Are there less toxic alternative fire retardant strategies?

FR Dilemma Part III
Berkeley, CA

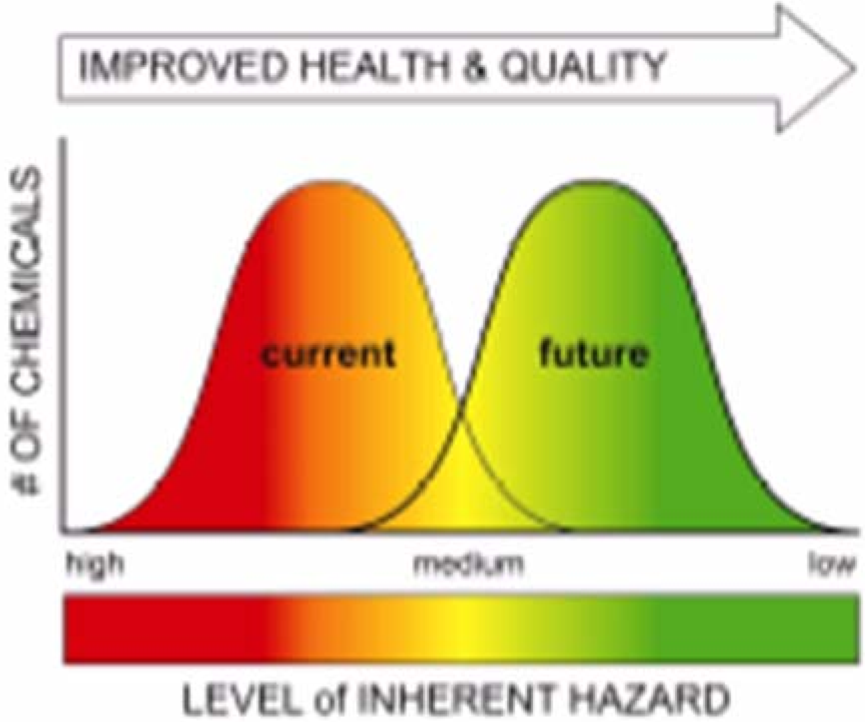
Lauren Heine, Ph.D.
Senior Fellow
Green Blue Institute (GreenBlue)
September 20, 2007

GreenBlue

Overview

- The US EPA Design for the Environment (DfE) Partnerships and Related Initiatives
  - Green Chemistry and the DfE Approach
  - DfE Projects and Related Initiatives
    - CleanGredients™
    - Furniture Flame Retardancy Partnership
    - The Green Screen for Safer Chemicals
    - Flame Retardants in Printed Circuit Boards

A Goal of Green Chemistry



What is a Sustainable Product?

‘Cradle to Cradle’ Design

- **Meets market requirements**
- **Positive social effects (for individuals and communities)**
- **Safe for human and ecological health**
- **Sourced from renewable or repeatedly recycled materials**
- **Sourced from renewable energy**
- **Designed for safe, productive return to nature or industry**
- **Recovered and recycled at highest quality after use**

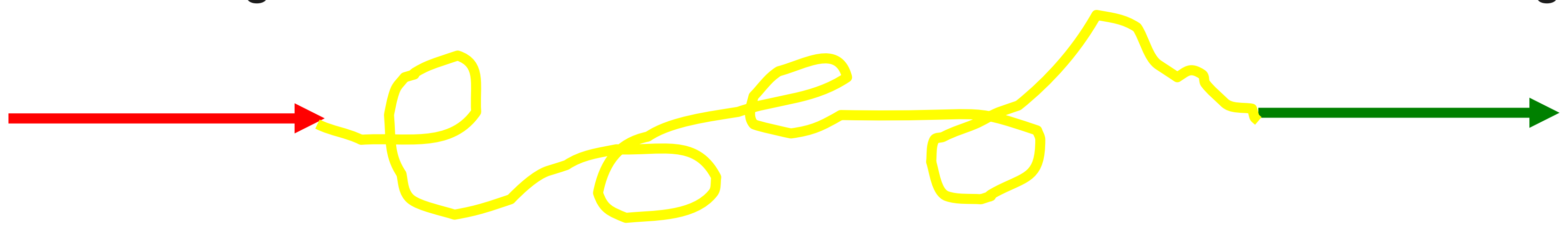
GreenBlue

The Path to Green Chemical Inventories

High Degree of Knowledge

Knowledge Gaps

High Degree of Knowledge



Chemicals of Concern (“Known Bads”)

Mixed hazard properties

Benign (“Known Goods”)

Reactive

Proactive

GreenBlue

U.S. EPA DfE Partnership Approach

- Engage diverse stakeholders in a common effort
- Provide needed information in a format that facilitates decision making (informed substitution)
- Protect confidential business information through third party review and careful design of information presentation
- Use EPA chemical information, models and new chemicals criteria
- Focus on hazard and not risk
- Tap into market mechanisms for promoting environmentally preferable products
  - DfE Formulator Program– product recognition
  - CleanGredients – ingredient review and listing

DfE and CleanGredients™

http://www.cleangredients.org

A database of Industrial & Institutional (I&I) cleaning product ingredients and their characteristics* to:

- **help formulators identify ingredients that may be useful for green product formulation**
- **provide opportunity for raw material suppliers to showcase their ingredients with especially positive environmental and/or human health and safety attributes**

* By ***characteristics*** we mean functional properties such as critical micelle concentration, physical properties such as biodegradability, and associated human and environmental health toxicological information.

