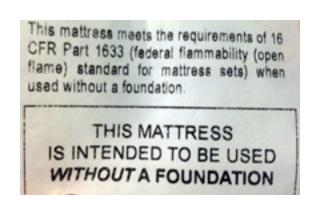


Definition:

"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





California Technical Bulletin 117 (TB 117)

- Applies to residential furniture in CA

CFR 1633- The Federal Mattress Flammability standard







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

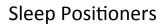


























- A research study conducted in the 1990s in Sweden identified PBDEs in human milk
- Levels were found to be doubling every few years while pesticide exposure was was decreasing

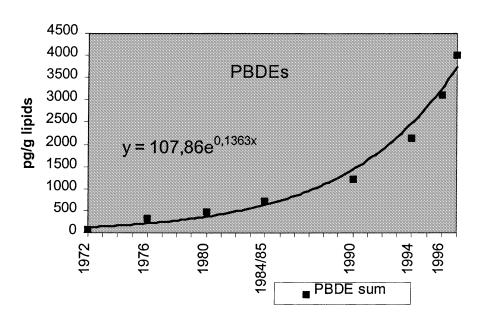


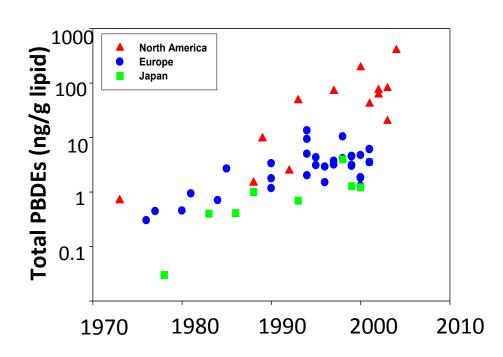
Fig. 4. Concentrations an time related trends of PBDEs in human milk expressed as an exponential curve.

(Source: Noren and Meironyte, 2000)



Flame Retardant Exposures Increasing Around the World

- PBDEs are detected in blood from more than 95% of the US population
- Exposure levels in the US population are an order of magnitude higher than levels measured in other populations around the world.
- PBDE exposure increased exponentially from the 1970s through 2003 until PentaBDE was phased-out from use in the US



From Hites et al., 2005



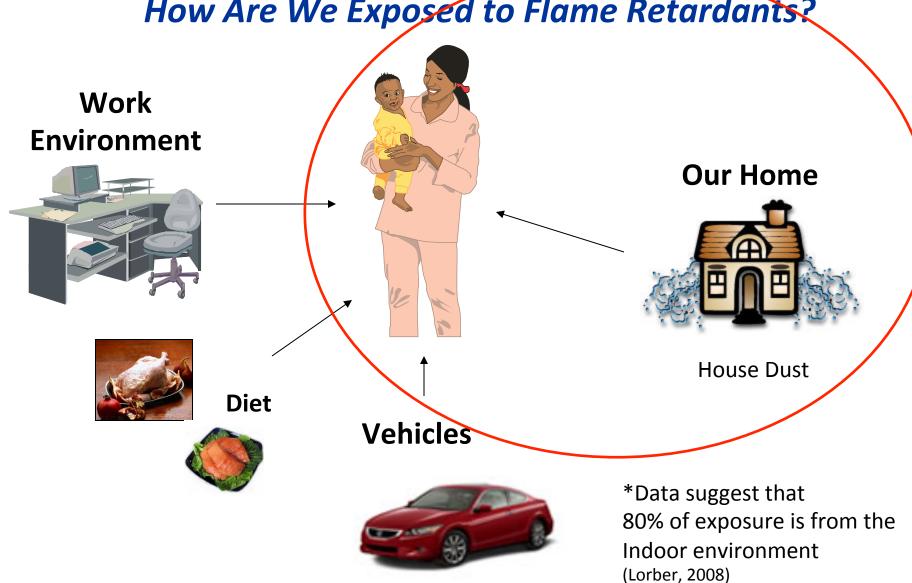
"PentaBDE" <u>Was</u> the Major Flame Retardant Mixture Used in Furniture Sold in the US

- "PentaBDE" was a flame retardant mixture applied to polyurethane foam to meet California TB 117
- 98% of the world market demand for PentaBDE was from North America (US and Canada), primarily to meet CA TB 117
- Concern about persistence, bioaccumulation and potential toxicity led to ban on use in Europe Union in 2002; voluntary phase-out agreement reached between EPA and US manufacturers in 2003





How Are We Exposed to Flame Retardants?





