Safer Alternatives to DecaBDE

Lansing, MI
February 12, 2008

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Senior Science Advisor
Clean Production Action

Outline

- The Problem
  - Why is deca-BDE a concern?
- What are others doing about it at the policy level?
- How are others managing without it at the technical level?
- Why can this bill be viewed as a driver for innovation and business-friendly?

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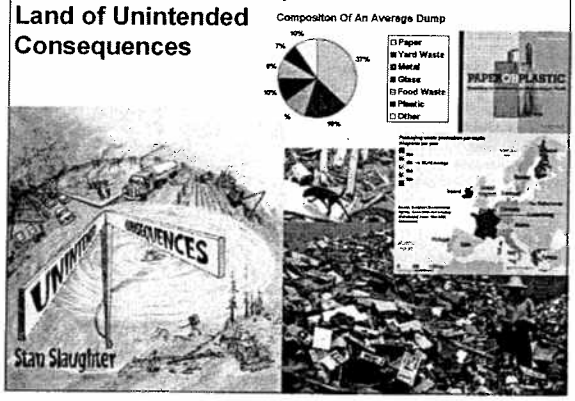
Mountains (and Rivers) of Waste in the Land of Unintended Consequences



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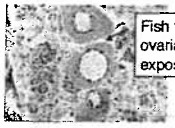
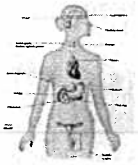
Endocrine Disruptors

- Chemicals that mimic or block the activities of hormones or alter the concentrations of natural hormones
- Examples commonly used in cleaning products
  - Alkylphenol ethoxylates degrade to alkyl phenols
    - Particularly in aquatic and anaerobic environments
    - Nonylphenol found in dust samples in study of homes
  - Some phthalates used in fragrances



Fish testes containing ovarian tissue due to exposure to ED compounds



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"Scientists Drug-Test Whole Cities"

Tamiflu Survives Sewage Treatment

- *"It's a community urinalysis," said Caleb Banta-Green, a University of WA drug abuse researcher who was part of the Oregon State team. The scientists presented their results at a meeting of the ACS in Boston (Aug 2007).*
- *"One of the early results of the new study showed big differences in methamphetamine (meth) use city to city. One urban area with a gambling industry had meth levels more than five times higher than other cities. Yet meth levels were virtually nonexistent in some smaller Midwestern locales", said Jennifer Field, the lead researcher and a professor of environmental toxicology at OSU.*
- *"The ingredient Americans consume and excrete the most was caffeine", Field said.*

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Growing Consumer Concern About Product Safety: "Which Companies Can I Trust?"

Body Burden testing raises public awareness of chemicals in products :

"Every single sample of mother or baby blood tested positive for an array of chemicals linked to birth defects or certain types of cancer."

http://www.wwf.org.uk/chemicals/biotourbaby.asp

Toy scandal only accentuates consumer concern

Deca BDE Fate and Toxicity

Slides Courtesy of Dr. Heather Stapleton, Duke University

Congener (# Br)	Percent of Total
Penta-BDE Commercial Mixture	
BDE-47 (4)	27
BDE-85 (5)	1.6
BDE-99 (5)	43
BDE-100 (5)	9.8
BDE-153 (6)	6.5
BDE-154 (6)	9.3
hexa-BDE	1.1
Octa-BDE Commercial Mixture	
BDE-153 (6)	6.7
BDE-154 (6)	1.7
BDE-183 (7)	44
2 hepta-BDEs	2.5
3 octa-BDEs	34
BDE-207	12
Deca-BDE Commercial Mixture	
BDE-209 (10)	>97

Phased out or banned

Phased out or banned

Types of Products

Slide courtesy of Dr. Heather Stapleton, Duke University

Uses of Commercial PBDE Mixtures in Various Plastics

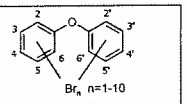
Resins and Polymers	DecaBDE	OctaBDE	PentaBDE
Acrylonitrile-butadiene styrene		X	
Epoxy-resin	X		
Phenolic resins	X		X
Polyacrylonitrile	X		
Polyamide	X	X	
Polybutylene terephthalate	X	X	
Cross Linked Polyethylene	X		
Polyethylene terephthalate	X		
Polypropylene	X		
Polystyrene/HIPS	X	X	
Polyvinylchloride			X
Polyurethane			X
Unsaturated polyesters	X		X
Rubber	X		X
Paints/lacquers	X		X
Textiles	X		X

Slides Courtesy of Dr. Heather Stapleton, Duke University

From: EBFRIP, 1996; Rahman et al., 2001

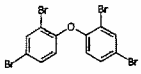
Slide courtesy of Dr. Heather Stapleton, Duke University

PBDE Nomenclature



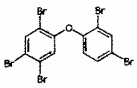
Polybrominated Diphenyl Ether (PBDE)

PentaBDE Congeners:



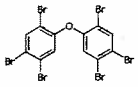
2,2',4,4'-tetrabromodiphenyl ether

BDE-47



2,2',4,4',5-pentabromodiphenyl ether

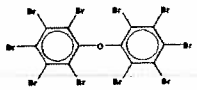
BDE-99



2,2',4,4',5,5'-hexabromodiphenyl ether

BDE-153

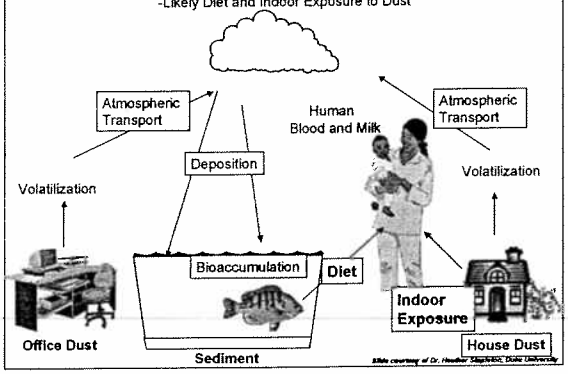
DecaBDE:



BDE 209

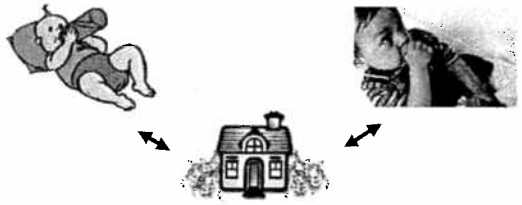
What Are The Major Routes of Human Exposure?