GreenBlue

DfE's Furniture Flame Retardancy Partnership

Multi-stakeholder effort

- American Fire Safety Council (AFSC),
- the American Home Furnishings Alliance (AHFA),
- the Business and Institutional Furniture Manufacturers Association (BIFMA),
- the Consumer Product Safety Commission (CPSC),
- GreenBlue Institute
- EPA's Design for the Environment (DfE) Program.

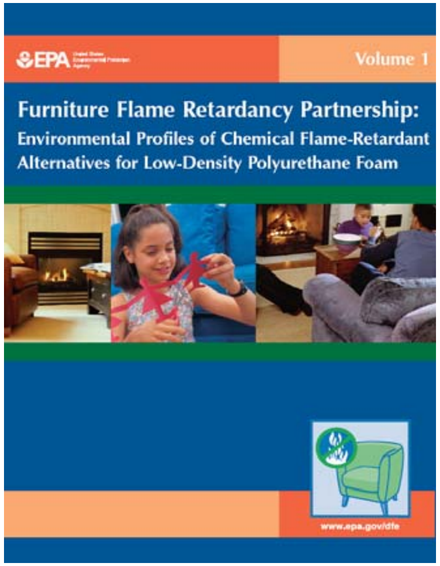
Focus on providing information on alternative ways to achieve fire safety in upholstered furniture

- Need for alternatives to (pentaBDE)
- Compare 14 chemical formulations identified as viable substitutes against a broad set of hazard endpoints

www.epa.gov/dfe/pubs/flameret/ffr-alt.htm

Results

- Phase I report: "Environmental Profiles of Chemical Flame-Retardant Alternatives for Low-Density Polyurethane Foam,"



- Did not perform Phase II work to assess other FR technologies such as barriers or fabric backcoatings due to uncertainty in planned CPSC national flammability standard.

GreenBlue

Innovation: Furniture Flame Retardancy Partnership Table 4-1

Table 4-1 Screening Level Toxicology and Exposure Summary

L = Low hazard concern
M[1] = Moderate hazard concern
H = High hazard concern
L, *M*[1], or *H* = Endpoint assigned using estimated values and professional judgment (Structure Activity Relationships)

N = No
Y = Yes
P = Yes for pure chemical

*Ongoing studies may result in a change in this endpoint
▲Persistent degradation products expected[2]

Company	Chemical	% in Formulation[3]	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	ANTIBLAZE 180 and ANTIBLAZE 195																				
	Tris(1,3-dichloro-2-propyl)Phosphate CAS # 13674-87-8	95%	M	L	M	M	L	M	M	M	M	M	*L*	N	Y	Y	N	Y	Y	Y	Additive
Albemarle	ANTIBLAZE 182 and ANTIBLAZE 205																				
	Proprietary A Chloroalkyl phosphate (1)		M	L	M	M	L	M	M	M	M	M	*L*	N	Y	Y	N	Y	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
Albemarle	ANTIBLAZE V500																				
	Proprietary C Chloroalkyl phosphate (2)		*M*	M	*M**	*M**	L	M	L	M	M	M	*L*	N	Y	Y	N	Y	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
Albemarle	SAYTEX RX-8500																				
	Proprietary D Reactive brominated flame retardant		*L*	*M*	*L*	*L*	*M*	*M*	L	*M*	*M*	*L*▲	*L*	N	Y	Y	N	N	Y	Y	Reactive
	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

GreenBlue

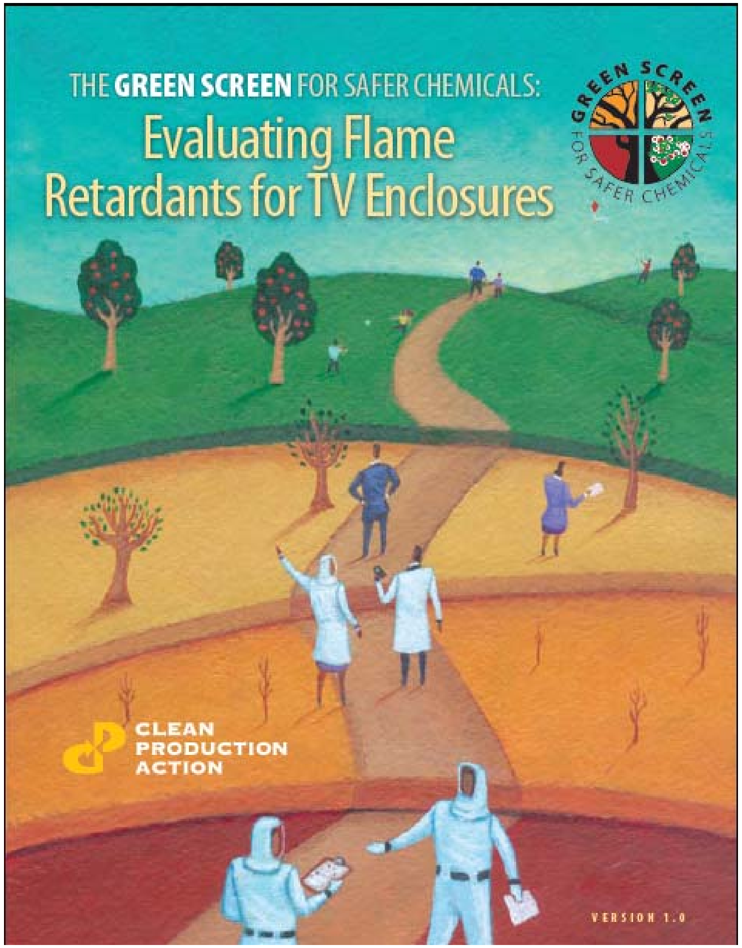
Challenge: where we left off…

- Which flame retardant is better? (Outside DfE scope)
- How would you evaluate and compare barriers and backcoating or inherently flame retardant alternative materials? (Drivers changed – did not address)
    - Ammonium polyphosphate (coated on various fibers)
    - Boric acid and Zinc borate (coated on cotton fiber)
    - Cellulosic fiber containing silicic acid (Visil®)
    - Fiberglass
    - Meta aramid fiber (Nomex®)
    - Melamine fiber
    - Modacrylic fiber (polymer contains antimony trioxide)
    - Oxidized PAN (PolyAcryloNitrile) fiber
    - Para aramid fiber (Kevlar®)
    - Polyetherimide resin
    - Vinylidene chloride fiber
    - Proprietary 1: Inert polymer coating (can be used on cotton woven substrate) (VersaShield II)

