



# U.S. EPA Design for the Environment Program

## *Flame Retardant Alternatives Analyses*

---

Kelly Grant, PhD

Portland EPA

February 25, 2010

# Presentation Outline

- **Action Plan for PBDEs**
  - Octa/penta
  - Deca
- **DfE's Alternatives Assessment**
  - Furniture flame retardants
- **Other flame retardants of concern and EPA actions**
  - Printed Circuit Boards, TBBPA
  - HBCD



# EPA Action Plan for PBDEs (12/09)



## Scientific findings:

- Phase out of manufacture of penta- & octa has not resulted in decreases in persistent/bioaccumulative (PB) congeners.
- Acknowledged that ecosystem exposure levels are near or match effect levels.
- Deca- partially debrominates to PB congeners.
- Importation of articles containing penta- & octa may also contribute to increasing PBDEs in environment.

# EPA Action Plan for PBDEs (12/09)

## Initiate rulemaking

- Add PBDEs to TSCA 5(b)(4) risk list, late fall 2010.
- SNUR importing articles containing penta, octa.
  - Significant New Use Rule
  - Deca will be SNUR'ed later
- TSCA §4 test rule for DecaBDE. Require laboratory studies to determine health and environmental effects.

# EPA Action Plan for PBDEs (12/09)

- Support voluntary phase out of deca, encourage full participation.
  - Two U.S. producers of decabromodiphenyl ether (decaBDE), Albemarle and Chemtura, and the largest U.S. importer, ICL Industrial Products, Inc., announced commitments to phase out decaBDE in the United States by 2013.

## DfE's plans:

- DfE's Alternatives Analysis for DecaBDE beginning Spring 2010. Report expected in late 2011.

# Furniture Flame Retardancy Partnership Alternatives Assessment (Completed 2005)



- **Predominant flame retardant (pentaBDE) was being found increasingly in human tissue, breast milk and the environment.**
  - Need for fire safety will likely increase based on planned national standards.
  - Decision-making for alternatives to this 19 million pound per year chemical.
- Market was in transition; industry is choosing alternatives. What are the potential risks of substitutes?



# Flame Retardant Alternatives Report

## Hazard Concerns



- Table summarizing EPA assessment for environmental and human health endpoints
  - High, Moderate, Low (hazard concern levels)
- Assessments of chemicals in flame retardant formulations
  - Detailed hazard reviews – publicly available information
  - Measured confidential data from EPA and chemical companies
  - Estimations from EPA New Chemicals Program
  - Professional judgment of EPA scientists
  - References if non-proprietary

# Furniture Flame Retardancy Partnership

## Results: Data Presentation



### Human Health Hazard Concern

### Ecotoxicity Hazard Concern

### Environmental Hazard Concern

| Company     | Chemical                                       | % in Formulation <sup>3</sup> | Human Health Effects |                 |              |               |              |          |              | Ecotoxicity |         | Environmental |                 | Potential Routes of Exposure |        |           |                    |        |           |         | Reactive or Additive? |
|-------------|------------------------------------------------|-------------------------------|----------------------|-----------------|--------------|---------------|--------------|----------|--------------|-------------|---------|---------------|-----------------|------------------------------|--------|-----------|--------------------|--------|-----------|---------|-----------------------|
|             |                                                |                               | Cancer Hazard        | Skin Sensitizer | Reproductive | Developmental | Neurological | Systemic | Genotoxicity | Acute       | Chronic | Persistence   | Bioaccumulation | Worker                       |        |           | General Population |        |           | Aquatic |                       |
|             |                                                |                               |                      |                 |              |               |              |          |              |             |         |               |                 | Inhalation                   | Dermal | Ingestion | Inhalation         | Dermal | Ingestion |         |                       |
| 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<br>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<br>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<br>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              |

# Other Brominated Flame Retardants of Concern



- PBDEs are not the only BFRs of potential concern.

- Key Activities:

- DfE is investigating alternatives to tetrabromobisphenol A (TBBPA) in electronics. Draft report available on website.

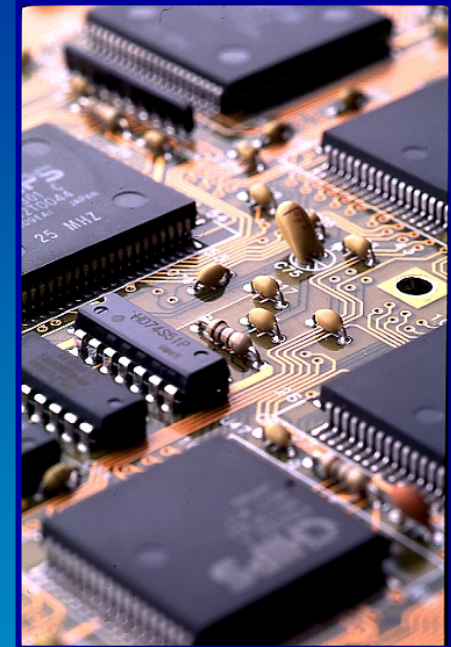
<http://epa.gov/dfe/pubs/projects/pcb/index.htm>

- HBCD, hexabromocyclododecane, is likely to be included in a future round of EPA Action Plans. HBCD is used in polystyrene foam.

