

AB289, Looking for Answers

The Case of TBPH, an “Alternative” Flame Retardant

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Human and Ecological Risk Division

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

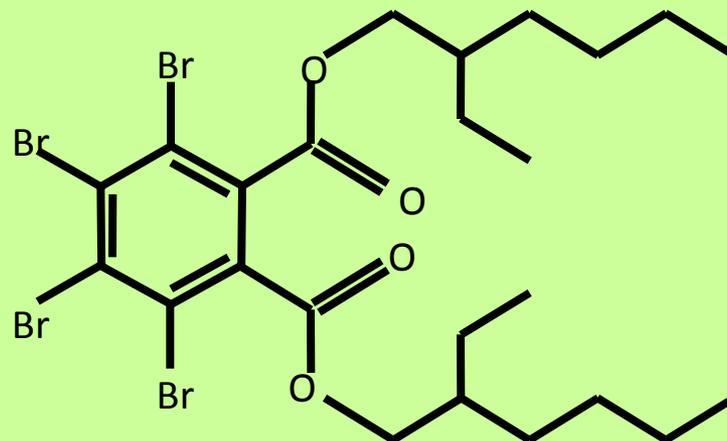
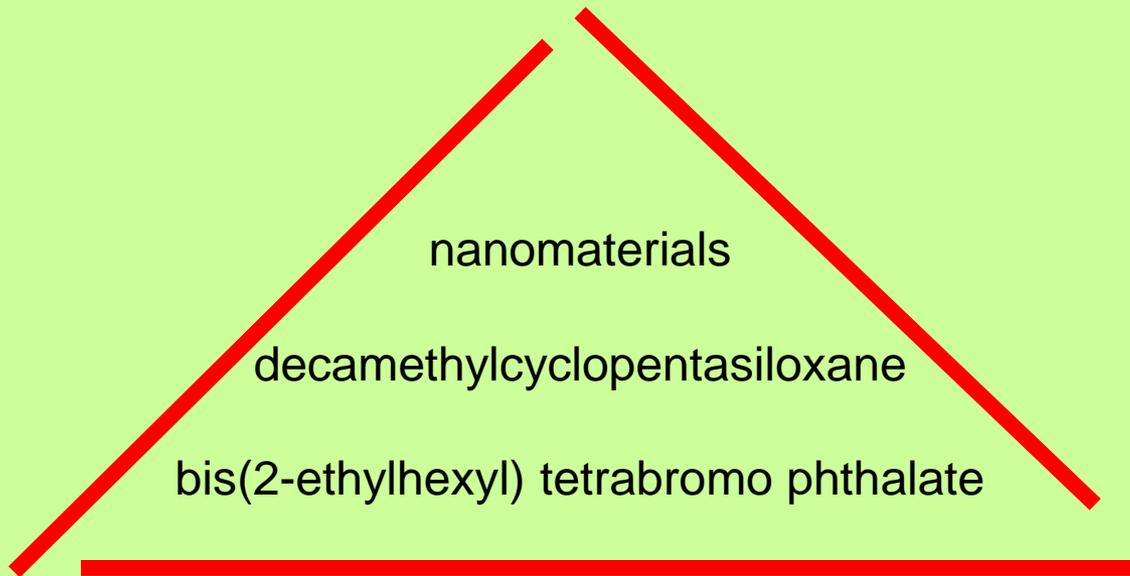
chemical **manufacturers**^(*) to provide specified information regarding (*but not limited to*) the fate and transport of chemicals into the environment.

- 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.*

Why?

It is the law



What? nano, D5, TBPH

- 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/m³.
*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