Research Questions:

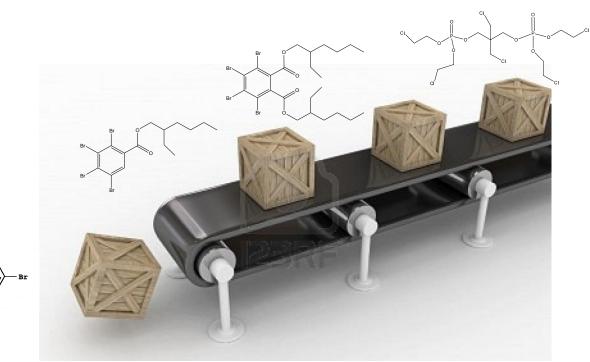
- With the phase-out of PentaBDE, what types of flame retardants would be used most frequently in residential furniture to meet CA TB117?
- Is the general public exposed to these new or alternate flame retardants and at what levels?
- Are there hazards/toxicities associated with these new flame retardants?

(Risk= exposure * hazard)



The Case of the Chemical Conveyor Belt.....

When one flame retardant is banned, another chemical moves in to take it's place, and less is known about the replacement chemical...









EPA Alternatives Assessment

- EPA's Design for the Environment program sought to characterize potential chemical replacements for PentaBDE in residential furniture
- However, most flame retardant chemicals are considered "Confidential Business Information" and are not disclosed.

	Ta	ble 4-1	1 Screening Level Toxicology and Exposure Summary																		
M ⁴ H :	= Low hazard concern = Moderate hazard concern = High hazard concern M', or H = Endpoint assigned using																				
Company		% in Formulation ⁶	Cancer Hazard					lect		LCOL	loxicity	LIIVIIO	1	Worker			General Population				
	Chemical			Skin Sensitizer	Reproductive	Developmental	Neurological	Systemic	Genotoxicity	Acute	Chronic	Persistence	Bioaccumulati	<u> </u>	Inhalation	Dermal	Ingestion	Aquatic	Reactive or Additive?		
Albemarle	SAYTEX RZ-243		Ĭ		Ī	Ī	Ī		Ĭ			_	_	Ī		_					
	Proprietary E Tetrabromophthalate did diester	ol	L	L	L*	L*	L	M*	L	L	H	L [*]	L	N	Υ	Υ	N	N	Υ	Υ	Additive
	Proprietary B Aryl phosphate		L	L	M*	M*	M	M*	L	Н	H	L	M	N	Υ	Υ	N	Υ	N	N	Additive
	Triphenyl Phosphate CAS # 115-86-6		L	L	L	L	L	М	L	н	H	L	L	Υ	Υ	Υ	Υ	Y	Υ	Υ	Additive
Ameribrom	FR513																				
	Tribromoneopentyl Alcohol CAS # 36483-57-5		M	L	M	M	M	М	М	M	M	L	L	Υ	Υ	Υ	N	N	Y	Υ	Reactive
Great Lakes	Firemaster 550																				
	Proprietary F Halogenated aryl ester		L	L	M	M	L	M	L	Н	H	L*	L	N	Υ	Υ	N	Υ	Υ	Υ	Additive
	Proprietary G Triaryl phosphate, isopropylated		L	L	M*	M*	M	M*	L	н	H	L	M	N	Υ	Υ	N	Y	N	N	Additive
	Triphenyl Phosphate CAS # 115-86-6		L	L	L	L	L	М	L	н	H	L	L	Υ	Υ	Υ	Y	Υ	Υ	Υ	Additive
	Proprietary H Halogenated aryl ester		L	L	M	M	L	M	L	Н	H	L [*]	L	N	Υ	Υ	N	Υ	Υ	Υ	Additive
Great Lakes	Firemaster 552																				
	Proprietary F Halogenated aryl ester		L	L	M	M	L	M	L	н	H	L*	L	N	Υ	Υ	N	Υ	Υ	Υ	Additive
	Proprietary G Triaryl phosphate, isopropylated		L	L	M*	M*	М	M *	L	н	H	L	M	N	Υ	Υ	N	Y	N	N	Additive
	Triphenyl Phosphate CAS # 115-86-6		L	L	L	L	L	М	L	н	H	L	L	Υ	Υ	Υ	Y	Υ	Υ	Υ	Additive
	Proprietary H Halogenated aryl ester		L	L	M	M	L	M	L	н	H	LA	L	N	Υ	Υ	N	Y	Υ	Υ	Additive