-Likely Diet and Indoor Exposure to Dust



Slide courtesy of Dr. Heather Stapleton, Duke University

Are Children Receiving Greater Exposure to DecaBDE from House Dust?



Children Place Their Hands, Bottles, Toys,(etc.) in Mouth

↓

Inadvertent Ingestion of PBDEs associated with Dust

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Slide courtesy of Dr. Heather Stapleton, Duke University

USA Today: July 12, 2005:

"Childhood Pastimes are Increasingly Moving Indoors"

-By Dennis Cauchon

-Children would rather play video games or surf the internet than play outside

-Children spend 87% of their time Indoors

-Thus, children experiencing an increasingly greater exposure to electronics, and indoor air and dust

**Children are experiencing a greater amount of time indoors and in closer contact with electronic products. Does this lead to increased exposure to flame retardant chemicals in plastics/electronics, in dust, in air?

More studies are needed on the levels of PBDEs in children's serum

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Slide courtesy of Dr. Heather Stapleton, Duke University

Children's Exposure to Lead: The Link to House Dust

**Lead in House Dust Positively Linked to Lead Poisoning in Children

*Exposure Models Assume Children Ingest Approximately 100 to 200 mg dust/day (EPA, *Child-Specific Exposure Handbook*, 2002)

•Studies have found that young children have hand to mouth contact at rates of about 10X per hour (Reed et al., 1999)

.....What levels of PBDEs are children ingesting from dust?

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Slide courtesy of Dr. Heather Stapleton, Duke University

Is DecaBDE found in Indoor Air?

•Yes, DecaBDE present in Indoor air

•DecaBDE is Inhaled in •Indoor Air

~ 3.5 ng/day of BDE 209
~10 ng/day of pentaBDE
(assumed inhalation rate of 20 m³/day).

**Presence of personal "Dust Clouds" results in higher exposure than predicted by large volume air samplers

GM PBDE Concentrations in Air (pg/m³)

Congener	Personal	Bedroom	Main living area
BDE 17	7.6	8.1	7.0
BDE 28/33	29.6	27.3	25.4
BDE 47	226.8	157.9 **	145.1 **
BDE 49	9.1	6.0 **	7.2
BDE 66	3.7	3.5	3.5
BDE 85/155	3.8	2.7	2.5
BDE 99	110.8	66.9 **	60.3 **
BDE 100	22.2	14.4 **	12.0 **
BDE 153	8.6	4.0 **	3.5 **
BDE 154	9.1	6.1 **	5.2 **
BDE 209	173.6	94.8 **	94.2 **
ΣBDE	765.7	460.4	452.8
ΣBDE (no 209)	469.1	324.7	288.6

(Data from Allen et al., 2007)
20 participants from Boston, MA

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Slide courtesy of Dr. Heather Stapleton, Duke University

What are the Levels of PBDEs in Children?
A Case Study from Berkeley, California

Data from Fisher et al., 2006

Blood Levels Measured in ppb lipid

	Date Measured	Penta	Deca	PBDEs
Father Age 35	Sept. 04	64	23	87
	Dec. 04	71	3	74
Mother Age 36	Sept. 04	106	14	120
	Dec. 04	142	4	146
Daughter Age 5	Sept. 04	247	143	390
	Dec. 04	244	11	255
Son Age: 18 mo	Sept. 04	418	233	651
	Dec. 04	482	23	505

This data Combined with Exposure Modeling Suggest Children are Receiving 10X greater exposure to PBDEs than Adults (Jones-Otazo et al., 2005)

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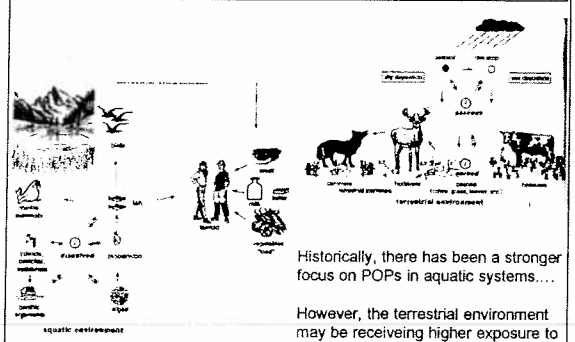
Environmental Levels of BDE 209: Terrestrial vs Aquatic Contamination



Historically, there has been a stronger focus on POPs in aquatic systems....

However, the terrestrial environment may be receiveing higher exposure to DecaBDE.

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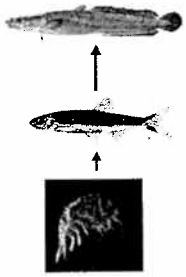
Slide courtesy of Dr. Heather Stapleton, Duke University

DecaBDE does accumulate in Aquatic Organisms and recent evidence Suggests Biomagnification



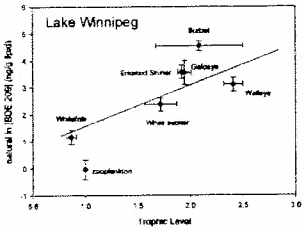
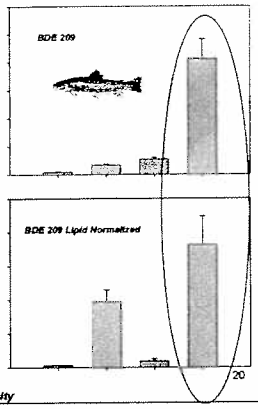


Fig. 5. Relationship between concentration (ng/g, lipid and control corrected; mean ± standard error) of decabromodiphenyl ether (BDE) 209 and trophic level (TL) for the Lake Winnipeg (Canada) food web. Regression analysis: ln [BDE 209] = 2.2894(TL) − 1.2225 (r^2 = 0.7359, p = 0.01).

