Decabromodiphenyl Ether

An Industry Overview

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House Environmental Committee
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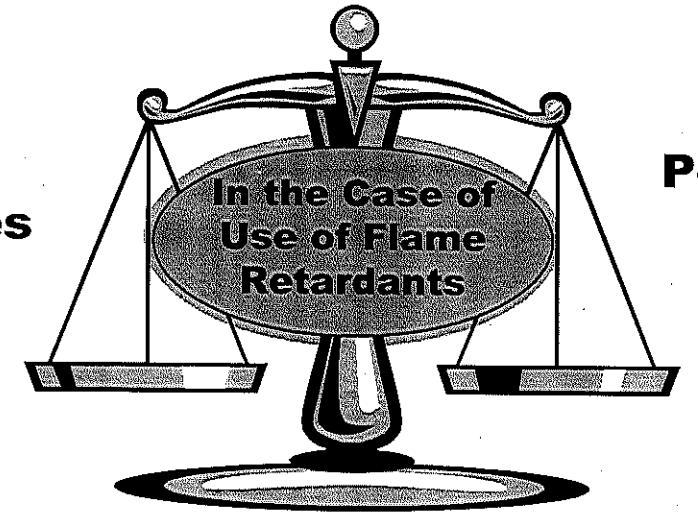
Flame Retardants?

Balancing Public Safety

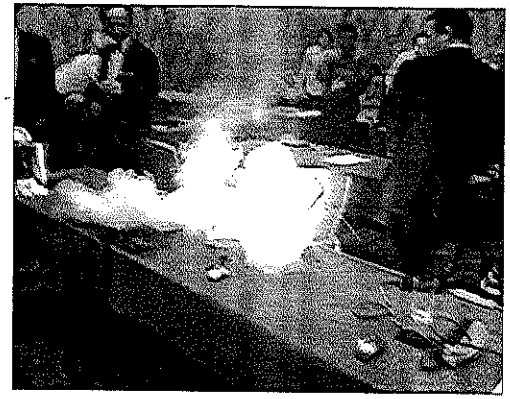
Risk and Consequences of Fire



Potential or Perceived Human Harm or Environmental Damage

Risk must be **assessed and balanced**

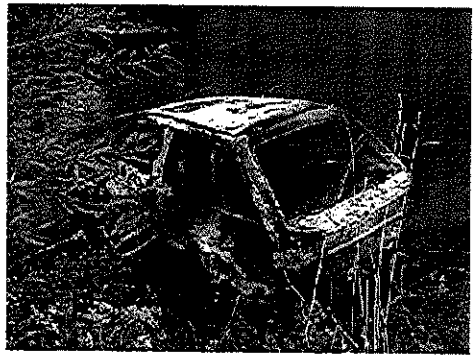
Flame Retardants are Important To Society



