

The Fire Retardant Dilemma

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The Problem: Most Chemicals are not Effectively Regulated in the U.S.

The U.S. Toxic Substances Control Act (1976)

- 62,000 chemicals in commerce “grandfathered”
 - Since then, EPA has restricted five of these
- 20,000 new chemicals have been introduced
 - 85% have no health data
 - 67% no data at all
 - EPA has six weeks to show cause for harm, often with no data

Brominated Tris Flame Retardant

Tris (2,3-dibromopropyl) phosphate



- Used to treat U.S. children's sleepwear from 1975 to 1977.
- Up to 10% of the weight of fabric
- Not covalently bonded to fabric
- Absorbed in children's bodies; metabolite found in their urine

Flame-Retardant Additives as Possible Cancer Hazards

The main flame retardant in children's pajamas is a mutagen and should not be used.

Arlene Blum and Bruce N. Ames

Thousands of chemicals to which humans have been exposed have been introduced into the environment without adequate toxicological testing.

Some chemical flame retardants provide a good example of a technological innovation where adverse environmental effects may outweigh some of the benefits.

Until recently, little attention was paid to the long-term biological effects of these flame-retardant compounds. The main organic chemicals used in flame retardants contain bromine or chlorine or they are phosphate esters. Some have chemical structures (discussed below) that are closely related to compounds known to cause cancer or to be toxic to animals. Several compounds previously used as flame retardants have been shown to be teratogenic, carcinogenic, mutagenic, or highly toxic (4).



**U.S. Consumer Product
Safety Commission**

CPSC Bans TRIS-Treated Children's Garments

FOR IMMEDIATE RELEASE

April 7, 1977

Flame Retardants in Consumer Products

- Use of fire retardant chemicals in household furniture and baby products foam driven by California's Technical Bulletin 117 (TB117)
 - Standard usually met with halogenated fire retardants
 - Some manufacturers comply with TB117 nationwide
 - Requires 12 second resistance to open flame
 - No enforced flammability standard for fabric



Formation of brominated furans and dioxins from combustion of flame-retarded plastics

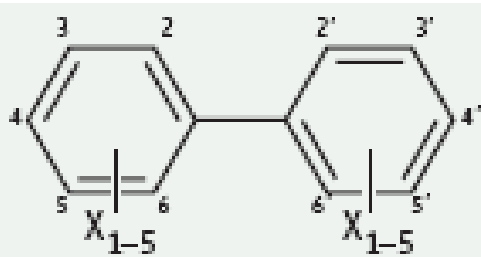
- Low temperature incinerations, as in home fires, produces high levels of brominated dioxins and furans.
- People in contact with fire residues are in danger of adverse health impacts.

Brominated Furan Yield From Combustion of Flame-Retarded (decaBDE) in Plastics

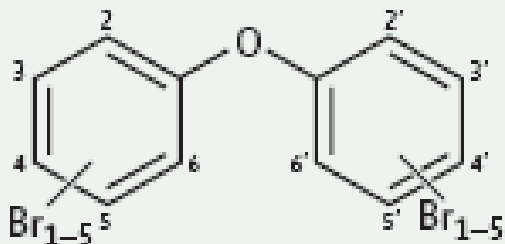
Temperature In degrees F	decaBDE alone (mg/kg)	In Polypropylene Matrix (mg/kg)
750 F	-	107,517 (11%)
1110 F	-	49,677 (5%)
1470 F	28 (.003%)	29,147 (3%)

Formation of Brominated Dioxins from decaBDE, octaBDE, decaBB, and TBBPA showed a similar dependence on temperature and/or matrix as seen with Brominated Furans (Kielhorn et. al. 1998).

