AB289, Looking for Answers
The Case of TBPH, an “Alternative” Flame Retardant

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Department of Toxic Substances Control
California Environmental Protection Agency

Analysis and conclusions contained herein are solely those of the author and do not represent official policy of the Department of Toxic Substances Control
Large amounts of chemicals are released in California each year.

Among the many chemicals commercially available, some are known to the State of California to cause cancer, damage to the brain and the nervous, and reproductive systems. In addition, for many others there is just not enough information.

Why? There is a lot of “stuff” out there.
AB 289 (Chan)

Health and Safety Code, Chapter 699, sections 57018-57020

chemical manufacturers (*) to provide specified information regarding (but not limited to) the fate and transport of chemicals into the environment.

- analytical methods, $K_{o/w}$, BCF for humans, and other fate and transport information
- requested information within one year
- release of a trade secret

(*) = the term “manufacturers” includes persons and businesses that produce chemicals in California or import chemicals into California for sale.
What? nano, D5, TBPH

- nanomaterials
- decamethylcyclopentasiloxane
- bis(2-ethylhexyl) tetrabromo phthalate
• In California, all upholstered furniture has to meet stringent flammability standards.

• To avoid expenses most furniture sold in other states have flame retardants.

• Prior to 2006, PBDEs were the main flame retardants in furniture foam. PBDEs migrated into indoor and outdoor environments.

• Highest levels of PBDE in California homes and residents.

• Since 2006, California banned pentaBDEs and octaBDEs.

• DecaBDE mix with about 3% nonaBDE, is banned in EU, Washington and Maine.
Heavy BFR (BDE-209) appeared in shrimp and catfish. Lighter congeners (BDE-100, -99, and -47) are more common in salmon and trout

van Leeuwen, Inst. Env. Studies,
Vrije Universiteit Amsterdam

PBDE concentrations in three Fords ranged from 126 to 2644 pg/m$^3$.

Stuart Harrad,
University of Birmingham, UK

elevated concentrations of PBDEs in house dust correlate with hormonal alterations associated with male infertility and performance impairments.

John Meeker, Dept. Env. Health Sc. , Univ. of Michigan

Why? “Old” BRF are everywhere
Fire Retardants in Toddlers and Their Mothers

Levels Three Times Higher in Toddlers Than Moms

Published on Environmental Working Group (http://www.ewg.org)

Published September 4, 2008
Researchers in China have detected DBDPE in red pandas, as well as giant pandas and five species of waterbirds.

Jiayin Dai, Inst. of Zoology
Chinese Academy of Sciences

Herring gull eggs from some portions of Lakes Michigan and Huron had the highest concentrations of DBDPE.

Craig Herbert, Environment Canada

Why? “New” BRF are everywhere
PBDE in mussels, NOAA April 2009

Legend:
- Colored dots indicate 2004-2007 mean tissue concentrations (ppb lipid weight):
  - 0
  - 1 - 270
  - 271 - 8202
  - Sediment or 1996 tissue data only
to provide the highest level of safety, and to protect public health and the environment from toxic harm
global leaders in environmental excellence, using **sound science**, promoting green technology and seeking continuous improvement, for a **healthy, sustainable and prosperous California**
TBPH
bis(2-ethylhexyl) tetrabromo phthalate

- flame retardant in polyurethane foam, electrical insulation, and other products.
- in house dust, possibly from furniture, electronics, and other consumer items within the home.

Other flame retardants may be added later
**Other Names:** Tetrabromophthalate Ester, DP-45™

**CAS Registry:** 26040-51-7

**Product Overview**

DP-45™ is a brominated liquid flame retardant plasticizer for polyvinylchloride adhesives, coatings and elastomers including SBR, Neoprene and EPDM. DP-45 is especially recommended as a **flame retardant plasticizer** for PVC applications such as wire and cable insulation, coated fabrics, film and sheeting. It is proven to be extremely effective in PVC jacketing for wire and cable meeting the plenum (UL910) standards. It can be used alone or, where allowed, in combination with antimony trioxide.
What are the fire retardant chemicals used in the foam?