(Law et al., 2006)

Slide courtesy of Dr. Heather Stapleton, Duke University

- BDE 209 preferentially accumulates in liver and in Serum. *This has the potential to induce greater toxicity than if it was accumulating in fat tissues*
- Similar to Findings by Morck et al. (2003) and Kierkegaard et al. (1999) exposing rats and rainbow trout to BDE 209, respectively



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Slide courtesy of Dr. Heather Stapleton, Duke University

What about Degradation and Metabolism of DecaBDE??

- Is DecaBDE breaking down into products that are more Persistent and toxic?

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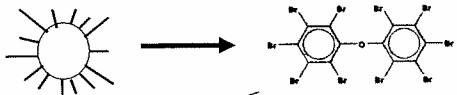
Slide courtesy of Dr. Heather Stapleton, Duke University

Exposure to Sunlight Leads to Degradation: (primarily "debromination")



BDE 209

Congeners found in OctaBDE

BDE 207

BDE 201

BDE 183

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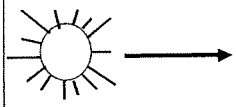
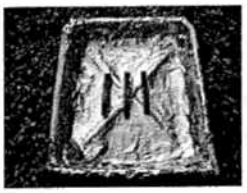
Slide courtesy of Dr. Heather Stapleton, Duke University

Does DecaBDE Degrade When Exposed to Sunlight?





(Stapleton and Dodder, 2007)
(In Review for Publication)

0.5 grams Dust in plastic curvettes

- Tested the ability of natural sunlight to degrade/debrominate DecaBDE in dust
- Will DecaBDE degradation lead to formation of congeners found in OctaBDE and PentaBDE commecial mixtures (which are more Persistent and potentially more toxic)

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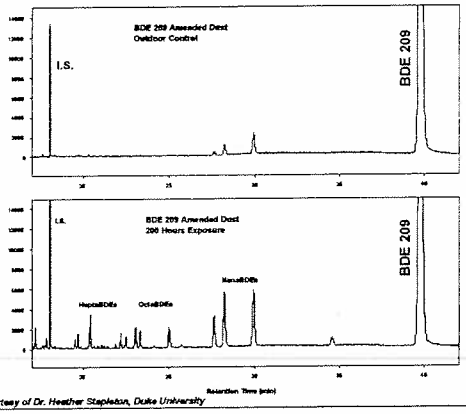
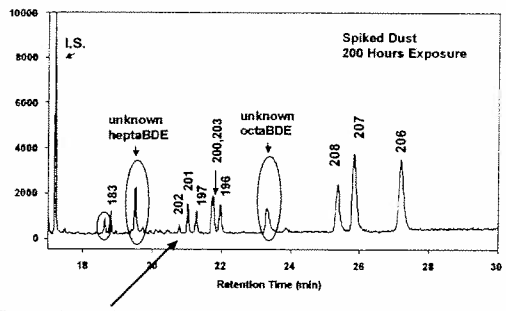
Slide courtesy of Dr. Heather Stapleton, Duke University



Slide courtesy of Dr. Heather Stapleton, Duke University



*Degradation products not found in any commercial mixtures: e.g. BDE 202 Indicators of DecaBDE debromination

*BDE 202 has been measured in house dust (Allen et al., 2006)

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Slide courtesy of Dr. Heather Stapleton, Duke University

Summary and Conclusions:

- DecaBDE, and its primary component, BDE 209 leach out of a variety of consumer products and enter the environment
- DecaBDE does accumulate in human and wildlife tissues
- Exposure to DecaBDE may be greater for children and toddlers relative to adults due to high levels in house dust (similar to lead exposure)
- People may be receiving exposure through inadvertent ingestion of dust, possibly from hand absorption and transfer to the mouth
- Terrestrial food webs may be receiving greater exposure to DecaBDE relative to aquatic species

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Slide courtesy of Dr. Heather Stapleton, Duke University

Summary and Conclusions:

- DecaBDE is bioavailable and does accumulate from dust ingestion
- DecaBDE does break down and form lower brominated congeners associated with the octaBDE mixture when exposed to natural sunlight
- DecaBDE is metabolized in fish and rodents to lower brominated congeners (associated with octaBDE) and to hydroxylated BDEs.
- The degradation and metabolism of DecaBDE is of concern because the metabolites are more persistent and toxic than DecaBDE itself.

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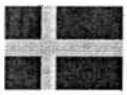
Slide courtesy of Dr. Heather Stapleton, Duke University

DecaBDE Restrictions

- Sweden



- European Union

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DecaBDE Restricted in Textiles & Other Applications in Sweden

KEMI
SWEDISH CHEMICALS INSPECTORATE

Application for exemption to use decaBDE

On 1 January 2007, the Swedish ban on the flame retardant decaBDE came into effect. The following products are exempted:

- electrical and electronic products to which harmonised regulations apply according to Directive 2005/95/EC (RoHS),
- vehicles as defined in the Act (2001:559) on Road Traffic Definitions.

The ban applies to all other articles.

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DecaBDE is Restricted based on Presence of Nona-BDE in Commercial Mixtures

EUROPEAN COMMISSION
DIRECTORATE-GENERAL
ENVIRONMENT
Directorate G - Sustainable Development and Integration
ENV.G.4 - Sustainable Production & Consumption

Brussels, 21 JUIN 2006
KwH/Sk D(2006) 12139

Subject: Scope of the exemption provided by item "DecaBDE in polymeric applications" in the Annex to Directive 2002/95/EC on the restriction of the use of certain hazardous substances in electrical and electronic equipment

The Commission services are of the opinion that -- with the exception of decaBDE -- all PBDEs, including nonaBDE that is introduced into a material as part of a decaBDE, have to comply with the substance ban of Article 4 of the Directive and with the maximum tolerance levels set by Decision 2005/618/EC.