GreenBlue

Which Flame Retardant is Better?
The Green Screen for Safer Chemicals

- Guidance for selecting greener chemicals
- Case Study: FRs used in television casings
  - decaBDE,
  - RDP
  - BPADP

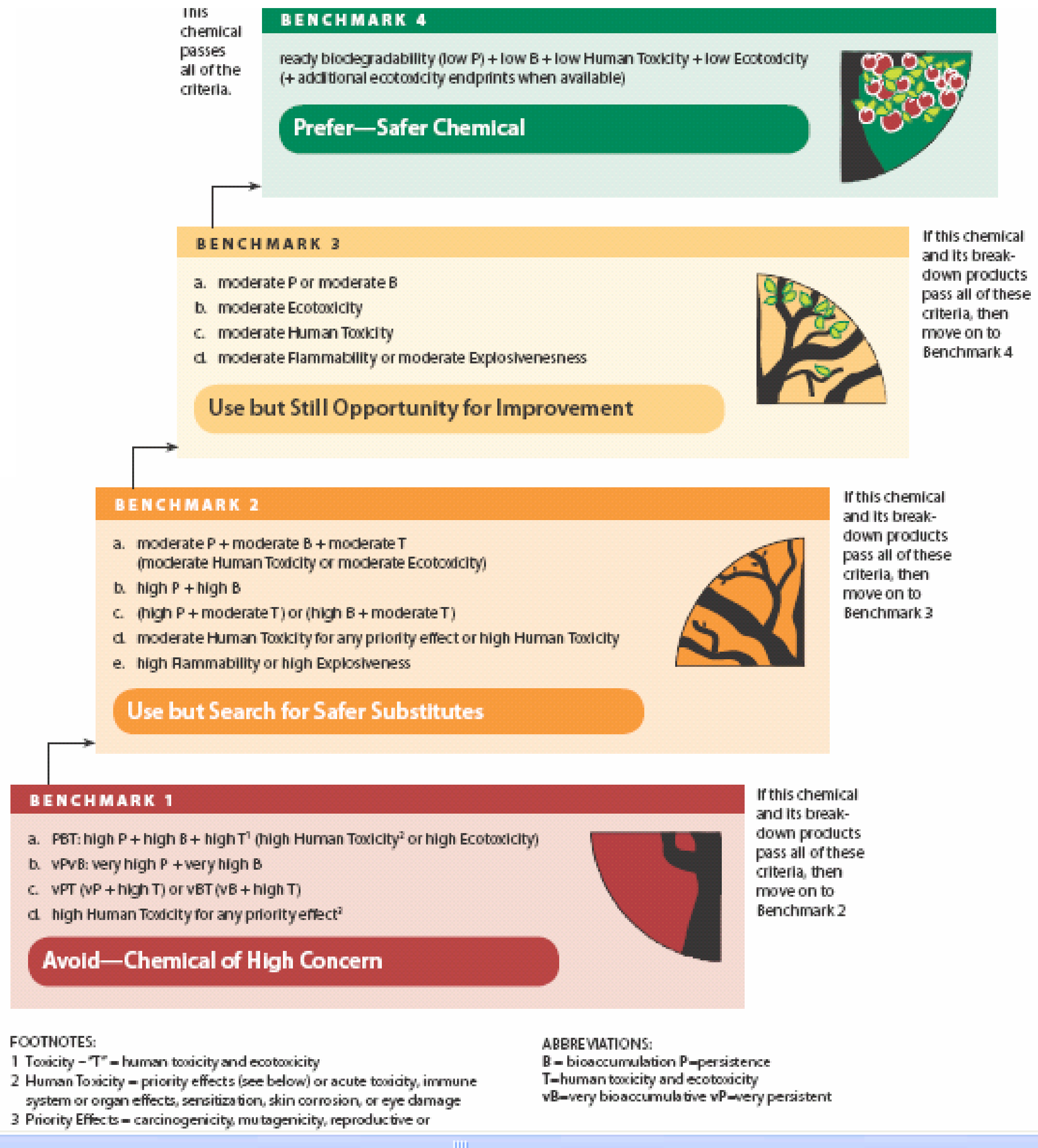


Download at: http://www.cleanproduction.org/Green.Greenscreen.php

GreenBlue

Green Screen for Safer Chemicals: Benchmarks

- Benchmark 1:
  Avoid—Chemical of high concern
- Benchmark 2:
  Use but search for safer substitutes
- Benchmark 3:
  Use but still opportunity for improvement
- Benchmark 4:
  Prefer—Safer chemical



Green Screen Hazard Thresholds

TABLE 3: **Threshold Values for Each Chemical Hazard Included in the Green Screen**