# Flame Retardants in Printed Circuit Boards Partnership Drivers



- Tetrabromobisphenol A / TBBPA
  - Highest volume brominated flame retardant used in printed circuit boards at ~ 330 million pounds/year
  - Reacted into the epoxy backbone of the PCB laminate
- Industry need for information on flame retardants
- Concern by some stakeholders over environmental impacts and combustion by-products



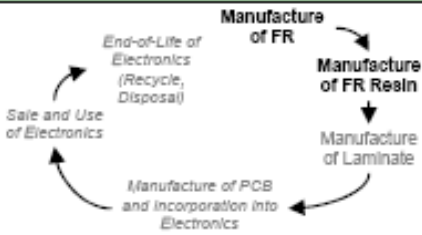
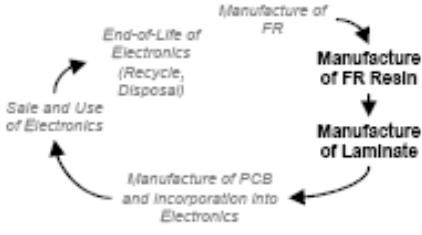
# Flame Retardants in Printed Circuit Boards

## Results: Data Presentation

### Human Health Hazard Concern

### Ecotoxicity Hazard Concern

### Environmental Hazard Concern

| Chemical                                                                                                                                                                               | CASRN       | Human Health Effects |                 |                |                |                |                |              |          |                | Aquatic Toxicity |         | Environmental |                 | Exposure Considerations                                                               |  |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------|----------------------|-----------------|----------------|----------------|----------------|----------------|--------------|----------|----------------|------------------|---------|---------------|-----------------|---------------------------------------------------------------------------------------|--|
|                                                                                                                                                                                        |             | Acute Toxicity       | Skin Sensitizer | Cancer Hazard  | Immunotoxicity | Reproductive   | Developmental  | Neurological | Systemic | Genotoxicity   | Acute            | Chronic | Persistence   | Bioaccumulation |                                                                                       |  |
| Availability of flame retardants (FRs) throughout the lifecycle for reactive and additive FRs chemicals and resins                                                                     |             |                      |                 |                |                |                |                |              |          |                |                  |         |               |                 |                                                                                       |  |
| Reactive Flame Retardant Chemicals <sup>2</sup>                                                                                                                                        |             |                      |                 |                |                |                |                |              |          |                |                  |         |               |                 |                                                                                       |  |
| Tetrabromobisphenol A (TBBPA) (Albemarle, Chemtura, and others)                                                                                                                        |             |                      |                 |                |                |                |                |              |          |                |                  |         |               |                 |                                                                                       |  |
| TBBPA                                                                                                                                                                                  | 79-94-7     | L                    | L               | L              | L              | L              | M              | L            | L        | L              | H                | H       | M             | L               |   |  |
| DOPO (6H-Dibenz[c,e][1,2] oxaphosphorin, 6-oxide) (Samko Co., Ltd. and others)                                                                                                         |             |                      |                 |                |                |                |                |              |          |                |                  |         |               |                 |                                                                                       |  |
| DOPO                                                                                                                                                                                   | 35948-25-5  | L                    | L               | L              | L              | L              | L              | L            | L        | L              | M                | M       | L             | L               |                                                                                       |  |
| Fyrolflex PMP (Aryl alkylphosphonate) (Supresta)                                                                                                                                       |             |                      |                 |                |                |                |                |              |          |                |                  |         |               |                 |                                                                                       |  |
| Fyrolflex PMP                                                                                                                                                                          | Proprietary | L                    | L               | L              | L              | L              | L              | L            | L        | L              | L                | L       | H             | L               |                                                                                       |  |
| Reactive Flame Retardant Resins <sup>2</sup>                                                                                                                                           |             |                      |                 |                |                |                |                |              |          |                |                  |         |               |                 |                                                                                       |  |
| Reaction product of TBBPA - D.E.R. 538 (Phenol, 4,4'-(1-methylethylidene)bis[2,6-dibromo-, polymer with (chloromethyl)oxirane and 4,4'-(1-methylethylidene)bis[phenol]] (Dow Chemical) |             |                      |                 |                |                |                |                |              |          |                |                  |         |               |                 |                                                                                       |  |
| D.E.R. 538                                                                                                                                                                             | 26265-08-7  | L                    | M               | M <sup>0</sup> | L              | M <sup>0</sup> | M <sup>0</sup> | L            | L        | M              | L                | L       | M             | L               |  |  |
| Reaction Product of DOPO - Dow XZ-92547 (reaction product of an epoxy phenyl novolak with DOPO) (Dow Chemical)                                                                         |             |                      |                 |                |                |                |                |              |          |                |                  |         |               |                 |                                                                                       |  |
| Dow XZ-92547                                                                                                                                                                           | Proprietary | L                    | M               | M <sup>0</sup> | L              | M <sup>0</sup> | M <sup>0</sup> | L            | L        | M <sup>0</sup> | L                | L       | H             | L               |                                                                                       |  |
| Reaction product of Fyrolflex PMP with bisphenol A, polymer with epichlorohydrin (Representative Resin)                                                                                |             |                      |                 |                |                |                |                |              |          |                |                  |         |               |                 |                                                                                       |  |
| Representative Fyrolflex PCB Resin                                                                                                                                                     | Unknown     | L                    | L               | M <sup>0</sup> | L              | M <sup>0</sup> | M <sup>0</sup> | L            | L        | M <sup>0</sup> | L                | L       | H             | L               |                                                                                       |  |