Homogenous materials containing above 0.1% by weight of nonaBDE therefore do not comply with the provisions of the Directive.

emphasis added

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Albemarle Plans to Comply with EU Deca Restriction

Albemarle Introduces Higher Purity Deca-bromodiphenyl Ether Flame Retardant, SAYTEX(R) 102HP

BATON ROUGE, La., Jan. 22 /PRNewswire-FirstCall/ – Albemarle Corporation (NYSE: ALB), the world leader in flame retardant solutions for polymers, has developed and is commercializing SAYTEX 102HP flame retardant, a new, high- assay form of decabromodiphenyl ether, or DecaBDE. Patent applications covering both the high-assay product and the processes for its manufacture are currently pending.

This new product is designed to help Albemarle customers and their downstream users ***meet the*** strictest interpretation of the ***European Union (EU) Restriction on the Use of Hazardous Substances (RoHS) Directive*** and related EU Commission Decisions regarding the use of polybrominated diphenyl ethers, or PBDEs.

http://www.albemarle.com/Products_and_services/Polymer_additives/?news=text&releaseID=952675

[emphasis added]

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Safer, Cost Competitive Alternatives are Available to DecaBDE

Product	Alternatives Available?	Cost-Competitive?	Safer Alternatives Available?
Electronic housings	Yes	Yes	Yes
Furniture applications	Yes	Yes	Yes

Washington State estimates that *"about 57% of TVs and 95% of computer products are PBDE-free"*

Example: Fight for the Status Quo, then Innovate!

Albemarle Expands Possibilities for Furniture Fire Safety

ALBEMARLE

Albemarle logo. (PRNewsFoto) (Nasdaq: Tag2: pmphoto0050000)

WASHINGTON, DC UNITED STATES

Replaces penta (not deca) BDE

New Hal-Free ANTIBLAZE(R) Flame Retardant Protects Flexible Foams at Lower Loadings

BATON ROUGE, La., Jan. 28 /PRNewswire-FirstCall/ -- Flexible foam producers and users now have an extremely effective and more environmentally appealing alternative for flame retarding the foams used in furniture and automobile seats, thanks to an innovation from the worldwide leader in flame retardants, Albemarle Corporation (NYSE: ALB).

(Logo: http://www.newscom.com/cgi-bin/prnh/20050801/ALBEMARLELOGO)

Albemarle has introduced ANTIBLAZE(R) 117MF, a new, halogen-free flame retardant designed to provide a safe and highly effective alternative to halogen-based flame retardants in flexible furniture and automotive foams. Additional benefits of ANTIBLAZE 117MF flame retardant are its high efficiency - achieving the same reliable protection as existing flame retardants with up to 30 percent less product - and excellent non-scorching performance.

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Progress towards PVC(1) and BFR(2) elimination by leading electronic manufacturers selling consumer electronic products in the US (February 2007)

Manufacturers	Market availability of DecaBDE* free products	Goal of partial BFR and PVC elimination	Goal of BFR elimination for new products	Goal of PVC elimination for new products
Apple(3)	√	√	by end of 2008	by end of 2008
Dell(3)	√	√	by 2009	by 2009
Lenovo(3)	√	√	by 2009	by 2009
Toshiba Personal Computing(3)	√	√	by 2008	by 2008
Acer(3)	X	√	by 2008	by 2008
Sony(3)	√	√	by 2010	by 2010
LG Electronics(3)	√	√	by 2010	by 2010
Samsung(3)	√	√	by 2010	by 2010
Sharp(3)	√	√	by 2010	by 2010
Philips(3)	√	√	by 2012	by 2012
Hewlett Packard(3)	√	by 2008 for PVC and BFR free computing products	X	X
Panasonic(3)	√	by 2011 for PVC free imaging and BFR free computers and mobile phones	X	X

Key: X means no publicly available data found on website and / or means goal has been met or accomplished
*Some products still might contain trace amounts of decaBDE due to the use of recycled plastics.

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Flame Retardant(s)	Example Uses
Resorcinol bis diphenyl phosphate (**RDP**)	**Europe -- ~20,000 metric tons in TVs**
Bisphenol A diphosphate or RDP	• Sharp AQUOS LCD TV • Philips flat panel TV
Phosphate esters	• Apple Monitor • Philips Plasma TV
Metal hydroxide	NEC
None, change design to eliminated FR need	Printers, copiers

Source: LCSP, 2005

halogen-free electronics

Flame Retardant	Resin Cost – average[1] TV front & rear	Resin cost as % of $300 TV
DecaBDE	**$11.21**	**3.7%**
Other BFRs	$14.55	4.9%
Bisphenol A diphosphate or RDP	$18.18	6.1%
Phosphate esters	$22.00	7.3%
RDP	**$23.03**	**7.7%**

[1]Average TVs: 27.5" unit, $300

Source: LCSP, 2005

costs of -- TV alts

Are the Phosphate Alternatives Safer?

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BSEF Members Manufacture Phosphate Alternatives to DecaBDE

Chemtura (formerly Great Lakes Chemical)

Manufactures phosphorous-based flame retardants for TV housings (www.e1.greatlakes.com):

_ TPP, BAPP/BPADP, & RDP

"**Reofos RDP** is recommended for use in modified polyphenylene oxide (mPPO), polycarbonate/ABS blends and polyurethane foams. **Reofos RDP** provides the following performance advantages:

- High phosphorus content
- High molecular weight and low volatility
- Reduced plasticization"

(http://www.e1.greatlakes.com/freb/common/pdf/Reofos_RDP_ds.pdf)

BSEF Members Manufacture Phosphate Alternatives to DecaBDE

Albemarle Corporation

Manufacturer of phosphorous flame retardant for TV housings BAPP/BPADP

"**Thermoplastic alloys** such as **PC/ABS** and **PPO/HIPS** are often required to meet stringent FR standards such as UL94 V0. **Phosphate based FR's work efficiently in these resins and give good physical properties and good UV stability"** (link from Albemarle webpage: www.specialchem4polymers.com/tc/phosphorus-flame-retardants/index.aspx)