Computer which spontaneously caught fire during a conference in Japan

House Fire

Air France Crash



Fire following an accident

Foam Factory Fire 2007

Bus fire in London

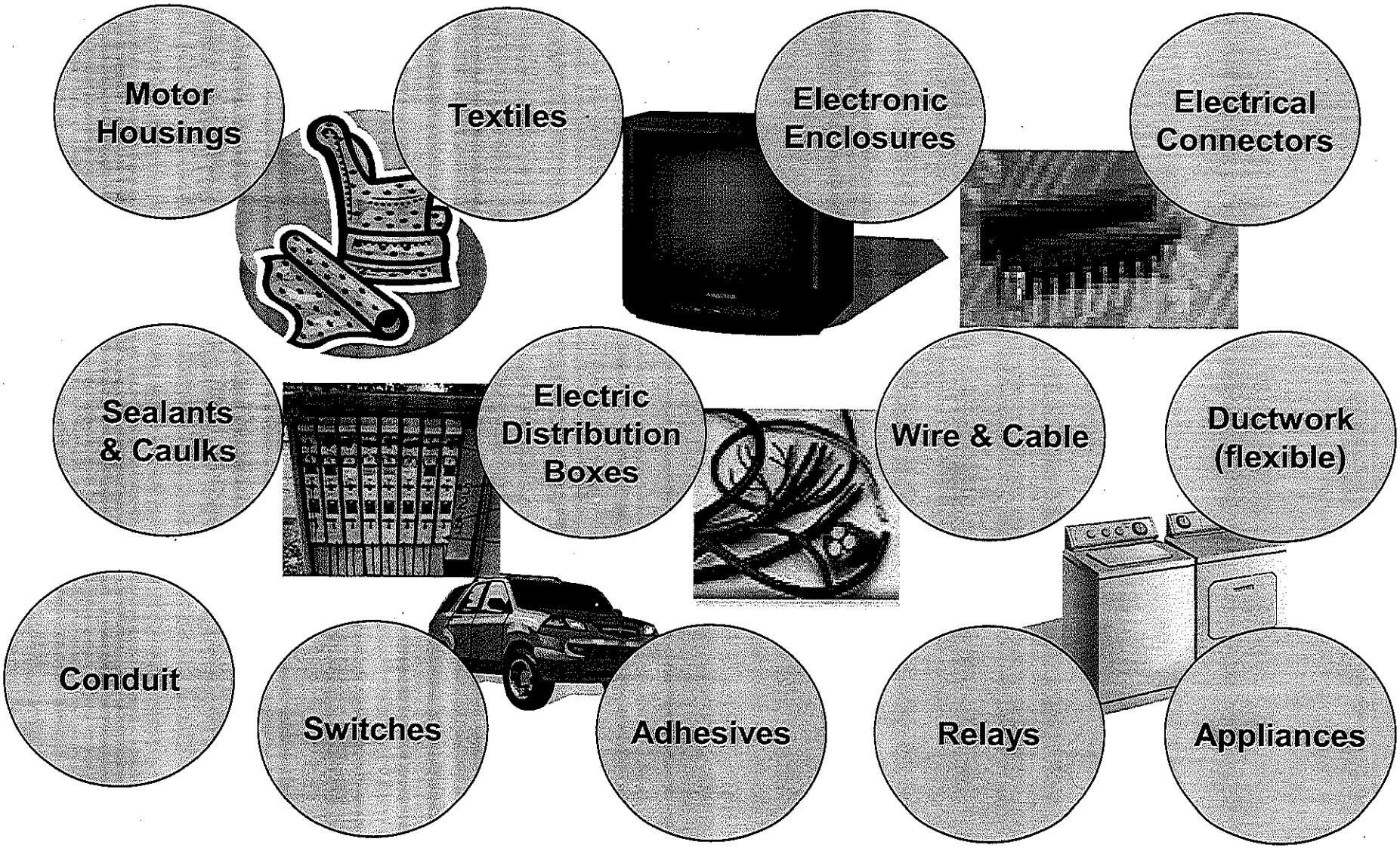
•Extract from a Dutch TV documentary, RTL 5, 2000

Why Use Flame Retardants?

- The use of flame retardants in plastics and textiles improves fire safety
  - Lives are saved
  - Injuries are reduced
  - Economic loss reduced
  - Reduction of immediate local pollution
    - Less fires ➔ less toxic gases ➔ reduced toxic emissions
    - The US National Bureau of Standards (NIST) tested a range of flame retardant (FR) containing and non FR containing products :
      - Total quantities of **toxic gases** released by flame retardant products 1/3 lower than for non-flame retardant products
      - **Smoke** production not significantly different
      - Total **carbon monoxide** (CO) emissions ~1/2 as low for flame retardant products

NIST 1988, "Fire-hazard comparison of fire retarded and non fire retarded products" (TV, PC, upholstered chair, cable, circuit board) http://fire.nist.gov/bfrlpubs/fire88/art003.html

Deca-BDE is Applicable to a Wide Variety of End Uses



The PBDE Family

- Decabromodiphenyl ether (Deca) is a member of the class of chemicals known as polybrominateddiphenyl ethers (PBDEs).
- There are 209 distinct chemical congeners in the PBDE family depending on the number and position of bromine atoms on the diphenyl ether skeleton.

The PBDE Family

- These congeners are identified as BDE-1 through to BDE-209.
- For example
  - BDE-47 is a tetrabrominated diphenyl ether
  - BDE-99 is a pentabrominated diphenyl ether
  - BDE-153 is a hexabrominated diphenyl ether
  - BDE-209 is the decabrominated diphenyl ether

Commercial products

- Historically there have been three distinct commercial flame retardants based on PBDEs:
  - Penta
  - Octa
  - Deca

Commercial products

- These three products are quite different in their properties and applications.
- Given these differences it is appropriate to evaluate each commercial product on its own merits.
- There is sufficient data on each commercial product to allow individual assessments of their impact on human health and the environment.
- Each has undergone extensive risk assessment particularly in the European Union.

Commercial Penta

- **Commercial production ceased in December 2004**
  - Penta was banned from use in Europe in August, 2004.
  - Several US States have also implemented bans.
- Commercial Penta is a viscous liquid.
- It is a complex mixture of BDE congeners.
- The major components of the mixture are BDE-47, BDE-99, BDE-100,BDE-153, and BDE-154.
- Its major application was in flame retarding polyurethane flexible foam.

Commercial Octa

- **Commercial production ceased in December 2004**
  - Octa was banned from use in Europe in August, 2004.
  - Several US States have also implemented bans.
- Commercial Octa is a white solid.
- It is a complex mixture of BDE congeners.
- The major components of the mixture are BDE-153, BDE-183, BDE-197, and BDE-207
- Its major application was in flame retarding ABS plastic found in automotive and electronic applications.