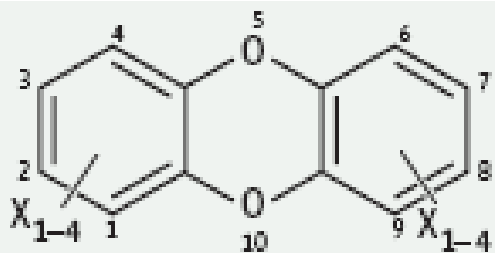
Source: Kielhorn, Dr. J., and Dr. C. Melber, Environmental Health Criteria 205: Polybrominated Dibenzo-*p*-dioxins and Dibenzofurans. World Health Organization (International Programme on Chemical Safety); Geneva, 1998. <<http://www.inchem.org/documents/ehc/ehc/ehc205.htm>>



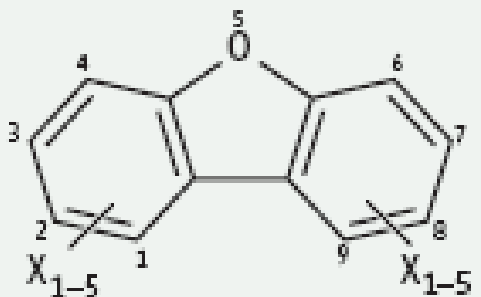
PCBs (X = Cl) and PBBs (X = Br)



PBDEs



Dioxins (X = Cl or Br)



Furans (X = Cl or Br)

Chemical flame retardants can slow but usually do not stop fires

Some brominated dioxins and furans are ten times more toxic than chlorinated dioxins.

Kielhorn, Dr. J., and Dr. C. Melber, Environmental Health Criteria 205: Polybrominated Dibenzo-p-dioxins and Dibenzofurans. WHO (International Programme on Chemical Safety); Geneva, 1998.

On the combustion and photolytic degradation products of some brominated flame retardants, Gunilla Söderström, University of Umea, Sweden

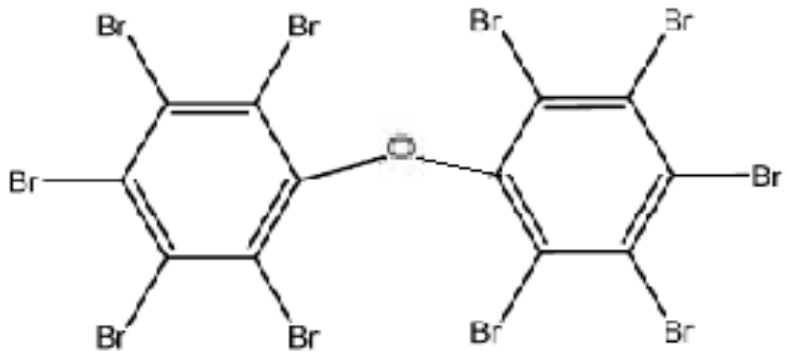
Could high levels of cancer in firefighters be related to exposure to combustion products from brominated fire retardants?



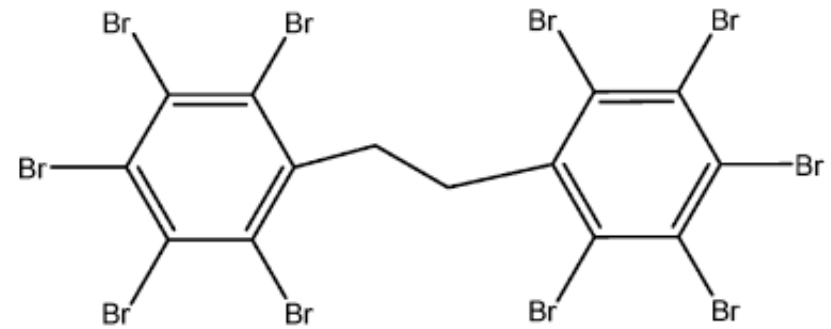
- Firefighters have significantly elevated rates of
 - multiple myeloma
 - non-Hodgkin's lymphoma
 - prostate
 - testicular cancer
- These four cancers can be related to exposure to dioxins and/or furans.

G.K. LeMasters, et al, Journal of Occupational and Environmental Medicine 48(11): 1189-202(2006).

Deca ether replaced by Deca ethane



Decabromodiphenyl ether



Decabromodiphenyl ethane

December 3, 2008

[Glut of data on “new” flame retardant documents its presence all over the world](#)



Now that DBDPE has been detected in more than a dozen species of animals in Asia and North America, scientists are calling for more research into its toxicology.

Major Flame Retardant Exposure Pathways

Consumer products

Waste streams
(e-waste, autoshredder)

Indoor exposure

Inhalation
&
Ingestion

Sewage Sludge

Household
Wastes

Biosolids

Agriculture

Food

Wildlife, food, water



Breast milk also a major source!