(Furniture Flame Retardancy Partnership V 1, EPA 2005)



Screening Consumer Products for FR Chemicals:

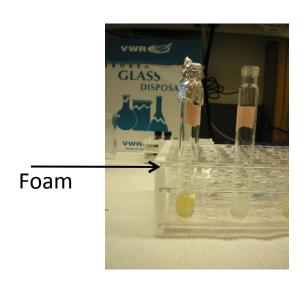
Project 1- Baby Products (2011)

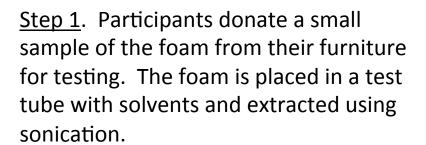
Project 2- Residential Sofas (2012)

Project 3 – Screening All Furniture (Current)



How We Test the Foam Samples







Step 2. The solvent containing the flame retardant is transferred to a vial which is injected into this piece of analytical equipment called a Mass Spectrometer. This device tells us the weight and structure of the chemical in the solvent.







Project 1: Flame Retardants in Infant Products

ENVIRONMENTAL Science & Technology

ARTICLE

)

(2011)

Identification of Flame Retardants in Polyurethane Foam Collected from Baby Products

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Ellen Cooper, '* Thomas F. Webster, " and Arlene Blum

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Supporting Information

 Many baby products are considered "furniture" and previously had to meet CA TB117

- In this study we screened 101 Baby products for flame retardant (FR) chemicals
- 80% contained a FR
- The flame retardants found most frequently were TDCPP and Firemaster® 550 (FM 550)
- Suggests greater exposure potential for infants sleeping on these types of products
- Now >5 infant/juvenile products exempted from TB 117





Car Seats







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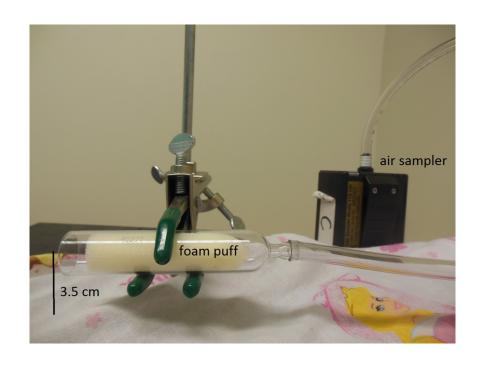






Will Infants be Exposed to Flame Retardants While Sleeping on Mattresses?

- Experiments were conducted to measure potential exposure from a treated mattress
- Levels measured 3.5 cm
 above the mattress were 20X
 higher than levels measured
 10 feet away in the room
- Infants will have significantly higher exposure than adults due to their closer proximity to treated products



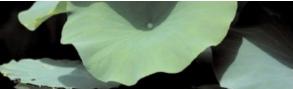
Measuring flame retardants in the air above a baby mattress



New Questions Raised

- 1. How Frequently are flame retardants used in other furniture items?
- 2. With addition of TDCPP to California Proposition 65, will it's use in furniture decrease?
- 3. How will use of flame retardants change in response to changes in TB 117 in 2013?







- New testing service launched in February 2014 for the general public
- Intended to screen foam samples for flame retardants
- Supported by the Superfund Research Program

Submit a Sample Our Findings Resources FAQ Bibliography What's in my foam? Scientists at Duke University's Superfund Research Center are examining the use of flame retardant chemicals in furniture. Be part of the study by submitting a foam sample from your home.

Who can send in samples?

Currently, we are only able to test foam sent to us from US residents

Why should I test my sofa?