Hazard	Very High (v)	High (H)	Moderate (M)	Low (L)
Environmental Fate				
Persistence—P (half-life in days)[1]	• Soil or sediment >180 days; or • Water >60 days	• Soil or sediment >60 to 180 days; • Water >40 to 60 days; or • Potential for long-range environmental transport	• Soil or sediment 30 to 60 days; or • Water 7 to 40 days	• Soil or sediment <30 days; • Water <7 days; or • Ready biodegradability
Bioaccumulation Potential—B[1]	• BCF/BAF >5000; or • Absent such data, log K_{ow} >5	• BCF/BAF >1000 to 5000; • Absent such data, log K_{ow} >4.5-5; or • Weight of evidence demonstrates bioaccumulation in humans or wildlife	• BCF/BAF 500 to 1000; • Absent such data, log K_{ow} 4-4.5; or • Suggestive evidence of bioaccumulation in humans or wildlife	• BCF/BAF <500; or • Absent such data, log K_{ow} <4
Ecotoxicity				
Acute Aquatic Toxicity[1]		• $LC_{50}/EC_{50}/IC_{50}$ <1 mg/l; or • GHS Category 1	• $LC_{50}/EC_{50}/IC_{50}$ 1-100 mg/l; or • GHS Category 2 or 3	• $LC_{50}/EC_{50}/IC_{50}$ >100 mg/l
Chronic Aquatic Toxicity[1]		• NOEC <0.1 mg/l; or • GHS Category 1	• NOEC 0.1-10 mg/l; or • GHS Category 2, 3 or 4	• NOEC >10 mg/l
Human Health				
Carcinogenicity*		• Evidence of adverse effects in humans; • Weight of evidence demonstrates potential for adverse effects in humans; • NTP known or reasonably anticipated to be human carcinogen; • OSHA carcinogen; • US EPA known/likely (probable); • California Prop 65; • IARC Group 1 or 2A; • EU Category 1 or 2; or • GHS Category 1A or 1B	• Suggestive animal studies; • Analog data; • Chemical class known to produce toxicity; • US EPA suggested evidence (possible); • IARC Group 2B; • EU Category 3; or • GHS Category 2	• No basis for concern identified or • IARC Group 3 or 4
Mutagenicity/ Genotoxicity*		• Evidence of adverse effects in humans; • Weight of evidence demonstrates potential for adverse effects in humans; • EU Category 1 or 2; or • GHS Category 1A or 1B	• Suggestive animal studies; • Analog data; • Chemical class known to produce toxicity; • EU Category 3; or • GHS Category 2	No basis for concern identified
Reproductive toxicity*		• Evidence of adverse effects in humans; • Weight of evidence demonstrates potential for adverse effects in humans; • NTP Center for the Evaluation of Risks to Human Reproduction; • California Prop 65; • EU Category 1 or 2; or • GHS Category 1A or 1B	• Suggestive animal studies; • Analog data; • Chemical class known to produce toxicity; • EU Category 3; or • GHS Category 2	No basis for concern identified
Developmental toxicity*		• Evidence of adverse effects in humans; • Weight of evidence demonstrates potential for adverse effects in humans; • NTP Center for the Evaluation of Risks to Human Reproduction; or • California Prop 65	• Suggestive animal studies; • Analog data; or • Chemical class known to produce toxicity	No basis for concern identified
Endocrine Disruption*		• Evidence of adverse effects in humans; or • Weight of evidence demonstrates potential for adverse effects in humans	• Suggestive animal studies; • Analog data; • Chemical class known to produce toxicity; • EU Draft List—Category 1 or 2; or • Japanese list	No basis for concern identified

TABLE 3: **Threshold Values for Each Chemical Hazard Included in the Green Screen** continued

Hazard	Very High (vH)	High (H)	Moderate (M)	Low (L)
Neurotoxicity*		• Evidence of adverse effects in humans; or • Weight of evidence demonstrates potential for adverse effects in humans	• Suggestive animal studies; • Analog data; or • Chemical class known to produce toxicity	No basis for concern identified
Acute Toxicity (oral, dermal, or inhalation)		• LD_{50} <50 mg/kg bodyweight (oral); • LD_{50} <200 mg/kg bodyweight (dermal); • LC_{50} <500 ppm (gas); • LC_{50} <2.0 mg/l (vapor); • LC_{50} <0.5 mg/l (dust or mist); • US EPA Extremely Hazardous Substance List; or • GHS Category 1 or 2	• LD_{50} 50-2000 mg/kg body-weight (oral); • LD_{50} 200-2000 mg/kg bodyweight (dermal); • LC_{50} 500-5000 ppm (gas); • LC_{50} 2-20 mg/l (vapor); • LC_{50} 0.5-5 mg/l (dust or mist); or • GHS Category 3 or 4	No basis for concern identified
Corrosion/Irritation of the Skin or Eye		• Evidence of irreversible effects in studies of human populations; • Weight of evidence of irreversible effects in animal studies; or • GHS Category 1 (skin or eye)	• Evidence of reversible effects in humans or animals; • GHS Category 2 or 3—skin irritation; or • GHS Category 2A or 2B—eye	No basis for concern identified
Sensitization of the Skin or Respiratory System		• Evidence of adverse effects in humans; • Weight of evidence demonstrates potential for adverse effects in humans; • GHS Category 1—(skin or respiratory); or • Positive responses in predictive Human Repeat Insult Patch Tests (HRIPT) (skin)	• Suggestive animal studies; • Analog data; or • Chemical class known to produce toxicity	No basis for concern identified
Immune System Effects		• Evidence of adverse effects in humans; or • Weight of evidence demonstrates potential for adverse effects in humans	• Suggestive animal studies; • Analog data; or • Chemical class known to produce toxicity	No basis for concern identified
Systemic Toxicity/Organ Effects (via single or repeated exposure)		• Evidence of adverse effects in humans; • Weight of evidence demonstrates potential for adverse effects in humans; • GHS Category 1—organ/systemic toxicity following single or repeated exposure	• Suggestive animal studies; • Analog data; • Chemical class known to produce toxicity; • GHS Category 2 or 3 single exposure; or • Category 2 repeated exposure	No basis for concern identified
Physical/Chemical Properties				
Explosive		• GHS Category: Unstable explosives or Divisions 1.1, 1.2, or 1.3	• GHS Category: Divisions 1.4 or 1.5	No basis for concern identified
Flammable		• GHS Category 1—Flammable Gases; • GHS Category 1—Flammable Aerosols; or • GHS Category 1 or 2—Flammable Liquids	• GHS Category 2—Flammable Gases; • GHS Category 2—Flammable Aerosols; or • GHS Category 3 or 4—Flammable Liquids	No basis for concern identified