An Overview of Research on Halogenated Fire Retardants

Linda S. Birnbaum, Ph.D., D.A.B.T., A.T.S.
Director

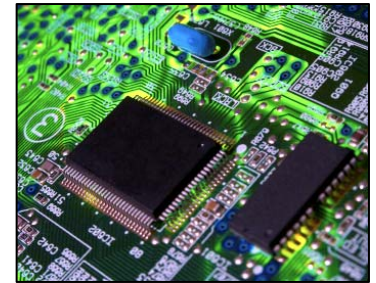
National Institute of Environmental Health Sciences/NIH
National Toxicology Program

Beijing, China – August 22, 2009



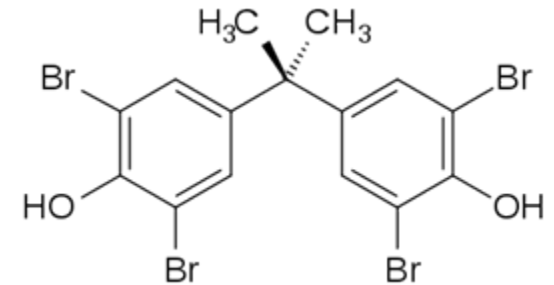
Three Examples of Fire Retardants of Concern and the Research on Their Health Effects

- TBBPA, primarily used in electronics/circuit boards
- HBCD, used in electronics, textile backings, and with insulation
- PBDEs, is or has been used in polymers, electronic equipment, textile backing, and flexible polyurethane foam

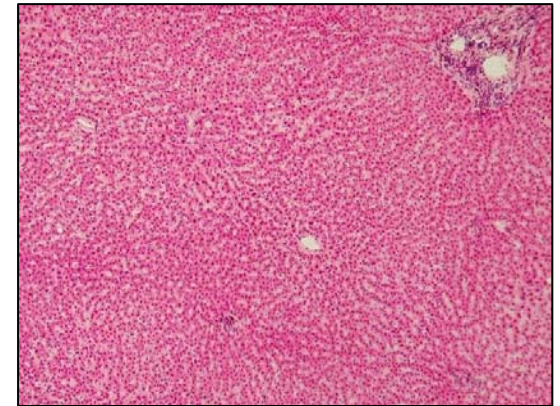


TBBPA : Health Effects

- Immunotoxic – inhibits T cell activation
- Hepatotoxic – toxic to primary hepatocytes, destroys mitochondria, causes membrane dysfunction
- Neurotoxic – oxidative stress, inhibits dopamine uptake, generates free radicals, increases calcium
- Causes hearing deficits in rats following perinatal exposure



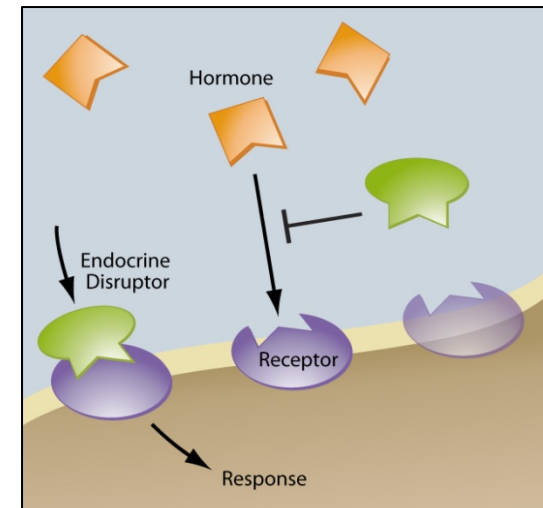
Hepatocyte - liver



Courtesy: Department of Histology, Jagiellonian University Medical College

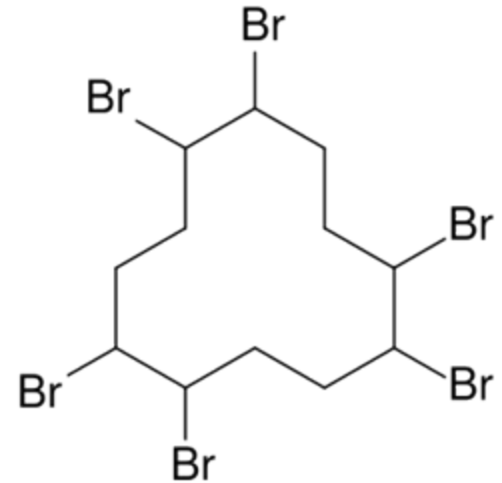
Tetrabromobisphenol A (TBBPA): Health Effects (continued) – Endocrine Disruption