"NcendX® P-30 liquid phosphorus (nonhalogen) flame retardant is an outstanding performer in PC/ABS and PPE/HIPS blends. It actually improves resin melt flow and exhibits outstanding thermal stability, excellent hydrolytic stability, low migration and low volatility." (www.albemarle.com/Products_and_services/Polymer_additives/Flame_retardants/Markets/Electronic_enclosures/)

Research is In: Safer Alternatives are Available

- Maine DEP and CDC
- Illinois EPA

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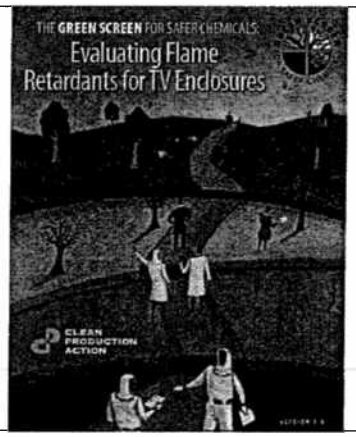

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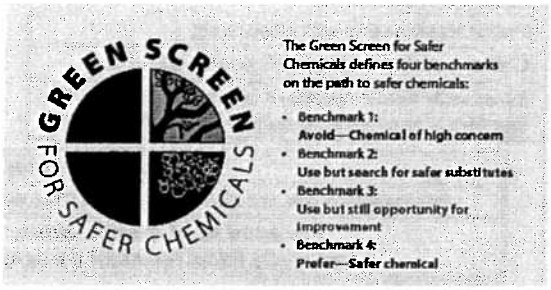

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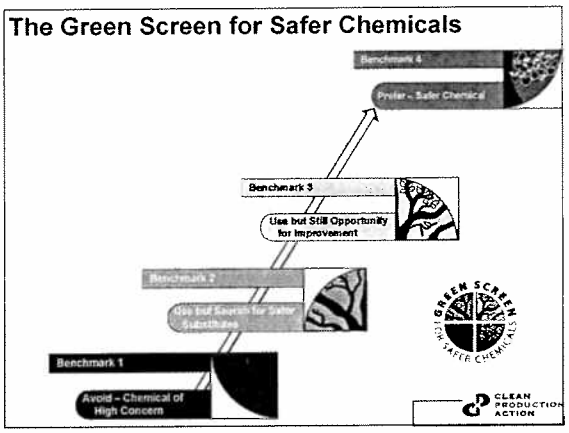
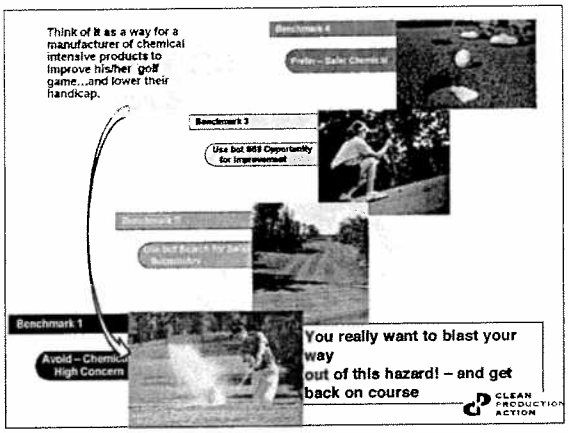
The Green Screen for Safer Chemicals





Green Screen: Comparison of DecaBDE & RDP

Chemical	Reasons for Benchmark	Benchmark Achieved
DecaBDE and its breakdown products	Issues with breakdown products • OctaBDE = vPT • Other lower brominated congeners with P, B and T characteristics	Benchmark 1: Avoid - Chemical of High Concern
RDP and its breakdown products	RDP constituents or breakdown products ***are not*** a PBT, vPvB, vPT, or vBT	Benchmark 2: Use but Search for Safer Substitutes

CLEAN PRODUCTION ACTION

Furnishings	Potential DecaBDE Use
Mattresses	Quilted fabric (or "mattress ticking")
Drapes & Upholstered Furniture	Commercial applications when required by building codes such as casinos, hotels, and schools

Source: LCSP, 2005

deca in textiles

Mattress Alternatives
Fabric backcoating with phosphate
Cotton padding treated with boric acid
Inherently flame resistant materials used as **fire barriers** – aramides, melamine, glass fibers, etc.

Mattress Notes
Halogen-free alts are common & often labeled
Preferred alt of manufacturers: inherently flame resistant barriers

Sources: LCSP, 2005; WA Dept of Ecology, 2006

mattresses: deca alts

Top 15 US Bedding Manufacturers – 2004

Rank	Company	PBDE?
1	Sealy	No
2	Simmons	No
3	Serta	No
4	Spring Air	*None applied at assembly factory*
5	Tempur-Pedic	No
6	Select Comfort	No
7	King Koil	No
8	Therapedic	*None applied at assembly factory*
9	Kingsdown	No
10	Englander	No
11	Int'l Bedding Corp	No
12	Restonic	No
13	Symbol	*Didn't know the answer*
14	Corsicana	No
15	Lady Americana	No

60% of U.S. Market

48

Source: WA Dept of Ecology, 2006

Upholstered Furniture Alternatives
Textile backings coated with phosphate material
Inherently flame resistant materials used as fire barrier

Furniture Notes
Very few manufacturers label their products as BFR-free

Source: LCSP, 2005

furniture: deca alts

Drapery Alternatives
Natural fibers (wool, cotton, linen) or natural/synthetic blends treated with phosphates
Inherently flame resistant materials or polymers w/phosphates

Drapery Notes
Natural/synthetic fiber blends are common
Higher % natural = better treatment results

Source: LCSP, 2005

drapes: deca alts

Examples of P Based Alternatives for Cotton: Proban and Pyrovatex

Rhodia

Ecolabel in Europe

Press Release

Rhodia receives approval from OEKOTEX, for their leading textile flame retardant polymer, PROBAN®

December 16th, Warford Rhodia's Phosphorus, Phosphates & Food Enterprise has received approval from OEKO TEX, the International Associations for Research and Testing in the Field of Textile Ecology for the PROBAN® polymer, which is produced using patented technology from its PROBAN® chemical.