In the US, flame retardant chemicals are sometimes intentionally added to the foam filling present in many types of furniture (including some baby furniture) to meet a California state flammability standard commonly known as Technical Bulletin 117 (TB 117). While only residential furniture sold in the state of California is required to meet this standard, manufacturers often make all their furniture to meet this standard [1]. The state of California is currently revising TB 117, and a new standard, referred to as TB 117-2013, will go into effect starting in January 2014 that should reduce the use of these flame retardants in furniture. However, it is currently unclear how the use of these chemicals will change starting in 2014.

How does this affect me?

Over the past 10-15 years, scientific evidence has demonstrated that some of these flame retardants are released from products and accumulate in indoor environments. People can be exposed to these chemicals indoors through inhalation and unintentional ingestion of dust particles [2.3.4]. The use of one flame retardant known as PentaBDE was phased out in 2004 due to concerns about the chemical's persistence, its tendency to concentrate in human tissues, and potential human health effects.

This means other chemicals are currently used to meet flammability standards, but little information is available on how we are exposed to these new flame retardants, or if there are potential health effects. Because manufacturers are not required to label products with the flame retardant applications used, consumers cannot determine if flame retardants are in their products without laboratory testing.

How does this help me?

Duke's Superfund Research Center can now help you find out what chemicals may be present in the furniture in your home with funding support provided by the National Institute of Environmental Health Sciences (NIEHS).

If you are interested in sending us a sample of your foam for analysis, please complete the sample submission process.

How does this help you?

Data collected from this testing will help us to understand which flame retarding chemicals are currently being used in furniture. Once we have a sense of what chemicals are being used, we'll be able to investigate how people are exposed to these chemicals in the home and understand if the chemicals may impact human health.

http://foam.pratt.duke.edu



Submitting a Foam Sample for Testing

- What type of product is being tested?
- In what year was it purchased?
- In what state was it purchased?
- Does it have a TB-117 label affixed to the product?
- Who is listed as the manufacturer?
- What country was it manufactured in?
- Since opening the program in February 2014 we have now received more than 1100 samples for screening.





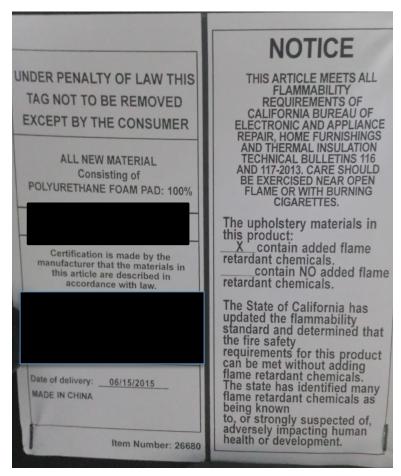
Current Results Suggest:

- PentaBDE use (and thus exposure) has significantly decreased since 2005;
- Use of alternate flame retardants has increased
- Currently TDCPP is most common flame retardant detected in furniture in US homes
- Over last two years, increasing detection of TCPP which has a similar structure to TDCPP
- Unclear how new TB117-2013 will change use in furniture- waiting for more data....



Changes to Flame Retardants Use Following Changes in CA TB 117

- In 2013 CA TB117 was amended from an open flame test to a smolder ignition test;
- In 2015, new labeling requirement initiated
- Impact of new TB 117-2013 on FR use and exposure still unclear





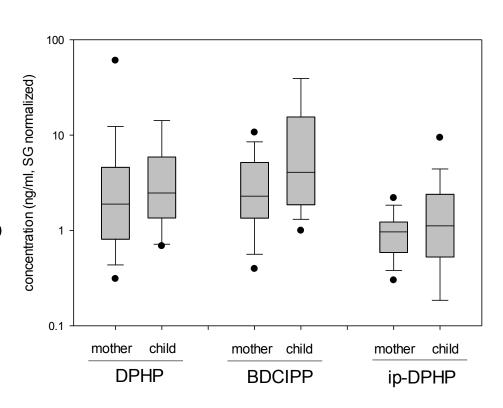
Now we have a better idea of which flame retardants are used in furniture.....

But are these alternate flame retardants also present in the home and are people exposed to them?