- AhR Effects – not relevant for commercial products (Contaminants? Combustion products?)
- Thyroid – Thyroid hormone agonist, antagonist, or no effect
- Estrogenic/Androgenic – inhibits sulfotransferase (decreases estrogen clearance), developmental effects including increased testis and pituitary weight



HBCD :Health Effects

- Mild acute toxicity, irritation, sensitization, mutagenicity (EU Commission, 2008)
- Liver hypertrophy: enzyme inducer (CAR/PXR)
- Repeated dose in rats increased liver weight, liver enzyme activity
- Two generation reproductive rat study showed decreased T4, increased TSH, reproductive effects, altered histology of ovary, decreased viability of pups (Ema, 2008)



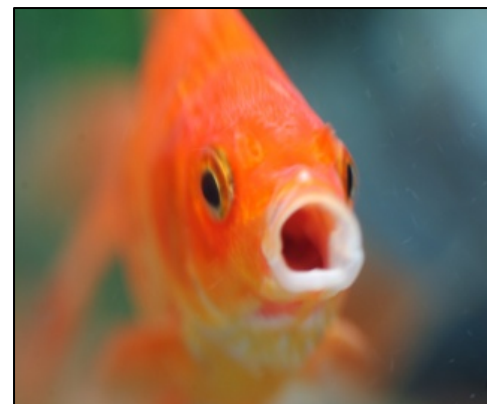
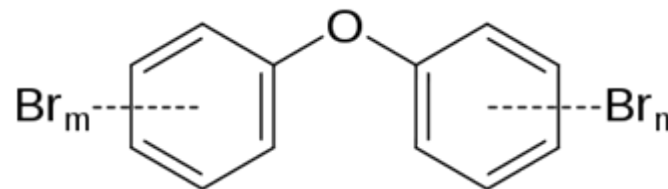
Hexabromocyclododecane (HBCD): Health Effects (continued)

- DNT effects in mice – spontaneous behavior, learning and memory deficits (Eriksson, 2006)
- *In Vitro* effects – anti-androgen, aromatase inhibitor, interactions with steroid hormone receptors; potentiates T3 effects in rat pituitary cell line/T-screen; neurotoxic to rat cerebellar granule cells; inhibits depolarization-evoked intracellular Ca^{++} increase and neurotransmitter release



PBDEs: Ecotoxicity

- Highly toxic to invertebrates
- Endocrine disruption in frogs, decreases testosterone, increases estradiol, increases phenotypic female frogs
- Developmentally toxic to fish, tail asymmetry, delayed hatching, behavioral changes, learning
- Baltic porpoise die-off related to lymphoid depletion



Polybrominated Diphenyl Ethers (PBDEs): Ecotoxicity (continued)

- Depletion of vitamin E in duck eggs
- Altered reproductive behaviors in Kestrels at environmental levels and decreased reproductive success
- PBDE levels measured in fish, sea turtles, birds, mammalian wildlife and domestic animals
- Decreases in T4/retinoids, and increases oxidative stress in Kestrels



Polybrominated Diphenyl Ethers (PBDEs): Endocrine Disrupting Effects

- Some PBDEs may be anti-estrogenic, others estrogenic
- Laboratory animal studies have shown decreased weight of epididymis, seminal vesicles and ventral prostate, decreased LH, sperm head deformities
- Decreased testosterone
- *In vitro* studies have shown antiandrogenic, non-competitive inhibition

PBDE Developmental and Reproductive Effects

- DE71 – pubertal exposures
- Delay in puberty
- Effects on male organs
- Anti-androgenic *in vitro*, especially BDE 100, 47
- BDE-99 and PBDE-47 – *in utero* exposures
- Delay in puberty
- Ovarian toxicity
- Male organ effects and decreased sperm