Green Screen Hazard Thresholds

Summary of Green Screen Modifications to DfE Approach

1. **Modified Thresholds**
   - Added a 4th level ((very) vP and vB) for persistence and bioaccumulation potential consistent with REACH
2. **Additional Endpoints**
   - Added endocrine disruption as an endpoint
   - Added flammability and explosiveness as endpoints
3. **Evaluated predicted and known degradation products along with the parent compound**
   - Degradation products weighed as heavily as the parent compound in final evaluation

Case Study: Comparing Flame Retardant Chemicals Used in Television Casings

TABLE 7: Green Screen Benchmarks for Phosphorous-based and DecaBDE Flame Retardants

Chemical	CAS #	Reasons for Benchmark	Benchmark Achieved
DecaBDE and its breakdown products	1163-19-5	Breakdown products stop decaBDE at Benchmark 1: • pentaBDE = PBT, vPvB, vPT, vBT, and high concern for endocrine disruption—Benchmarks 1(a)/(b), (c)/(d) • octaBDE = vPT and high concern for developmental toxicity—Benchmark 1(c)/(d)	Benchmark 1: Avoid—Chemical of High Concern
BPADP/BAPP and its breakdown products	181028-79-5	Breakdown product and formulation contaminant, bisphenol A, is of high concern for endocrine disruption—stopping BPADP at Benchmark 1(d)	Benchmark 1: Avoid—Chemical of High Concern
RDP and its breakdown products	125997-21-9	• Chemical constituents have high persistence or high bioaccumulation and moderate/high toxicity (but not for priority effects)—stopping RDP at Benchmarks 2(a) and 2(c) • Breakdown product, phenol, has high systemic effects—stopping RDP at Benchmark 2(d)	Benchmark 2: Use but Search for Safer Substitutes

- Of the 3 FR chemicals, only RDP passed all criteria under Benchmark 1 of the Green Screen.
- An integral element of the Green Screen is taking into account potential breakdown products.
  - The other FRs scored lower because of concern for degradation products.
- While RDP is not a “green chemical” per se, based on assessment via the Green Screen, it is a safer chemical.

Latest FR Partnership

- Industry need for information on flame retardants
  - Highest volume brominated flame retardant used in printed circuit boards - at approx. 330 million pounds/year (Tetrabromobisphenol A/TBBPA)
- Concern by some stakeholders over environmental impacts and combustion by-products

DfE: Flame Retardants in Printed Circuit Boards

Goal:

- To identify and characterize commercially available flame retardants and their environmental, health, safety and environmental fate aspects in FR-4 printed circuit boards
- Apply life-cycle thinking to consider hazards and exposures **including degassing and combustion**
- Use EPA New Chemicals Program criteria to evaluate hazard and environmental fate concerns

Partnership Test Materials

Flame Retardant Chemicals

- TBBPA
- DOPO
- Melapur 200 (Melamine Polyphosphate)
- Clariant OP930 (Phosphinate)
- Silica
- Aluminum Hydroxide
- Supresta Fyrolflex PMP
- Dow Proprietary Chemical

Laminate Materials

- Conventional FR-4 Laminate
- NanYa NPG-TL
- NanYa NPG-170TL
- Hitachi BE-67G(R)
- Isola DE156*
- Isola IS500*
- TUC TU-642*
- TUC TU-742
- MEW R1566W
- ITEQ IT170G*
- ITEQ IT140G**
- ITEQ IT155G**
- Nelco 4000-7EF*
- Shengyi S1155**

Included on original iNEMI List Only
** *New on iNEMI List*

STATUS

Chemical Reviews – Hazard Assessment

- ✓FIRST DRAFT COMPLETED

Combustion Testing

- ? Under negotiation ($, ownership)

Partnership Report – Life Cycle Considerations

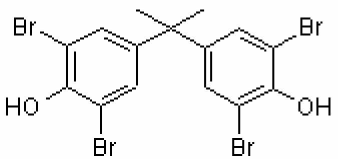
- ? Under development

Innovation

- Revised format for summarizing chemical hazard information and justifying levels (H/M/L)
- Proposed combustion study (2 phases) using quartz reactors and cone calorimetry to compare potential end-of-life impacts (concern for uncontrolled combustion)