THE POWER OF INFORMATION

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

Fire Retardants in Toddlers and Their Mothers

Levels Three Times Higher in Toddlers Than Moms

Published September 4, 2008

Why? Our children

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*

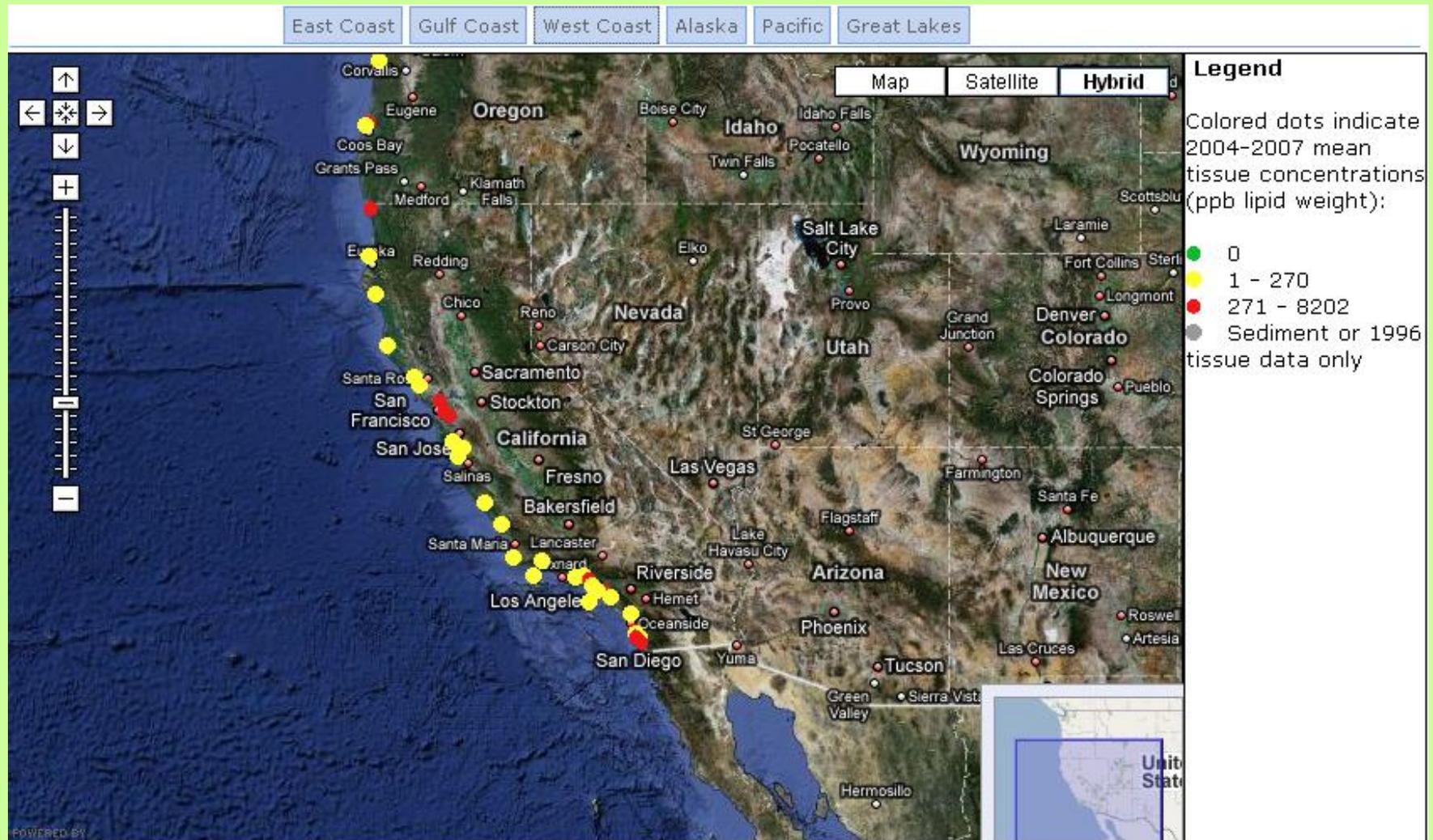
Environ. Sci. Technol., **2009**, 43 (2), 236-237

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



AB289, Looking for Answers: TBPH

to provide the highest level of safety, and to protect public health and the environment from toxic harm