PBDE Developmental Neurotoxicity

- DE-71, in rats, causes deficits in sensory and cognitive function
- Altered sex-dependent behaviors
- Effects on thyroid, cholinergic, and dopaminergic systems
- BDE-99, 209, 47, 153, 203, and 206 in mice and rats
- Infantile exposure during a period of “rapid brain growth” causes learning effects
- Perinatal exposure causes delay in sensory development
- Additive effects observed following co-exposure of BDE-99 and PCB-52, PFOA or MeHg, in mice



PBDE Developmental Neurotoxicity (continued)

- A number of mechanisms may be at work
- Depression in serum T4
- Anti-cholinergic/anti-dopaminergic
- Alterations in key proteins involved in normal brain maturation
- Detrimental effects on cytoskeletal regulation and neuronal maturation
- Oxidative stress
- PBDEs alter cell signaling in vitro – DE71, BDEs 47, 99, 153
- Altered PKC and calcium homeostasis associated with learning, memory
- Altered phorbol ester binding



NIEHS and NTP DE71 Studies (pentaBDE)

- DE71 subchronic studies using F344/N rats and B6C3F1 mice
- Primary toxicity to liver (hepatocytic hypertrophy, fatty change, single cell necrosis)
- Thyroid effects in rats
- DE71 *in utero*/postnatal/adult exposure cancer study in Wistar rats (ongoing)
- DE71 2-year traditional cancer study in B6C3F1 mice (ongoing)
- DE71 administered by oral gavage in corn oil



Developmental Effects of DBDE

- Developmental Reproductive Toxicity – decrease in sperm function, increase in oxidative stress
- Developmental Immunotoxicity – continuous exposure to high-dose PBDE-209 in female rats during pregnancy and lactation results in possible adverse effect on the immune function of offspring
- Changes in lymphocyte subsets
- Developmental Neurotoxicity – permanent effects on behavior, learning and memory



PBDE Effects in People

- Cryptorchidism (Main et al 2007)
- Reproductive hormone effects – decrease in androgens and LH, increase in FSH and Inhibin (Meeker et al 2009)
- Decrease in testosterone (BDE-47) (Meijer et al 2008)
- Decrease in sperm quality (Akutsu et al 2008)
- Associated with diabetes (Lim et al 2008, Turyk et al 2008)
- Thyroid Homeostasis – decrease TSH, decrease TT3, elevated T4, elevated rT3 (Yuan et al 2008, Herbstman et al 2008, Turyk et al 2007, Meeker et al 2009, Dallaire et al 2009)



Recent Findings: PBDE Effects in People

- Cryptorchidism
 - Main et al, 2007
- Reproductive Hormone Effects
 - Meeker et al., 2009 –
Decrease in Androgens and
LH; Increase in FSH and Inhibin
 - Meijer et al, 2008 –
Decrease in Testosterone
- Decreased Sperm Quality
 - Akutse et al, 2008
- Diabetes
 - Lim et al, 2008
- Thyroid Homeostasis
 - Yuan et al, 2008 –
elevated TSH
 - Herbstman et al, 2008 –
decrease in TT4
 - Turyk et al, 2007 –
elevated T4
 - Meeker et al, 2009 –
elevated T4, TBG
 - Dallaire et al, 2009 –
elevated T3 ~BDE47

Birnbaum, L. 2009, "Green Chemistry and Environmental Health", ACS Green Chemistry and Engineering Conference. College Park, Maryland.
<<http://acs.confex.com/acs/green09/recordingredirect.cgi/id/536>>



Regulation of Brominated Flame Retardants

- TBBPA – not regulated
- HBCD banned in Norway, European Union “SVHC”
- PBDEs – Penta/Octa Commercial Products – voluntarily withdrawn in U.S. at end of 2004, bans in several U.S. states, SNUR in place; Europe banned July 31, 2004, use stopped in many EU countries about ten years ago; **targeted for elimination under the Stockholm Convention May 9, 2009.**
- Deca Product – US – HPV, banned in Washington State and Maine, proposed bans in many other states; Canada ban upheld March 30, 2009; banned in Sweden January 2007; banned in EU July 2008.