Commercial Deca

- **Many jurisdictions have evaluated Deca:**
  - The European Union recently published its risk assessment that identified no reasons to limit its use.
  - Canada believes its continued use is acceptable under a risk management program.
  - Over the past few years a total of 60 bills has been introduced at state level aimed at limiting the use of Deca. Only two have passed – Washington and Maine, and these states still allow use in many applications.

Commercial Deca

- Commercial Deca is a white solid.
- It is a relatively pure product made up of > 97% BDE 209 with minor quantities of lower brominated congeners.
- Its major use is flame retarding HIPS plastic used in electronics. But, due to its efficiency and associated economics it finds wide use across many applications.
- Deca has undergone more studies and evaluations than any other flame retardant.

European Risk Assessment

- The most extensive evaluation of commercial Deca has been carried out in the EU.
- The assessment has extended over more than 12 years.
- Hundreds of scientific papers have been reviewed, and numerous first intent studies initiated with the guidance of technical experts representing member states.
- The risk assessment is thoroughly up to date – annual reviews of new data.

European Risk Assessment

- Consensus from member state experts is that there is no justification for limiting the use of Deca in its current applications.
- A number of studies are in progress at the request of the European authorities to address some areas of concern:
  - Environmental Monitoring study
  - Human bio-monitoring study
  - Developmental neurotoxicity study

Deca and the RoHS Directive

- On April 1, 2008, the European Court of Justice annulled the exemption that allowed use of Deca in electrical equipment.
- The annulment was based on procedural grounds and did not question the validity of the risk assessment.
- The court decision requires the Commission to reconsider the status of Deca under RoHS. We anticipate this will be done as part of the RoHS revision process to start soon.

Federal EPA

- Federal EPA has seen no reason to limit the use of Deca in current applications
- A plan for regular review of Deca is in place
- An enforceable consent agreement is in place to develop additional data:
  - Anaerobic Degradation
  - Photolysis in the indoor environment
- A recent IRIS review has recommended a new reference dose of 0.007 mg/kg/day
  - Reference dose is the estimated level of exposure that a person can have everyday of their lives with no ill effects to be expected.

Issues – Exposure to Deca

- There have been many reports of analyses showing levels of PBDEs in the environment, biota or humans.
- Detection in and of itself is not indicative of risk
  - Risk = f (exposure, hazard)
- Reference dose is a measure of hazard, and we can use this to estimate whether daily exposure to the levels detected give rise to an unacceptable risk

Exposure to Deca – a breast fed baby

- Even at the highest levels of Deca reported found in breast milk, a baby would have to digest many times its own weight of milk each day to approach the reference dose.
  - For example, based on the highest level found by Schechter (8.2 ng/g lipid) a 3 kg. Baby would have to digest more than 13 gallons of milk each and every day.

House Dust

- Often cited as a major source of exposure to DecaBDE
- Calculated exposures based on the highest reported levels of DecaBDE in house dust in the U.S. by Sjodin et al. (2008):
  - Adult: 31 ng/kg/d
  - Children: 140 ng/kg/d
- Calculated exposures by Goodman et al. (2008):
  - Adult: 0.26-7 ng/kg/d
  - Children: 2.3 to 57 ng/kg-day
- Calculated exposures versus U.S. EPA's Reference Dose of 0.007 mg/kg-d
  - 7,000 ng/kg/d
  - Calculated exposures far below that of Reference Dose
- Reference dose defined as amount all groups, including children, could be exposed to daily for a lifetime with the expectation of no adverse effects

Exposure to Deca in the Diet

- Based on reported Deca levels found in food, a child or adult could eat many times his or her own body weight each day without any appreciable risk of deleterious effects from Deca exposure during a life time.
  - For example, based on the highest levels detected by Schechter in fish, a 100 kg man would need to eat over half a tonne of fish each day to reach the reference dose.

The PBDE pattern

- Many reports of PBDE levels in fat tissues and human milk show the same pattern.
- There are high levels of tetra-, penta-, and hexa-brominated species. In particular BDE-47, BDE-99, BDE-100, BDE-153, BDE-154 – the so called congeners of concern.
- This pattern is very similar to the congener distribution in the commercial Penta product
- The commercial Octa product also contains a significant proportion of the hexa-brominated congeners
- Deca contains vanishingly small quantities of these congeners.

Debromination of Deca

- Under laboratory conditions Deca will debrominate under exposure to UV light in the presence of a hydrogen donating solvent.
- But, to what extent can Deca debrominate in the environment to contribute to these congeners of concern?
- The real world is very different to required lab. conditions

Debromination of Deca in the real world

- It is estimated that 97% of Deca released into the environment goes to sediment. This material is not exposed to UV light
- Experiments following debromination where Deca is exposed to UV light in the real world have not detected the formation of any tetra-, penta- or hexa-brominated congeners.