The PROBAN® polymer formed in the fabric, gives cotton and cotton rich fabrics their wash durable flame retardant properties. OEKO TEX has declared it harmless to human health and will include it in the company's list of active chemical products.

A textile labeled with the Oeko-Tex Standard 100 offers the consumer assurance the textile does not contain any amounts of harmful substances, which are detrimental to health.

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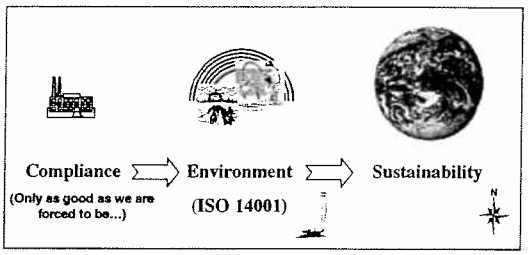
Why is a decaBDE ban good for business?

Responsible Organization Trend: Focus on Sustainability



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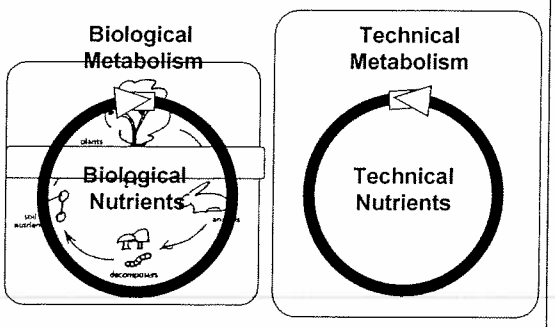
Cradle-to-Cradle Design: Focus on Nutrients and Metabolisms



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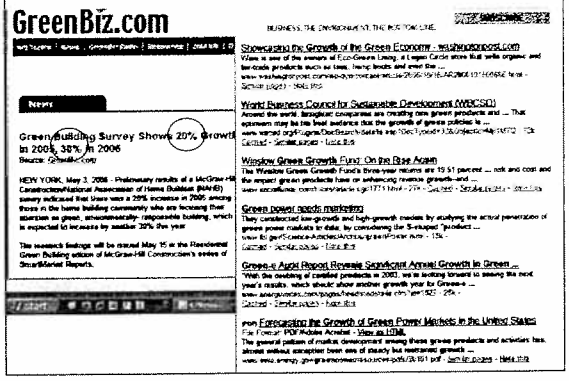
A Growing Green Economy



Wal-Mart's Principles for Preferred Chemical Intensive Products

Safe Products for Mother, Child, and the Environment

> *When we suspect that an ingredient in a product or the product itself is capable of causing harm to human health and the environment, we will act to find better alternatives.*

> *We will favor those products that do not contain the following:*

Chemicals Harmful to Human Health (CMRs)
- Carcinogens – can cause cancer
- Mutagens – can damage genetic material
- Reproductive Toxicants – may affect reproduction or the unborn

Chemicals Harmful to the Environment (PBTs)
- Persistent – do not break down in the environment
- Bioaccumulative – builds up in the food chain
- Toxic – causes death or damage in organisms in the environment

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NSF International Ann Arbor, MI

- New Green Chemistry and Sustainable Assessment Standards
  - USEPA DfE Formulator Program
  - CleanGredients
  - *Carpet
  - *Furnishing Fabrics
  - *Resilient Flooring
  - *Furniture

  No pBDEs permitted
- Growth
  - 12%/yr for last 7 years
  - Doubled employees (~1200 in 2008 incl. contractors; ~100 in 1990)
  - Doubled lab space (to 180,000 ft², large on global scale!)
  - Fledgling green chemistry programs already responsible for 0.5% annual growth

* *New programs, nearing start*

What are you doing?

- Cutting stone
- Making perfect cuts
- Building a cathedral (temple, mosque)

Aspects of non halogenated & halogenated flame retardants

Both halogenated and non halogenated flame retardants are in widespread use as additives in a variety of applications including electronics and furniture. There are major differences in the chemical structures of halogens and non-halogens. The non-halogen flame retardants do not contain any bromine or chlorine.

The halogenated flame retardants are persistent and poorly biodegradable due to their molecular structure and very low water solubility. Therefore, they will accumulate in the environment, will bio-accumulate in fatty tissues and then bio-magnify up the food chain. The combination of bio-accumulation and apparent chronic toxicity can make halogenated flame retardants a high concern for the environment and human health. It is also beyond debate that a select group of halogenated flame retardants form dioxins and furans during their production, use, in the case of fire, and when they are disposed of or recycled in an improper manner.

Non halogenated flame retardants tend to biodegrade easily and do not generate these toxic intermediates or hazardous degradation products in case of fire or disposal. Due to their structure, they do not accumulate in the environment. They do not appear to end up in animals or humans via the food chain and therefore are not likely to cause chronic exposure to animals or humans via that route.

National Black Chamber of Commerce
1350 Connecticut Avenue NW Suite 405, Washington DC 20036
202-466-6888 202-466-4918fax www.nationalbcc.org info@nationalbcc.org

February 8, 2008

Rebekah Warren
Chair, Great Lakes & Environment Committee
S0987 House Office Building
P.O. Box 30014
Lansing, MI 48909-7514

Re: HB 4465

Dear Representative Warren:

The National Black Chamber of Commerce has over 151 chapters located within 41 states in this nation and has direct access to over 100,000 Black owned businesses.

The NBCC is standing by a growing national coalition opposing legislation like HB 4465 which we feel seriously threatens public safety and especially the safety of individuals and businesses in low income communities. HB 4465 mandates the removal of critical flame retardants found in a variety of products. Further, the bill does so without any safeguards with respect to untested replacement products. This is not cost protective and is, indeed, playing with fire. Low income and minority communities already bear a disproportionate share of fire related injuries and deaths due in large part to the lack of fire safety resources directed at their communities.