The fire retardant in this foam is Firemaster 550 which meets California standards and is PBDE free.
DTSC *looks forward* to working with the manufacturers and end users of TBPH, and other interested parties to identify

- available information;
- potential data gaps;
- information in publicly available government databases;
- other specific information from manufacturers, academic researchers, or other sources that may address potential data gaps;
- information on other manufacturers who may not be aware of this *call-in*; and
- new information that may be required to ensure these chemicals can be used safely.
Characterization of the Brominated Chemicals in a PentaBDE Replacement Mixture and their Detection in Biosolids Collected from Two San Francisco Bay Area Wastewater Treatment Plants

Susan Klosterhaus,1 Alex Konstantinov,1 and Heather Stapleton3
1 San Francisco Estuary Institute, Oakland, CA, USA
2 Wellington Laboratories, Guelph, Ontario, Canada
3 Duke University, Nicholas School of the Environment & Earth Sciences, Durham, NC, USA

Alternate and New Brominated Flame Retardants Detected in U.S. House Dust

Heather M. Stapleton,* Joseph G. Allen,* Shannan M. Kelly,* Alex Konstantinov,* Susan Klosterhaus,* Deborah Watkins,* Michael D. McClean, and Thomas F. Webster*
Nicholas School of the Environment & Earth Sciences, Duke University, Durham, North Carolina, Department of Environmental Health, Boston University School of Public Health, Boston, Massachusetts, Environmental Health & Engineering, Inc., Needham, Massachusetts, Wellington Laboratories Inc., Guelph, Ontario, Canada, and San Francisco Estuary Institute, Oakland, California

Received April 17, 2008. Revised manuscript received June 11, 2008. Accepted June 12, 2008.

Why TBPH is out there
DTSC looks forward to working with the manufacturers and end users of TBPH, and other interested parties to identify

(i) available information on these chemicals;

(ii) potential data gaps;

(iii) specific information in publicly available government databases that addresses potential data gaps;

(iv) other specific information from manufacturers, academic researchers, or other sources that may address potential data gaps;

(v) information on other manufacturers who may not be aware of this call-in; and

(vi) new information that may be required to ensure these chemicals can be used safely.
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Introduction
Over the past decade there has been a large focus on the prevalence and fate of the brominated flame retardant chemicals known collectively as polybrominated diphenyl ethers (PBDEs). Historically these chemicals have been used in high volumes to reduce the flammability of numerous types of polymers and resins commonly found in furniture and electronic components. However, many studies have now reported on their ubiquitous presence in the environment (1–3), their accumulation in human tissues (4–6), and their potential toxicity (7–9). For these reasons, two of the three commercial PBDE mixtures, PentaBDE and OctaBDE, have been voluntarily withdrawn or banned from use in some parts of the world. The third and last commercial mixture, DecaBDE, is the subject of ongoing and controversial debate as to whether it should also be banned. DecaBDE is an example of the shift in flame retardants from brominated to halogenated flame retardants as one of the most commonly used commercial flame retardants. Recently, cadmium and lead have been found in high concentrations in some cases, raising significant health concerns. Additionally, other brominated flame retardants have been identified in many countries that have banned PBDEs due to their higher toxicity or their ability to bioaccumulate. These include Hexabromocyclododecane (HBCD), a brominated cyclic hydrocarbon flame retardant with the chemical formula C12H12Br6. The basis for this study is to determine the prevalence and fate of brominated flame retardants in U.S. house dust.
High Production Volume (HPV) Challenge Program

Test Plan

For

PHTHALIC ACID TETRABROMO BIS 2-ETHYLHEXYL ESTER
(CAS# 26040-51-7)

Prepared for:

Brominated Phthalate Ester Panel (BR PEP)
American Chemistry Council
1300 Wilson Blvd
Arlington, VA 22209

Prepared by:

Health & Environmental Horizons, Ltd.
2851 South Haven Road
Annapolis, MD 21401

Date

July 1, 2004
High Production Volume (HPV) Challenge Program

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Date

July 1, 2004
What we know

US EPA - HPV

AB289, Looking for Answers: TBPH

Not so fast ...