Report DRAFT ONLY - Chemical Summary Assessments

5.2 Chemical Summary Assessments

Record ID: Tetrabromobisphenol A	**CAS No.** 79-94-7
	**MW:** 543.88 **MF:** $C_{15}H_{12}Br_4O_2$ **Physical Forms:** **Neat:** Solid **Use:** Flame retardant, additive or reactive
SMILES: Oc1c(Br)cc(cc1Br)C(C)(C)c2cc(Br)c(O)c(Br)c2	
Name: Phenol, 4,4'-(1-methylethylidene)bis[2,6-dibromo-	
Synonyms: Tetrabromobisphenol A; TBBPA; 4,4'-Isopropylidenebis(2,6-dibromophenol)	
Life-Cycle Considerations: TBBPA is used as both an additive and reactive flame retardant in a wide variety of electronic equipment. As indicated in Section 3.2, TBBA is most commonly used as a reactive flame retardant in PCBs and is incorporated into this product through chemical reactions with the epoxy resin. Potential exposure or release if TBBPA particulates may occur during dust forming operations during its manufacture or subsequent loading/unloading, transfer, or mixing operations (those that occur before its incorporation into the epoxy resin). Depending on the method of manufacture, there may be unreacted TBBPA present in the epoxy resins and therefore, free TBBPA may also be present in the laminate and PCBs subsequently produced. The amount of free TBBPA is generally anticipated to be relatively low when it is used as a reactive flame retardant although quantitative data on the amount of free TBBPA present in PCBs is currently limited. The following studies are representative (also see section 6.2). Sellstrom and Jansen (1995) found approximately 0.7 micrograms per gram in a basic extraction of PCB filings from an off-the-shelf product purchased in Sweden (approximately 4 micrograms per gram TBBPA used). Extraction of a prepreg sample with an unidentified organic solvent did not lead to the detection of free TBBPA (PSB, 2006). Release of free TBBPA may occur during the disposal of PCBs. TBBPA has been detected in the air of electronic recycling plants (Sjodin et al., 2001, 2003), although these facilities also recycled products where TBBPA is used as an additive flame retardant. Although its water solubility is low under neutral conditions, it may be released from PCBs in landfills that come in contact with basic leachate. The potential for TBBPA and other compounds to be released from the incineration or open burning of PCBs is discussed in Section 6.1.	

Tetrabromobisphenol A			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
PHYSICAL/CHEMICAL PROPERTIES			
Melting Point (°C)	206 (Estimated)	EPI	
	181 (Measured)	WHO, 1995; Albemarle Corporation, 1999	Inadequate, the submitter comment

Tetrabromobisphenol A			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
			indicated that the measurement was performed on the commercial product which was not 100% pure.
Boiling Point (°C)	Decomposes at 316 (Measured)	Stenger, 1978; WHO, 1995	Adequate, TBBPA will decompose before boiling based on measurements on the commercial product, which may not have been 100% pure.
Vapor Pressure (mm Hg)	<8.9x10^{-8} (Measured)	Lezotte and Nixon, 2001	Adequate
	<1 (Measured)	WHO, 1995; Hardy and Smith, 1999	Inadequate
Water Solubility (g/L)	1.2x10^{-6} (Estimated)	EPI	
	4.6x10^{-3} to 8.2x10^{-3} (Measured)	NOTOX, 2000; Submitted confidential study	Inadequate, the measured water solubilities were dependent on the flow rates through the column. Higher flow rates gave higher solubilities, which indicate that the flow rate dependency is not caused by a failure to reach equilibrium. The study was properly performed, and the actual water solubility is probably near this range.
	1.48x10^{-4} at pH 5 1.26x10^{-3} at pH 7 2.34x10^{-4} at pH 9 (Measured)	MacGregor and Nixon, 2002; Submitted confidential study	Inadequate, the samples were not assessed for the presence of colloidal material before analysis.
	7.2x10^{-4} at 15 °C 4.16x10^{-3} at 25 °C 1.77x10^{-3} at 35 °C (Measured)	WHO, 1995	Inadequate, study details and test conditions were not available. The original study was in an unpublished report submitted to the WHO.

Tetrabromobisphenol A			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
Log K_{ow}	7.2 (Estimated)	EPI	
	4.5-5.3 (Measured)	WHO, 1995	Inadequate, study details and test conditions were not available. The original study was in an unpublished report submitted to the WHO.
	5.903 (Measured)	MacGregor and Nixon, 2001; Submitted confidential study	Adequate
Flammability (Flash Point)			No data
Explosivity	Dust Explosivity: Maximum Explosion Pressure (P_{max}) = 7.7 bar; Maximum Rate of Pressure Rise $(dP/dt)_{max}$ = 379 bar/s; K_{st} Value = 103 bar.m/s (weak explosion) (Measured)	Churchwell and Ellis, 2007; Submitted confidential study	Adequate
pH			No data

PROPERTY/ENDPOINT		DATA	REFERENCE	DATA QUALITY
ENVIRONMENTAL FATE				
Transport		**The estimated water solubility of $1.2x10^{-6}$ g/L, vapor pressure of <10^{-6} torr, and estimated K_{oc} of $5.6x10^{5}$ indicate that TBBPA will partition predominantly to soil and sediment. The estimated Henry's Law constant of $2.31x10^{-13}$ atm-m^{3}/mole indicates that TBBPA will not volatilize from water to the atmosphere. The estimated K_{oc} of $5.6x10^{5}$ indicates that TBBPA is not anticipated to migrate through soil into groundwater and also has the potential to adsorb to sediment.**		
	Henry's Law Constant – HLC (atm-m^{3}/mole)	$2.31x10^{-13}$ (Estimated)	EPI	
	Sediment/Soil	$5.6x10^{5}$ (Estimated)	EPI	