Debromination of Deca in the real world

- The pattern of congeners that would be expected from debromination of Deca is not found in the environment
- An expected marker compound indicative of Deca debromination has not been found in the EU environmental monitoring studies
- Expected correlations between levels of different congeners that might be expected if debromination of deca is contributing significantly to the presence of lower brominated congeners are not found.

Debromination of Deca in the real world

- Conclusion: Deca is not significantly contributing to levels of lower brominated PBDEs found in the environment
- Ongoing environmental monitoring will further test this
- Studies with federal EPA will also further test this conclusion.

Metabolism

- Recent papers claim BDE-209 metabolized to lower BDEs
- Putative metabolites do NOT include BDE-47, 99; *e.g.*, the major BDEs in biota
- Primary 'metabolites' said to be nonaBDEs
  - NonaBDEs are the main impurities in commercial Deca products
  - Any nonaBDEs detected in biota likely from impurities in commercial product

Evidence for Metabolism

- Questionable; Main studies in rats claiming metabolism did so without
  - Analysis of impurities in test article
  - Identification of 'metabolite's' structure, and/or
  - Determination that 'metabolites' did indeed originate from BDE-209 molecule
- Primary fish studies claiming metabolism indicate formation of <0.1% of dose
- Multiple studies demonstrate BDE-209 eliminated primarily as the parent molecule without prior absorption or metabolism
  - Absorption is VERY poor; Probably <1% of an oral dose
  - Any conversion to 'metabolites' would be < than this

Developmental Neurotoxicity

- Academic studies have suggested that there may be a neurotoxicological effect when new born mice or rats are exposed to Deca.
- While raising questions, the study designs had major flaws.
- These studies have been reviewed by national experts within the context of the EU risk assessment, and found to be of insufficient quality to draw firm conclusions
- As a result a larger study that will allow allow appropriate statistical analysis is in progress, and finalized results will be available in February

Addressing Firefighters' Concerns

- Will a firefighter contact brominated FRs (BFRs) in a fire?
  - BFRs act on fire to slow it down. They break down during a fire and are consumed in order to do this
- Does Deca cause cancer?
  - Deca-BDE has been tested by the US National Toxicology Program (NTP), the US Occupational Safety and Health Commission (OSHA) and the International Agency for Research on Cancer (IARC) and is not considered a carcinogen.

Addressing Firefighters' Concerns

- Toxic Byproducts from Fire
  - The major killer in fire situations is carbon monoxide inhalation.
  - Many other toxic products are formed from incomplete combustion. These include polyaromatic hydrocarbons, acrolein, cyanides, acids, and dioxins and furans.
  - Removal or replacement of Deca will not make the fire scenario substantively safer. For example, The US Toxicology Program has stated that wood combustion is one of the greatest unintentional sources of chlorinated dioxins.
  - Wearing proper turnout gear and keeping it clean to prevent exposure to smoke and soot is recommended to limit exposure to any substances of concern.

Deca is not a substance of very high concern

- Global chemical regulation is being led by the European Union and its REACH initiative.
- Under reach ALL chemicals used in Europe will undergo examination to determine certain fundamental properties
- The key properties that will drive replacement of chemicals have been defined and chemicals that have these properties will be designated as "substances of very high concern".

Deca is not a substance of very high concern

- Substances of very high concern:
  - Substances that are persistent, bioaccumulative and toxic
  - Substances that are very persistent and very bioaccumulative
  - Substances that are carcinaogenic, mutagenic, or reprotoxic to category 1 or 2 levels.
  - Substances of equivalent concern
- Deca does not meet these criteria.

Emissions Control

- As an industry it is recognized that it is desirable to minimize any unintended emissions of chemicals into the environment.
- A code of practice has been developed and is now being applied to the manufacture and downstream use of various flame retardants, including Deca.

VECAP – Voluntary Emissions Control Action Program

- Introduced into Europe, Unites States, Canada, and China this program seeks to reduce emissions by a process of continuous improvements in manufacturing, handling and downstream use.
- Forms the basis of an Environmental Performance Agreement with Environment Canada.
- Has significantly reduced emissions
  - For example a 97% reduction to water by the UK textiles sector over two years.

Conclusions

- Much is known about Deca
- Commercial deca should be evaluated in terms of its own characteristics, and should not be confused with the penta-, and octa-commercial products

Conclusions

- There are areas of concern that require further study, but the concerns are not sufficient to limit its use.
- Studies to address concerns are underway in Europe and North America
- The consensus of major reviews of Deca's properties is that continued use in its current application areas is acceptable.