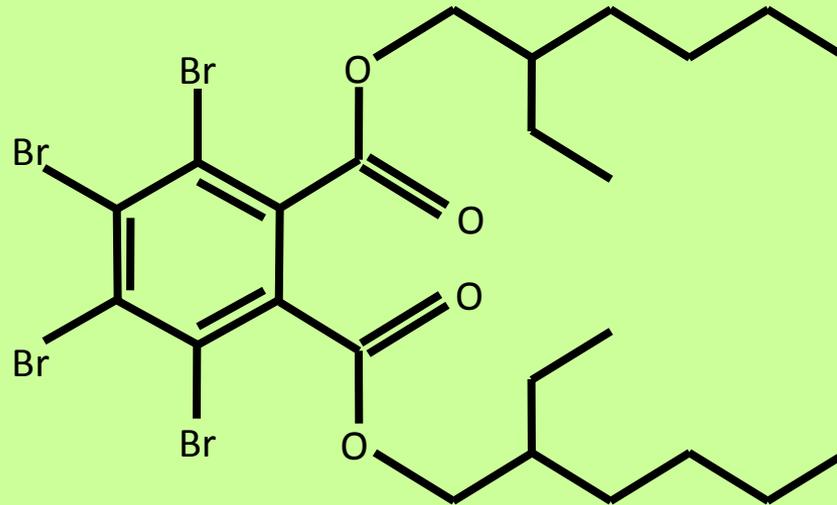
global leaders in environmental excellence, using **sound science**, promoting green technology and seeking continuous improvement, for a **healthy, sustainable and prosperous California**

Why?

Protect human health and the environment

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

What? TBPH

TBPH

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.

Where? TBPH

TBPH

A screenshot of a website header with an orange background. On the left, a circular badge contains the text "safe", "easy", and "soft". In the center, there is a blue rectangular box followed by ".com". On the right, there is a cartoon bee character sitting on a cloud. Below the header, a light blue bar contains the text "bed bug bumper" and "faq".



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.

Where? TBPH

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.

How? Call-in



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 Klosterhaus¹, Alex Konstantinov², 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

Environ. Sci. Technol. 2008, 42, 8910-8916

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

HEATHER M. STAPLETON,^{*,†}
JOSEPH G. ALLEN,^{‡,§}
SHANNON 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.

transport within the home. Analysis of paired dust samples collected from different rooms in the same home suggests HBCD, TBB, and TBPH are higher in dust from the main living area compared to dust collected in bedrooms; however, BTBPE and DBOPE levels were comparable between rooms. This study highlights the fact that numerous types of brominated flame retardants are present in indoor environments, raising questions about exposure to mixtures of these contaminants.

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,

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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.

Is it safe? available information



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Information sources

literature



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

04 AUG -5 PM 1:38

RECEIVED
HPV CHALLENGE



Great Lakes Chemical Corporation

PA

Business Unit or Division: Polymer Additives
One Great Lakes Boulevard, P.O. Box 2200, West Lafayette, IN 47996-2200

Document Type: **Technical Information**

Product Name: **Great Lakes Firemaster® BZ-54**



Great Lakes
POLYMER ADDITIVES

Technical Information

Firemaster® 550
Phosphorus-Bromine Flame Retardant
Firemaster 550 is a low viscosity liquid flame retardant for polyurethane foams and other applications, which require a liquid product. Firemaster 550's high efficiency as a flame retardant is a result of phosphorus-bromine synergy. It is based on proprietary Great Lakes technology and does not contain brominated diphenyl ethers.

Page: 1 of 4
Issue Date: 6/13/00
Supersedes: 3/5/01
MSDS No.:



MATERIAL SAFETY DATA SHEET

1. CHEMICAL PRODUCT AND COMPANY IDENTIFICATION

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

MANUFACTURER:	EMERGENCY TELEPHONE NUMBERS:
Unitex Chemical Corporation 520 Broome Road P.O. Box 16344 Greensboro, NC 27406	Emergency Telephone Number: CHEMTREC 1 (800) 424-9300 International 1 (703) 527-3887 Telephone Number for Information: (336) 378-0965 (Monday - Friday 8:00 a.m. - 5:00 p.m.)



Great Lakes Chemical Corporation

MATERIAL SAFETY DATA SHEET

MSDS Number: 01688
Product Name: **Pyronil® 45**

Effective Date: 05/21/2004
Page: 1 of 6

SECTION I - CHEMICAL PRODUCT AND COMPANY IDENTIFICATION

Product Name: Pyronil® 45
Manufacturer: Great Lakes Chemical Corporation
Address: P.O. Box 2200 City: West Lafayette



MATERIAL SAFETY DATA SHEET

MSDS Number: 00896
Product Name: **FIREMASTER® 550**

Effective Date: 06/20/2006
Page: 1 of 8



MATERIAL SAFETY DATA SHEET

PYRONIL® 45 FLAME RETARDANT

Page 1
Printed: 6/14/04

PRODUCT IDENTIFICATION AND USE

MANUFACTURER: ATOFINA CANADA INC.