Tetrabromobisphenol A				
PROPERTY/ENDPOINT		DATA	REFERENCE	DATA QUALITY
	pK_a	pK_a = 9.40 (Measured)	Lezotte and Nixon, 2002; Submitted confidential study	Adequate
		pK_{a1} = 7.5 and pK_{a2} = 8.5 (Measured)	WHO, 1995	Inadequate, study details and test conditions were not available. The original study was in an unpublished report submitted to the WHO.
Bioaccumulation		**LOW: The measured fish BCFs are less than 1000.**		
	Fish BCF	13,550 (Estimated)	EPI	
		30-485 (*Cyprinus carpio*) (Measured)	CITI, 1992; CERIJ, 2006	Adequate
		A BCF (*Pimephalus promelas*) of 1200 was measured based on total ^{14}C radioactivity; however, extraction and thin layer chromatograph of the residue in the body of the fish determined that only 24.9% of the ^{14}C radioactivity was due to TBBPA, with the remainder due to metabolites, giving a BCF of 300 for TBBPA. Elimination half-life < 24 hours for total ^{14}C radioactivity. (Measured)	Fackler, 1989a; Submitted confidential study	Adequate
	Daphnids BCF			No data
	Green Algae BCF			No data

Tetrabromobisphenol A				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
	Earthworms BCF			No data
	Metabolism in fish			No data
Persistence		**MODERATE: Experimental aerobic biodegradation studies in soil and sediment indicate that the aerobic primary biodegradation half-life is less than 180 days, but not less than 60 days. Experimental anaerobic biodegradation studies in soil and sediment indicate that the anaerobic primary biodegradation half-life is less than 60 days. Mineralization under both aerobic and anaerobic conditions in soil and sediment is low, indicating that persistent degradation products are formed. An experimental photolysis half-life of 24 minutes at pH 7.4 in water indicates that TBBPA may photolyze rapidly; however, it is not anticipated to partition significantly to water. Although adequate experimental data are not available, degradation of TBBPA by hydrolysis is not expected to be significant as the functional groups present on this molecule do not tend to undergo hydrolyze. The atmospheric half-life for the gas phase reactions of TBBPA is estimated at 3.6 days, though it is expected to exist primarily as a particulate in air.**		
Water	**Aerobic Biodegradation**	Primary: weeks-months (Estimated)	EPI	
		Ultimate: recalcitrant (Estimated)	EPI	
	Volatilization Half-life for Model River	>1 year (Estimated)	EPI	
	Volatilization Half-life for Model Lake	>1 year (Estimated)	EPI	
	Ready Biodegradability	No biodegradation was observed according to a Japanese MITI test using TBBPA (100 mg/L) in activated sludge (30 mg/L) for 2 weeks. (Measured)	CITI, 1992; CERIJ, 2006	Adequate
Soil	**Aerobic Biodegradation**	Aerobic biodegradation of TBBPA was measured in three soil types. After 64 days, the amount of ^{14}C-TBBPA in the soil ranged	Fackler, 1989b; Submitted confidential study	Adequate

Tetrabromobisphenol A			
PROPERTY/ENDPOINT	**DATA**	**REFERENCE**	**DATA QUALITY**
ECOTOXICITY			
ECOSAR Class	Phenols		
Acute Toxicity	**HIGH: The measured LC_{50} for fish, the estimated LC_{50} for daphnids and the estimated EC_{50} for green algae are all less than 1 mg/L.**		
Fish LC50	14-da LC_{50} = 0.291 mg/L (Estimated)	ECOSAR	
	Rainbow trout 96-hour LC_{50} = 0.40 mg/L (Measured)	Calmbacher, 1978	Adequate
	Bluegill sunfish 96-hour LC_{50} = 0.51 mg/L (Measured)	Calmbacher, 1978	Adequate
	Fathead minnow 96-hour LC_{50} = 0.54 mg/L (Measured)	Surprenant, 1988	Adequate
	Killifish 48-hour LC_{50} = 8.2 mg/L (Measured)	CITI, 1992	Inadequate, study details and test conditions were not available.
	Lepomis macrochirus 96-hour NOEC = 0.1 mg/L (Measured)	Simonsen et al., 2000	Inadequate, study details and test conditions were not available.
	Salmo gairdneri 96-hour NOEC = 0.18 mg/L (Measured)	Simonsen et al., 2000	Inadequate, study details and test conditions were not available.
	Pimephales promelas 96-hour NOEC = 0.26 mg/L (Measured)	Simonsen et al., 2000	Inadequate, study details and test conditions were not available.
	Oncorhynchus mykiss 96-hour LC_{50} = 1.1 mg/L (Measured)	Blankinship et al., 2003a; Submitted confidential study	Inadequate, the effect concentration is greater than 10 times the NOTOX, 2000 water solubility.

Tetrabromobisphenol A				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
Toxicokinetics		**Experimental studies indicate TBBPA, administered an in vitro dermal absorption assay, had an absorbed dose of 0.73% and dermal delivery of 1.60%. The total unabsorbed dose was 102.26% of the applied dose. When administered as an oral dose to rats, 91.7% of the dose was excreted in the feces within 72-hours, 0.3% in the urine, and 2% remained in the tissues of the small and large intestine. Over 95% of the extractable fecal ^{14}C was TBBPA. Metabolites included glucuronic acid and sulfate ester conjugates.**		
Dermal Absorption in vitro		Human split-thickness skin: Absorbed dose = 0.73% applied dose (14.06 $\mu g/cm^2$); Dermal delivery = 1.60% applied dose (32.05 $\mu g/cm^2$) (Measured)	Roper, 2005, Submitted confidential study	Adequate
Metabolism, Excretion, & Distribution	**Oral**	Oral Dosing to Rat: Fecal excretion = 91.7% of dose Urine excretion = 0.3% of dose Residue in tissue = 2% of dose (Primarily large and small intestines) Oral Dosing to Bile-duct Cannulated Rat: Fecal excretion = 26.7% of dose Biliary excretion = 71.3% of dose Residue in tissue < 1% of dose Primary metabolites: Glucuronic acid and sulfate ester conjugates. Over 95% of extractable fecal ^{14}C was parent TBBPA (Measured)	Hakk et al, 2000	Adequate
Acute Toxicity		**Low: Experimental study indicates TBBPA, administered orally to rats and mice and dermally to rabbits, does not produce substantial mortality at levels up to 50,000 and 10,000 mg/kg, respectively.**		
Acute Lethality	**Oral**	Rat oral LD50 >50,000 mg/kg (Measured)	Int. Bio-Res., 1967a	Adequate
		Rat oral LD50 >10,000 mg/kg (Measured)	Hill Top, 1966	Adequate
		Rat oral LD50 >5000 mg/kg (Measured)	Pharmakon, 1981a	Adequate