HB 4465 would make an already bad situation worse. The NBCC supports these lifesaving products – products that have reduced the number of fire fatalities by over 64% nationally. The benefits of keeping these productive products far outweigh any of the reasons the bill presents to remove them.

We strongly ask you to remove your support from this bill and vote NO on HB 4465.

Sincerely,

HARRY C. ALFORD
President/CEO

CC: Members of the committee
CC: Lansing Black Chamber of Commerce, Idlewild Black Chamber of Commerce, and Detroit Black Chamber of Commerce

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Albemarle Expands Possibilities for Furniture Fire Safety

ALBEMARLE

Albemarle logo. (PRNewsFoto) (Newscom TagID: prnphotos055805)

WASHINGTON, DC UNITED STATES

New Hal-Free ANTIBLAZE(R) Flame Retardant Protects Flexible Foams at Lower Loadings

BATON ROUGE, La., Jan. 24 /PRNewswire-FirstCall/ -- Flexible foam producers and users now have an extremely effective and more environmentally appealing alternative for flame retarding the foams used in furniture and automobile seats, thanks to an innovation from the worldwide leader in flame retardants, Albemarle Corporation (NYSE: ALB).

(Logo: http://www.newscom.com/cgi-bin/prnh/20050801/ALBEMARLELOGO)

Albemarle has introduced ANTIBLAZE(R) 117HF, a new, halogen-free flame retardant designed to provide a safe and highly effective alternative to halogen-based flame retardants in flexible furniture and automotive foams. Additional benefits of ANTIBLAZE 117HF flame retardant are its high efficiency - achieving the same reliable protection as existing flame retardants with up to 30 percent less product - and excellent non-scorching performance.

The human health and environmental profile of ANTIBLAZE 117HF flame retardant has been tested extensively. Using U.S. Environmental Protection Agency criteria, the product also has been found to be non-persistent and non- bioaccumulative.

"As a socially responsible producer of flame retardants, we recognize the need for foam and furniture makers to offer products that ensure consumers the highest level of safety and value," said Steve LeVan, Albemarle division vice president of flame retardants.

"Our new ANTIBLAZE 117HF flame retardant lets foam makers and end-users achieve exceptional fire safety and material performance, as well as a strong health, safety and environmental profile, which is consistent with our mission to provide innovative and sustainable products to the marketplace," LeVan said.

Critical fire safety performance; lower usage levels; and an excellent health, safety and environmental profile, make ANTIBLAZE 117HF flame retardant an ideal solution for foam makers.

ANTIBLAZE 117HF flame retardant is produced at Albemarle's Orangeburg, S.C. facility and is now commercially available.

Albemarle Corporation, headquartered in Richmond, Virginia, is a leading global developer, manufacturer and marketer of highly engineered specialty chemicals for consumer electronics; petroleum and petrochemical processing; transportation and industrial products; pharmaceuticals; agricultural products; and construction and packaging materials. The Company operates in three business segments-Polymer Additives, Catalysts and Fine Chemicals, and serves customers in approximately 100 countries. Learn more about Albemarle at http://www.albemarle.com.

"Safe Harbor" Statement under the Private Securities Litigation Reform Act of 1995: Statements in this press release regarding Albemarle Corporation's business which are not historical facts are "forward-looking statements" that involve risks and uncertainties. For a discussion of such risks and uncertainties, which could cause actual results to differ from those contained in the forward-looking statements, see "Risk Factors" in the Company's Annual Report on Form 10-K.

SOURCE Albemarle Corporation

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Progress towards PVC[1] and BFR[2] elimination by leading electronic manufacturers selling consumer electronic products in the US (February 2007)				
Manufacturers	**Market availability of DecaBDE* free products**	**Goal of partial BFR and PVC elimination**	**Goal of BFR elimination for new products**	**Goal of PVC elimination for new products**
Apple[3]	√	√	by end of 2008	by end of 2008
Dell[4]	√	√	by 2009	by 2009
Lenovo[5]	√	√	by 2009	by 2009
Toshiba Personal Computing[6]	√	√	by 2009	by 2009
Acer[7]	X	√	by 2009	by 2009
Sony[8]	√	√	by 2010	by 2010
LG Electronics[9]	√	√	by 2010	by 2010
Samsung[10]	√	√	by 2010	by 2010
Sharp[11]	√	√	by 2010	by 2010
Phillips[12]	√	√	by 2012	by 2012
Hewlett Packard[13]	√	**by 2009** for PVC and BFR free computing products	X	X
Panasonic[14]	√	**by 2011** for PVC free internal wiring and BFR free computers and mobile phones	X	X

Key: X means no publicly available data found on website and √ means goal has been set or accomplished
*Some products still might contain trace amounts of decaBDE due to the use of recycled plastics.

CLEAN PRODUCTION ACTION

REFERENCES

[1] Polyvinyl Chloride
[2] Brominated Flame Retardants
[3] http://www.apple.com/environment/materials/
[4] http://www.dell.com/content/topics/global.aspx/corp/environment/en/prod_design?c=us&l=en&s=corp&~section=016
[5] http://www.pc.ibm.com/ww/lenovo/about/sustainability/environment/Lenovo_2006.2007_Sustainability_Report.pdf
[6] http://www.toshiba.co.jp/pc_env/eco/lca.html#comm5.
[7] http://global.acer.com/about/sustainability13.htm
[8] http://www.sony.net/SonyInfo/Environment/activities/products/index.html
[9] http://www.lge.com/about/sustainability/hazardous_substances_detail.jsp
[10] http://www.samsung.com/us/aboutsamsung/corpcitizenship/environmentsocialreport/environmentsocialreport_ManagementOfTargetSubstances.html
[11] http://sharp-world.com/corporate/eco/data/chem.html.
[12] http://www.philips.com/about/sustainability/howwework/ourproductsandprocesses/chemicalsubstances.page
[13] http://www.hp.com/hpinfo/globalcitizenship/environment/productdesign/materialuse.html
[14] http://www.panasonic.net/eco/gp/chemical.html