We have all we need!
2.0 EVALUATION OF EXISTING DATA FOR PHTHALIC ACID TETRABROMO ESTER:

The available data for phthalic acid tetrabromo bis 2-ethylhexyl ester have been evaluated in accordance with the guidance developed by EPA and have been prepared as robust summaries. Most of the data were generated using chemically pure phthalic acid tetrabromo ester (e.g. >95%). Robust summaries of these files are appended.

PHYSICAL and CHEMICAL PROPERTIES:

Melting Point

The melting point has been determined to be 229.19 degrees C (mean or weighted MP; derived from MPBPWIN v1.40).

Acceptable scientific information is available; no additional testing is proposed.

Boiling Point

The boiling point has been determined to be 539.75 degrees C (adapted Stein & Brown method; derived from MPBPWIN v1.40).

Acceptable scientific information is available; no additional testing is proposed.

Vapor Pressure

The vapor pressure is 1.71E-011 mmHg @ 25 degrees C (modified Grain method; derived from MPBPWIN v.1.40).

Acceptable scientific information is available; no additional testing is proposed.

Partition Coefficient

The octanol/water partition coefficient is 11.95 Log Kow (KOWWIN v1.66 estimate).

Acceptable scientific information is available; no additional testing is proposed.
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MATERIAL SAFETY DATA SHEET

1. CHEMICAL PRODUCT AND COMPANY IDENTIFICATION

Product Name: Uniplex FRP-45
Synonyms: Di-2-ethylhexyl tetrabromo phthalate

MANUFACTURER: Unitex Chemical Corporation
520 Broome Road
P.O. Box 16344
Greensboro, NC 27406

2. COMPOSITION/INFORMATION ON INGREDIENTS

<table>
<thead>
<tr>
<th>Components</th>
<th>% (optional)</th>
<th>OSHA PEL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Di-2-ethylhexyl tetrabromo phthalate</td>
<td>&gt; 99.5%</td>
<td>Not</td>
</tr>
</tbody>
</table>

3. PHYSICAL AND CHEMICAL PROPERTIES

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vapor Pressure</td>
<td>&lt; 0.001 mHg @ 25°C</td>
</tr>
<tr>
<td>Specific Gravity</td>
<td>1.5</td>
</tr>
<tr>
<td>Solubility in Water</td>
<td>Insoluble</td>
</tr>
<tr>
<td>pH</td>
<td>8 - 10</td>
</tr>
<tr>
<td>Boiling Point</td>
<td>&gt; 400°C</td>
</tr>
<tr>
<td>Viscosity</td>
<td>ND</td>
</tr>
<tr>
<td>Physical State</td>
<td>Liquid</td>
</tr>
</tbody>
</table>

8. EXPOSURE CONTROL/PERSONAL PROTECTION

Engineering Controls: Local exhaust ventilation recommended.

Personal Protection: Chemical splash-proof goggles, with rubber, PVC, or plastic gloves.

Respirator: None required under normal conditions of use. NIOSH/MSHA-approved organic vapor cartridge respirator can be used.

Protective Clothing: Standard work clothing and work shoes/boots.
BCF Estimate from LogKow [BCFWIN v2.14]

Log BCF = 0.500 (BCF = 3.162)

Log Kow used: 11.95 (estimated)

Philip H. Howard, William Meylan,
Dallas Aronson, & Sarah Stewart
Syracuse Research Corporation
Bioaccumulation Database Workshop
November 11, 2005
<table>
<thead>
<tr>
<th>ECOSAR Class</th>
<th>Organism</th>
<th>Duration</th>
<th>End Pt</th>
<th>Predicted mg/L (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neutral Organic SAR</td>
<td>Fish</td>
<td>14-day</td>
<td>LC50</td>
<td>2.04e-006 *</td>
</tr>
<tr>
<td>(Baseline Toxicity)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Esters</td>
<td>Fish</td>
<td>96-hr</td>
<td>LC50</td>
<td>0.000508 *</td>
</tr>
<tr>
<td>Esters</td>
<td>Daphnid</td>
<td>48-hr</td>
<td>LC50</td>
<td>4.95e-007 *</td>
</tr>
<tr>
<td>Esters</td>
<td>Green Algae</td>
<td>96-hr</td>
<td>EC50</td>
<td>5.83e-005 *</td>
</tr>
<tr>
<td>Esters</td>
<td>Green Algae</td>
<td></td>
<td>ChV</td>
<td>5.55e-005 *</td>
</tr>
<tr>
<td>Esters</td>
<td>Fish</td>
<td></td>
<td>ChV</td>
<td>2.37e-007 *</td>
</tr>
</tbody>
</table>