Tetrabromobisphenol A				
PROPERTY/ENDPOINT		**DATA**	**REFERENCE**	**DATA QUALITY**
		Non-sensitizing, humans (Measured)	Jessup, 1978; Submitted confidential study	Adequate
		Non-sensitizing, guinea pigs (Measured)	Pharmakon, 1981e	Adequate
		Non-sensitizing, guinea pigs (Measured)	IRDC, 1978b	Adequate
Reproductive Effects		**LOW: An experimental study indicates TBBPA, administered orally to rats, produces no adverse effects on reproductive performance or outcomes at levels up to 1000 mg/kg/day.**		
	Reproduction/ Developmental Toxicity Screen			No data
	Combined Repeated Dose with Reproduction/ Developmental Toxicity Screen			No data
	Reproduction and Fertility Effects	20-Week, 2-generation reproductive assay, rats, oral gavage, no effects on reproductive performance or outcomes, NOAEL = 1000 mg/kg/day (Measured)	MPI Research, 2002b	Adequate
Developmental Effects		**MODERATE: Nonstandard experimental studies indicate TBBPA, administered orally to mice, produces adverse hepatic effects at 140.5 mg/kg/day during gestation and 379.9 mg/kg/day during lactation.**		
	Reproduction/ Developmental Toxicity Screen			No data
	Combined Repeated Dose with Reproduction/ Developmental Toxicity Screen			No data

Lists Endocrine Disruption References

Tetrabromobisphenol A			
PROPERTY/ENDPOINT	DATA	REFERENCE	DATA QUALITY
Endocrine Disruption	Several studies were found related to endocrine disruption; however, they were not reviewed as part of this assessment. Citations for these studies are included in the reference list found at the end of this table.		

GreenBlue

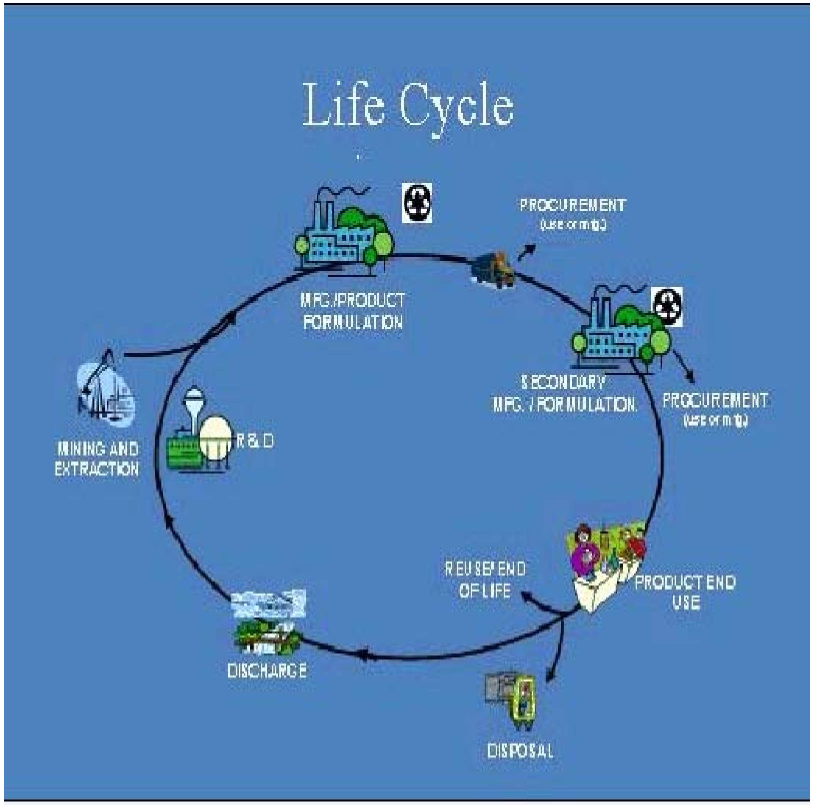
Challenge: Comparative Hazard Assessment and Life Cycle Thinking

Comparative Hazard Assessment

- Hazards associated with chemical via direct exposure such as during manufacture
- Hazards associated with chemical when reacted or added into laminate
- Hazards associated with chemical when product is combusted (landfilled, composted, littered or recycled)

Examples

- TBBPA
- Inorganic FRs, nanotech FRs



GreenBlue

Value of DfE Partnership Approach for Identifying and Promoting Less Toxic Alternative FRs

- Engages diverse stakeholders
- Provides needed information in a format that facilitates decision making (informed substitution)
- Protects confidential business information through third party review and careful design of information presentation
- Uses EPA chemical information, models and new chemicals criteria
- Focuses on hazard and not risk
- Taps into market drivers for promoting environmentally preferable products
  - DfE Formulator Program– product recognition
  - CleanGredients – ingredient review and listing

END

Life Cycle Impacts