Flame Retardant Urinary Metabolites in Mothers and their Toddlers

- Measurements of flame retardant metabolite levels in toddler's urine were higher than in mother's
- For TDCPP, urinary metabolite levels were 5X higher in toddlers relative to their moms
- Mom and toddlers had the same source of exposure

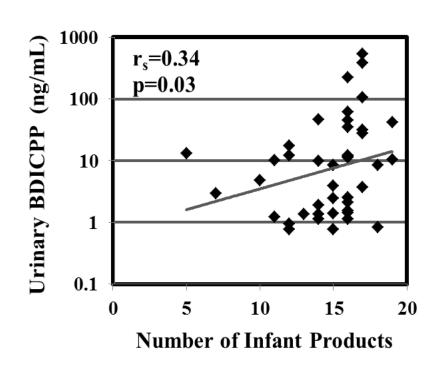


(Source: Butt et al. 2014)



Are Infant Products a Source of Exposure?

- We collected urine from 43 infants in 2014-2015
- The urinary metabolite of TDCPP (chlorinated Tris) was found in every sample and was higher (on average) than levels measured in toddlers
- Urinary metabolite levels were significantly correlated with the number of foam containing products in the home



(Hoffman et al., 2015)



What are the Potential Health Effects from Exposure to these New-Use Flame Retardants?



Tris (1,3-dichloroisopropyl) phosphate

- TDCPP was used as a flame retardant 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 could be greater than acceptable levels for increased risk of cancer (Babich, 2006)
- Studies conducted at Duke Univ. suggest TDCPP may also be a neurotoxicant with similar toxic effects observed to organophosphate pesticides (Dishaw et al. 2011).







Firemaster® 550 (FM 550)

- Manufactured by Chemtura
- Advertised as replacement for PentaBDE

- EPA Issued a Consent Order and required more testing in 2005, but only tested effects of two of the four components
- Before 2012, no studies on health effects of FM 550 in rodents/mammals





Firemaster® 550 Polyurethane Foam Market

Great Lakes Chemical introduces Firemaster[®] 550 for polyurethane foam applications. Firemaster 550 is a new, non-scorch, phosphorus-bromine flame retardant based on proprietary Great Lakes technology which has a favorable environmental profile and provides the improved fire safety protection currently met by Great Lakes DE-60F™ Special. The Environmental Protection Agency's (EPA) assessment¹ of the DE-60F replacement concludes that it is not persistent in the environment, bioaccumulative in organisms or eco toxic. (see EPA press release at www.epa.gov/newsroom - click on press releases link)

Firemaster® 550 Exhibits

- Outstanding Scorch Resistance
- Excellent Processing
- ✓ Better Flame Retardant Efficiency
- Resistance to Center Softening
- √ Favorable environmental profile (Not a P B, or T)



Applications

- ✓ Cal 117 Furniture Foam
- ✓ MVSS 302 Automotive Foam
- ✓ UL 94 HF1 Foam Packaging
- ✓ Flame Lamination Auto Headliners











Chemtura Corporation 199 Benson Road Middlebury, CT 06749 USA

203-573-2000 tel www.chemtura.com

May 27, 2010

Polyurethane Foam Association 334 Lakeside Plaza Loudon, TN 37774

Dear PFA membership,

We are please to inform you that the review by the US EPA of all required studies on the proprietary brominated flame retardant contained in the Firemaster®550 and Firemaster®500 product families have been completed with favorable results. Since their introduction these new products have been produced under a consent order pending, a two generation reproduction study, a review of studies on migration from foam and a prenatal developmental toxicity study.

The results of the 2-generation reproduction study showed no reproductive effects being noted. The results of the migration study from polyurethane foam, which was designed to evaluate the potential for exposure to the FR, indicated no detectable migration of the flame retardant. Although some effects were noted in the prenatal developmental study, the lack of migration of the flame retardant noted in the migration study would indicate that the risk of exposure to the FR is negligible.

Based on these results, it has been concluded by the EPA that no additional testing is required at this time and there are no further production limits on these products.

We are very pleased to have successfully completed this extensive review of the safety of Firemaster®550 and Firemaster®600. These products provide a unique balance of fire resistance and polyurethane foam quality, while providing a favorable environmental profile.