Kelly Grant  
grant.kelly@epa.gov  
202-564-9910



<http://www.epa.gov/dfe>

**U.S. Environmental Protection Agency**

# Flame Retardant Alternatives

## Report Human Health Effects Criteria



### Cancer Health Effects

|          |                                                                                                          |
|----------|----------------------------------------------------------------------------------------------------------|
| High     | Positive experimental data in humans                                                                     |
| Moderate | Positive cancer bioassay in experimental animals or chemical class known to produce carcinogenic effects |
| Low      | Negative experimental data                                                                               |

### Non-Cancer Health Effects

|          |                                                                                                             |
|----------|-------------------------------------------------------------------------------------------------------------|
| High     | Evidence of adverse effects in human populations or conclusive evidence of severe effects in animal studies |
| Moderate | Suggestive animal studies, analog data, or chemical class known to produce toxicity                         |
| Low      | No concern identified                                                                                       |

# Flame Retardant Alternatives

## Report Aquatic Toxicity Criteria



### Acute

|          |                                            |
|----------|--------------------------------------------|
| High     | $LC50 \leq 1 \text{ mg/L}$                 |
| Moderate | $1 \text{ mg/L} < LC50 < 100 \text{ mg/L}$ |
| Low      | $LC50 > 100 \text{ mg/L}$                  |

### Chronic

|          |                                                     |
|----------|-----------------------------------------------------|
| High     | $ChV \leq 0.1 \text{ mg/L}$                         |
| Moderate | $0.1 \text{ mg/L} < ChV < 10 \text{ mg/L}$          |
| Low      | $ChV > 10 \text{ mg/L}$ or No Effects at Saturation |

# Short Term Project Ideas

Accept slightly discolored foam.

Fire barrier technologies are already in use in mattresses, can similar technologies be used for other applications.

California is the only state with a residential furniture flammability standard - is it necessary?

Hickory Springs Converted Connover, N.C. plant to non-halogenated Phosphorous-based compound

# Downsides

- Non regulatory
  - Industry may not choose the best alternative
  - Need to have more out of the box thinking, like better ways to prevent fires, data indicating whether FRs really save lives now that there are other fire safety standards.
  - An informed (and outraged) public helps to prod industry and federal government into action.

# Potential Long Term Project - Developing Safe, Inherently Flame Retardant Foam



## UMASS Polymer Science Industry Research Program - Cluster F: Fire Safe Polymers and Polymer Composites

In 1996, the University of Massachusetts Amherst, in conjunction with the Federal Aviation Administration and Industry, joined together in a multi-year, multi-investigator program in an attempt to create a new generation of Fire-Safe materials.

*Sponsors: Boeing - Commercial Airplane Group, Federal Aviation Administration, NIST, Schneller, Inc., Solvay Advanced Polymers, US Army*

<http://www.pse.umass.edu/cumirp/fpart1.html>

# Uses of PBDEs

- PentaBDE (phased out 2004)
  - Foam in furniture, mattresses, automobile seats
  - 8,000 tons/year worldwide; 95% used in the U.S.
- OctaBDE (phased out 2004)
  - Plastics in electronics (e.g. TVs, computers)
  - 4,000 tons/year worldwide; 40% used in U.S.
- DecaBDE
  - Plastics in electronics (e.g. TVs, computers), wire and cable insulation, textiles
  - 62,000 tons/year worldwide; 44% used in U.S.

(industry data for 2001)