High Production Volume (HPV) Challenge Program

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2-ETHYLHEXYL ESTER
(CAS# 26040-51-7)**

Prepared for:

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American Chemistry Council
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Arlington, VA 22209**

Prepared by:

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

Date

July 1, 2004

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RECEIVED
HPV PEP

TABLE 1: HPV SIDS DATA REQUIREMENTS/CRITICAL STUDIES: Phthalic Acid Tetrabromo Ester (CAS #26040-51-7)

HPV Data Category	Test Endpoint	Data Available	Data Acceptable	Data to be Generated	
Physical and Chemical Properties	Melting Point	Yes ¹	Yes	No	
	Boiling Point	Yes ¹	Yes	No	
	Vapor Pressure	Yes ¹	Yes	No	
	Partition Coefficient	Yes ¹	Yes	No	
	Water Solubility	Yes ²	Yes	No	
Environmental Fate and Pathways	Photodegradation	No		No	
	Stability in Water	Yes ²	Yes	No	
	Biodegradation	Yes	Yes	No	
	Transport/Distribution	Yes ¹	Yes	No	
Ecotoxicity	Acute toxicity to fish	Yes ³	Waiver	No	
	Acute toxicity to aquatic invertebrates	Yes	Yes	No	
	Toxicity to Aquatic Plants	No ⁴	Waiver	No	
	Chronic aquatic invertebrate test	NR ⁵	NR	No	
	Terrestrial toxicity	NR ⁵	NR	No	
Human Health Effects	Acute toxicity	Yes	Yes	No	
	Repeated Dose	Yes	Yes	No	
	Genetic Toxicity	Gene Mut.	Yes	Yes	No
		Chrom. Ab	Yes	Yes	No
	Reproductive Toxicity	Yes ⁶	Yes	No	
	Developmental Toxicity	No ⁷	Waiver	No	

We have all we need !

Not so fast ...

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 v1.40**).

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

Partition Coefficient

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

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

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Synonyms: **Di-2-ethylhexyl tetrabromo phthalate**

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International 1 (703) 527-3887
Telephone Number for Information:
(336) 378-0965 (Monday - Friday 8:00 a.m. - 5:00 p.m.)

2. COMPOSITION/INFORMATION ON INGREDIENTS

Components	% (optional)	OSHA PEL
Di-2-ethylhexyl tetrabromo phthalate	> 99.5%	Not

Product Name: Uniplex FRP-45

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.

9. PHYSICAL AND CHEMICAL PROPERTIES

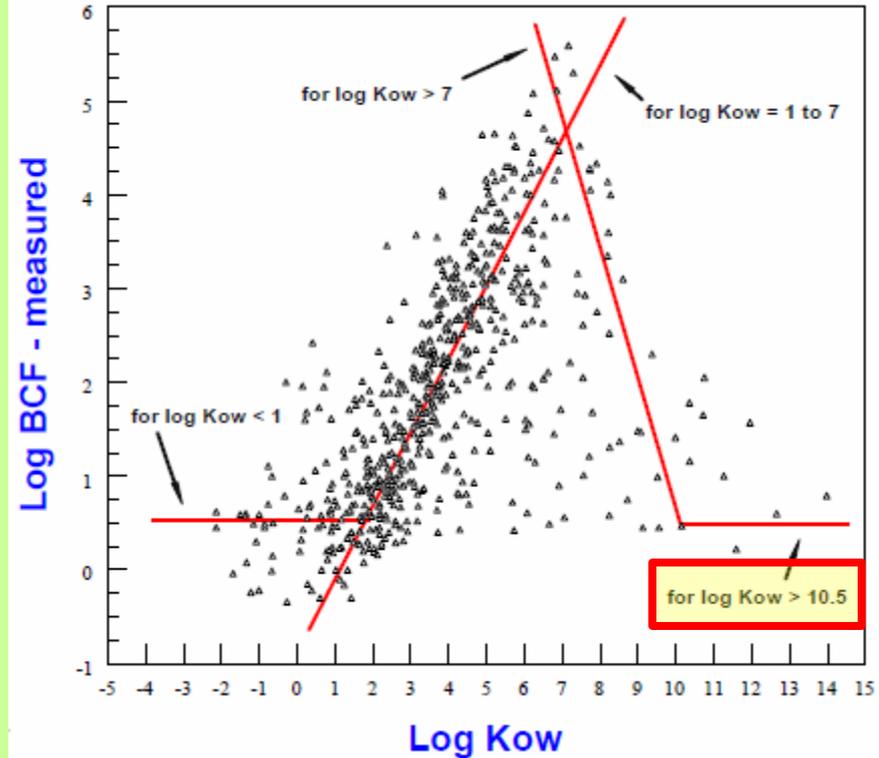
Vapor Pressure	: < 0.001 mHg @ 25°C	Vapor Density (Air = 1):	ND
Specific Gravity	: 1.5	Evaporation Rate	: < 1
Solubility in Water	: Insoluble	Freezing Point	: Approximately - 20°C
pH	: 8 - 10	Odor	: Characteristic
Boiling Point	: > 400°C	Appearance	: Clear, yellow liquid
Viscosity	: ND	Physical State	: Liquid