Toxicity Study Conducted by Duke and NC State on FM 550

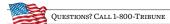
(Patisaul et al 2013)

- Rats were exposed to increasing levels of FM550 during pregnancy and pups were followed until adulthood.
- Pregnant rats had significant changes in thyroid hormone levels
- Female pups born to rats in the high dose group tested had early onset of puberty
- All pups born to rats 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

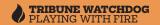








THURSDAY, MAY 10, 2012





SAPA D. DAVIS/PHOTO FOR THE TRIBLINE

Flame retardants get a pass from regulators with little assessment of potential health risks

Flame retardants get EPA pass

Continued from Page 1

The previously unreleased documents also show how the nation's chemical safety law, the 1976 Toxic Substances Control Act, gives the government little power to assess or limit dangers from the scores of chemicals added to furniture, electronics, toys, cosmetics and household products.

At a time when consumers clamor for more information about their exposure to toxic substances, the chemical safety law allows manufacturers to sell products without proving they are safe and to treat the formulas as trade secrets. Once health effects are documented, the law makes it almost impossible for the EPA to ban chemicals, its of critics.

A growing list of critics including the nation's leading group of pediatricians and the Government Accountability Office, the investigative arm of Congress—are calling for a sweeping overhaul of the law. Some compare the situation to Whac-A-Mole, the carnival game where plastic moles keep popping out of holes even after a player smacks one down.

"By the time the scientific community catches up to one chemical, industry moves on to another and they go back to their playbook of delay and denial," said Deborah Rice, a former EPA toxicologist who works for the Maine Center for Disease Control



Heather Stapleton, one of the nation's leading experts on flame retardant chemicals added to consumer products, seals liquid samples of foam in bottles before testing them at Duke University.



SARA D. DAVIS/PHOTOS FOR THE TRIBUNE

Stronger oversight proposal kept at bay

White House office stalls EPA chief's plan

By MICHAEL HAWTHORNE | Tribune reporter

With efforts to revamp the nation's chemical safety law stalled in Congress, the Obama administration's top environmental regulator vowed three years ago to act on her own to beef up the oversight of toxic substances.

But key parts of the initiative by Lisa Jackson, the administrator of the U.S. Environmental Protection Agency, are still bottled up in an obscure White House office under intense pressure from industry lobbyists to back off.

Since Jackson sent the EPA's proposed changes to the Office of Information and Regulatory Affairs, the gatekeeper for federal rules, industry representatives have met 18 times with administration officials about the initiative, according to records posted on the White House website.

Under her proposal, the EPA would create a formal list of "chemicals of concern" that "may present an unreasonable risk of injury to health or the environment." The agency said creating the list would be the first step toward improved regulation of toxic chemicals, including rules that would prevent them from being used in new types of products or in imported goods.

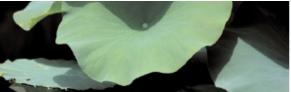
importer goods.

Topping Jackson's proposed list are flame retardants called polybrominated diphenyl ethers, or PBDEs. Others targeted include eight types of plastic-softening chemicals known as phthalates as well as bisphenol A, a compound added to food container limines.

EPA officials said there is considerable evidence that chemicals on the list interfere with natural hormones, trigger reproductive problems and cause developmental and neurological damage. For those reasons, certain PBDEs already have

Story was one of three finalists for the Pulitzer prize!







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



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 ROP

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

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 cials that spent more than a 6-week-old patient who he told Alaska lawmakers was fatally ourned in her crib in 2010.

Heimbach is not just a prom-

inent burn doctor. He is a star vitness for the manufacturers

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 results of textile above the property of the proper with pounds of toxic chemicals linked to cancer, neurological deficits, developmental prob-lems and impaired fertility.

The tactics started with Big Tobacco, which wanted to shift focus away from cigarettes as

from household products and

haven't declined in the U.S. ever



Discussion Points

- Flame retardants may provide an important benefit in some applications, but we need to identify alternative strategies to reduce fire risk AND human exposure/health concerns.
- Where do we really need flame retardants and where can their use in products be eliminated? (e.g. mattresses, TVs?)
- More transparency in chemical use may help to identify risks/ concerns earlier.
- We should avoid the use of small molecule additive flame retardants....they will always migrate out and lead to exposure. If you remove the exposure, you remove the risk.







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Dr. Scott Belcher (University of Cincinnati)

Dr. Jennifer Schlesinger (Boston University)

Dr. Andreas Sjodin (CDC)

Gretchen Kroeger (Duke University)



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