Note: * = asterick designates: Chemical may not be soluble enough to measure this predicted effect.

- Fish and daphnid acute toxicity: log Kow cutoff: 5.0
- Green algal EC50 toxicity: log Kow cutoff: 6.4
- Chronic toxicity: log Kow cutoff: 8.0
- MW cutoff: 1000

Log Kow: 11.95 (KowWin estimate)
SUMMARY FACT SHEET

PBT WORKING GROUP – PBT LIST NO. 116

TC NES SUBGROUP ON IDENTIFICATION OF PBT AND VPVP SUBSTANCES

RESULTS OF THE EVALUATION OF THE PBT/VPVB PROPERTIES OF:

Substance name: Phthalic acid, tetrabromo, bis(2-ethylhexyl) ester
EC number: 247-426-5
CAS number: 26040-51-7
Molecular formula: C_{24}H_{34}Br_4O_4
Structural formula:

![Structural formula image]

**Status:** Deferred (Low Production Volume chemical)

**Summary of the evaluation:**
In the course of discussion, the PBT Expert Working Group of the Technical Committee of New and Existing Chemicals has deferred the decision on the substance from the list of potential PBT or vPvB substances.
Summary of the evaluation:

According to Annex I to Directive 67/548/EEC, bis(2-ethylhexyl)phthalate (DEHP) is classified as toxic to reproduction, Repr. Cat. 2; R60-61 (May impair fertility; May cause harm to the unborn child).
The Safe Drinking Water and Toxic Enforcement Act of 1986 requires that the Governor revise and republish at least once per year the list of chemicals known to the State to cause cancer or reproductive toxicity. The identification number indicated in the following list is the Chemical Abstracts Service (CAS) Registry Number. No CAS number is given when several substances are presented as a single listing. The date refers to the initial appearance of the chemical on the list. For easy reference, chemicals which are shown underlined are newly added. Chemicals or endpoints shown in strikeout were placed on the Proposition 65 list on the date noted, and have subsequently been removed.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Type of Toxicity</th>
<th>CAS No.</th>
<th>Date Listed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Di(2-ethylhexyl)phthalate (DEHP)</td>
<td>cancer, developmental, male</td>
<td>117-81-7</td>
<td>January 1, 1988 October 24, 2003</td>
</tr>
</tbody>
</table>
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AB289, Looking for Questions
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The Case of TBPH, an “Alternative” Flame Retardant

Donald Rumsfeld 02/12/02, Department of Defense news briefing

As we know,

There are known knowns.

There are things we know we know.

We also know that there are known unknowns.

That is to say we know there are some things we do not know.

But there are also unknown unknowns, the ones we don't know we don't know.

AB289 data gaps?
AB289, Looking for Questions
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Donald Rumsfeld 02/12/02, Department of Defense news briefing

As we know,

There are known knowns.

There are things we know we know.

TBPH is found in the environment and in house dust
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Donald Rumsfeld 02/12/02, Department of Defense news briefing

We also know that there are known unknowns.

That is to say we know there are some things we do not know.

chemico-physical properties
environmental fate & transport
degradation/metabolic pathways
long-term health effects (e.g., endocrine disruption, cancer)
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Donald Rumsfeld 02/12/02, Department of Defense news briefing

But there are also unknown unknowns, the ones we don't know we don't know.

Any suggestion?
AB289, Looking for Questions

The Case of TBPH, an “Alternative” Flame Retardant

Jeff Wong
Bill Ryan
Bruce LaBelle
Myrto Petreas
Marty Snider

Thank you!

AB289 Team