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



What we know US EPA - HPV

ECOSAR Class	Organism	Duration	End Pt	Predicted mg/L (ppm)
Neutral Organic SAR (Baseline Toxicity)	: Fish	14-day	LC50	2.04e-006 *
Esters	: Fish	96-hr	LC50	0.000508 *
Esters	: Daphnid	48-hr	LC50	4.95e-007 *
Esters	: Green Algae	96-hr	EC50	5.83e-005 *
Esters	: Green Algae		ChV	5.55e-005 *
Esters	: Fish		ChV	2.37e-007 *

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)

What we know US EPA - HPV

TC NES SUBGROUP ON IDENTIFICATION OF PBT AND VPVP SUBSTANCES

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

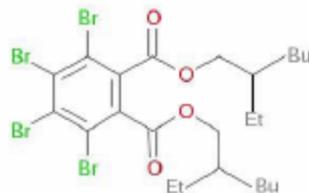
Substance name: Phthalic acid, tetrabromo, bis(2-ethylhexyl) ester

EC number: 247-426-5

CAS number: 26040-51-7

Molecular formula: C₂₄H₃₄Br₄O₄

Structural formula:



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.

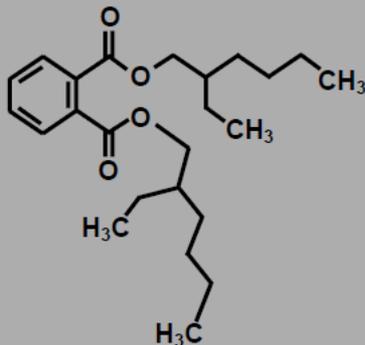
European Union deferred decision

European Union Risk Assessment Report

CAS No: 117-81-7

EINECS No: 204-211-0

bis(2-ethylhexyl)phthalate (DEHP)



2nd Priority List

Volume: 80



EUR 23384 EN

Summary of the evaluation:

According to Annex I to Directive 67/548/EEC, bis(2-ethylhexyl)phthalate (DEHP) is classified as substance **toxic to reproduction** Repr. Cat. 2; R60-61 (May impair fertility; May cause harm to the unborn child).

European Union DEHP (the non-brominated analog of TBPH)

STATE OF CALIFORNIA
ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF ENVIRONMENTAL HEALTH HAZARD ASSESSMENT
SAFE DRINKING WATER AND TOXIC ENFORCEMENT ACT OF 1986

CHEMICALS KNOWN TO THE STATE TO CAUSE CANCER OR REPRODUCTIVE TOXICITY
DECEMBER 19, 2008

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.

Chemical	Type of Toxicity	CAS No.	Date Listed
Di(2-ethylhexyl)phthalate (DEHP)	cancer developmental, male	117-81-7	January 1, 1988 October 24, 2003

California

DEHP (the non-brominated analog of TBPH)

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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.

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

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.

TBPH is found in the environment and in house dust

AB289 data gaps ?

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

We also know that there are known unknowns.

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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

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Any suggestion ?

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Jeff Wong

Bill Ryan

Bruce LaBelle

Myrto Petreas

Marty Snider

Thank you !

AB289 Team