29th International Symposium on
Halogenated Persistent Organic Pollutants
August 23-28, 2009 Beijing, China



- 19 Persistent Organic Pollutants banned under the Stockholm conventions
- Twelve more under consideration
- All are halogens
- When halogens burn, they produce dioxins and furans
- More than 100 papers and posters presented in Beijing relating to flame retardants (accumulation, toxicity, measurement, etc)

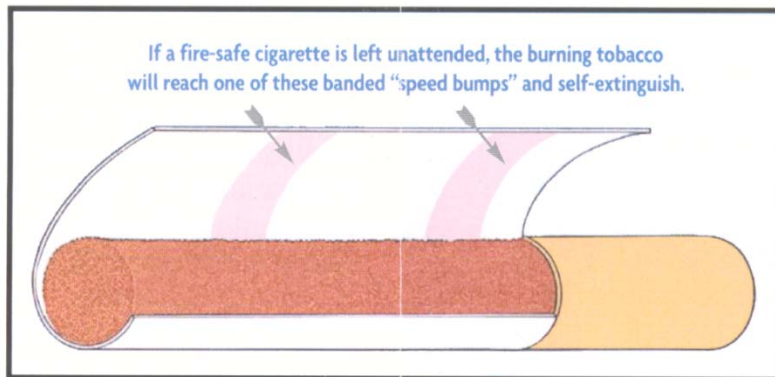
Solutions

Use flame retardant chemicals only when a fire safety need is established and alternative technologies are not available.

Move away from toxic or potentially toxic flame retardants to safer alternatives.

Fire Safety Without Toxic Chemicals

- Preventing ignition is less expensive, more effective, and healthier than adding chemicals to slow ignition
- Fire deaths in the US are rapidly declining due to:
 - 50% decrease in cigarette consumption since 1980
 - Enforcement of improved building, fire and electrical codes
 - Increased use of sprinklers and smoke detectors
 - Introduction of fire-safe cigarettes and candles



CPSC Candle Standards 1997- 2008

1990-1998

350% growth in candle production

13-42% increase in candle fires injuries / deaths

How to improve safety?

85% of candle fires caused by: :

- Excessive flame heights
- End of life issues when the candle burns out.
- Stability of candles not tipping over
- Secondary ignition caused from by nearby items burning in or on the candle

1997 1998 1999 2000 2001 2002 2003 2004 2005 2006 2007 2008

F15.45 sub committee formed to focus on candle product safety
Focus on fire causes of:
-abandonment
-combustible
-child play

Standard
Guide for Terminology Relating to Candles and Associated Accessory Items

Standard
Specification for Candle Fire Safety Labeling:
• keep candles insight
• out of reach of children/pets
• not to burn near combustible materials

Standard
Specification for Annealed Soda-Lime-Silicate Glass Containers That Are Produced for Use as Candle Containers

Standard
Specification for Fire Safety for Candles addressing 4 root cause areas

Standard
Specification for Fire Safety for Candle Accessories

Baby Products Can Contain Fire Retardants



Graco baby stroller with 3% TDCP or chlorinated Tris in the foam found within the padding.



Brestfriend said that **the chemical in its nursing pillow** wasn't a PBDE. It was Albemarle Antiblaze V6 and perfectly safe.

A V6 is 2,2-Bis(Chloromethyl) Trimethylene Bis(Bis(2-Chloroethyl) Phosphate). It's 37% chlorine.

No fire hazard has been demonstrated for these baby products



U.S. Consumer Product Safety Commission

In December 2007 the Consumer Product Safety Commission (CPSC) proposed a national furniture flammability standard that can be met without fire retardant chemicals in foam.

“No one wants to trade fire risks for chemical toxicity risks.”

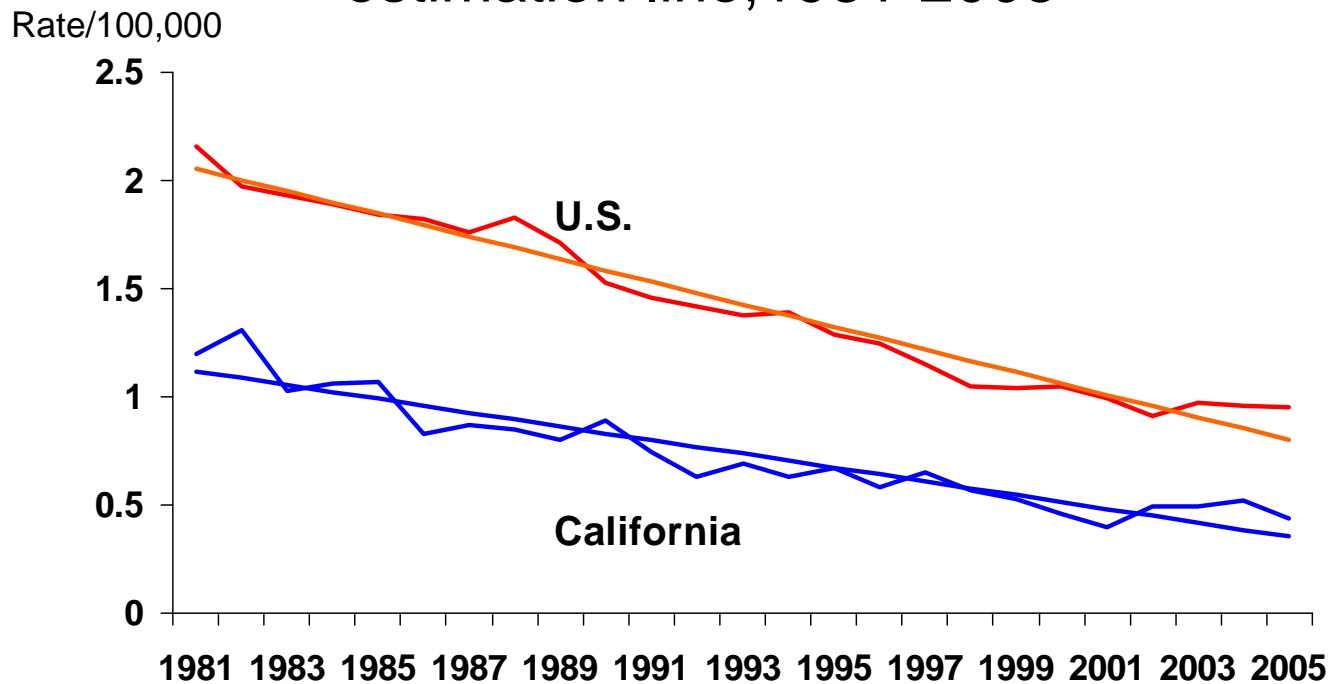
CPSC Commissioner Thomas Moore

Is TB 117 Effective?

- **Is there evidence that TB 117 has had any greater effect in preventing fire deaths in California than in other states (which do not have furniture flammability standards)**

U.S. Home Fire Deaths, 1981-2005

Residential Fire and Flame Death Rates in U.S. and California, trend data with linear estimation line, 1981-2005



Source: WISQARS, Centers for Disease Control and Prevention

Prepared by: California Department of Public Health, EPIC Branch

Decline in Fire Deaths

2000-2004 compared to 1980-1984

California	- 40%
Georgia	- 36%
Illinois	- 45%
Michigan	- 38%
New York	- 48%
Ohio	- 41%
Pennsylvania	- 41%
Texas	- 37%

*“US Unintentional Fire Death Rates by State”
National Fire Protection Association, 2008*



National Fire Protection Association

The authority on fire, electrical, and building safety

NFPA estimates 750 lives/year could have been saved by fire-safe cigarettes

On October 25, 2007, Reynolds American Inc. announced product-wide switch to fire-safe cigarettes. Jim Shannon, NFPA's president, said in an **“If cigarette manufacturers had begun producing only fire-safe cigarettes 20 years ago an estimated 15,000 lives could have been saved by now.”**

NFPA press release

No Data to show a Reduction in Fire Deaths from Retardants in Furniture Foam in California

“U.S. fire data is not detailed or complete enough to show whether adding fire retardant chemicals to furniture foam in California has made a measurable difference in fire deaths in that state.”

Marty Ahrens, Fire Analysis Services, NFPA



www.greensciencepolicy.org