Halogen-free Flame Retardants in E&E Applications

A growing toolbox of materials is becoming available

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Layout
Stolz Grafisches Atelier · Karlsruhe

Print
Wilhelm Stober GmbH · Eggenstein

Status: October 2007

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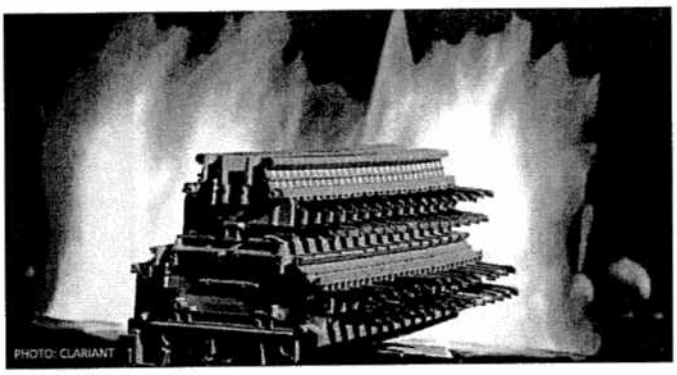
1 Introduction – Why Halogen-free Flame Retardants?



This brochure is meant to illustrate the technical properties and advantages of halogen-free flame retardants (FRs) for key application areas like housings, cables, connectors and switches as well as printed wiring boards. After many years of research and development a whole toolbox of halogen-free chemistries is now available for the materials engineer. In some areas, the development of commercial solutions is moving quickly.

Flame retardants have become a class of chemicals which receive more and more scientific and public attention. The discussions about flame retardants started, when brominated flame retardants (BFRs) became a topic of environmental concern in the early 1990ies, when it was discovered that some BFRs could form halogenated dioxins and furans under severe thermal stress or when they were burnt in accidental fires or uncontrolled combustion[1]. Findings in the environment and biota and the suspicion that some flame retardants bioaccumulate in organisms have added to these concerns[2 3 4 5]. Meanwhile, the environmental and health properties of not only BFRs but also other types of flame retardants have been studied extensively. The most widely used organic flame retardants have become the subject of official risk assessments in Europe[6].

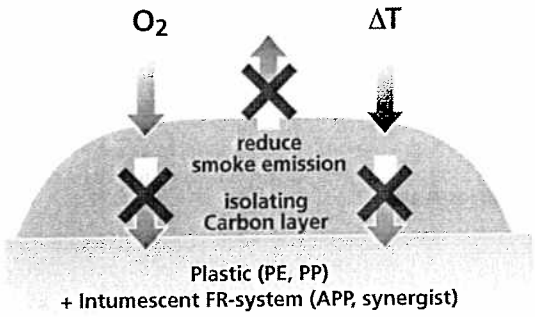


Figure 1: The mechanism of Intumescent flame retardant systems which are typically a combination of phosphorus and nitrogen compounds (Budenheim).

What are halogen-free flame retardants[7]? This group covers a diverse range of chemicals which are commonly classified as:

- Inorganic: This category comprises mainly metal hydroxides like aluminium hydroxide and magnesium hydroxide. Other compounds like e.g. zinc borate are used to a much lesser extent.
- Phosphorus based flame retardants include organic and inorganic phosphates, phosphonates and phosphinates as well as red phosphorus, thus covering a wide range of phosphorus compounds with different oxidation states.
- Nitrogen based flame retardants are typically melamine and melamine derivatives (e.g., melamine cyanurate, melamine polyphosphate, melem, melon). They are often used in combination with phosphorus based flame retardants.

1 *Söderström G, Marklund S (2002): PBCDD and PBCDF from incineration of waste-containing brominated flame retardants. ES&T, Vol. 36. pp. 1959-1964*

2 *de Wit C (2002): An overview of brominated flame retardants in the environment. Chemosphere. pp. 583-624*

3 *Ikonomou M, Rayne S, Addison R (2002): Exponential increases of the brominated flame retardants Polybrominated diphenyl ethers, in the Canadian Arctic from 1981 to 2000. ES&T, Vol. 36, No. 9. pp. 1886-1892*

4 *Law R, Allchin C, Boer J, Covaci A, Herzke D, Lepom P, Morris S, Tronczynski J, de Wit C. (2006): Levels and trends of brominated flame retardants in the European environment. . Chemosphere Vol, 64. pp. 187-208*

5 *Sjödin A, Patterson D, Bergman A (2001): Brominated Flame Retardants in Serum from U.S. Blood Donors. ES&T, Vol. 35, No. 19. pp. 3830-3833*

6 *http://ecb.jrc.it/existing-chemicals/*

7 *The proper designation is actually non-halogenated flame retardants, meaning that no halogens are intentionally added and contained in the products. Trace amounts of halogens are found everywhere and also in commercial chemicals.*

Intumescent flame retardants (mechanism see Figure 1) are an example of a typical mechanism for halogen-free flame retardants. The combustible material is separated from the fire or heat source by an insulating foam which forms at the surface. Intumescent flame retardant systems can be applied to decrease flammability of thermoplastic polymers such as Polyethylene, Polypropylene, Polyurethane, Polyesters and Epoxy resins.

Figure 2 shows the current European consumption of different flame retardant types – halogen-free FRs do already present the major market share. In addition, Figure 3 illustrates the variety of polymer types used for E&E installations, which explains why so many different FR technologies are necessary, because FRs need to match polymer properties and specific processing requirements. The total European plastics demand for E&E applications was estimated at 3.15 million tons in 2004 (source: PlasticsEurope).

For cables the estimated total polymer consumption for 2007 will be 1.3 mio. tons, dominated by PE (52 %) and PVC (40 %). Other materials make up the remaining 8 %. Low smoke, zero halogen cables have been growing strongly in Europe and reached a consumption of 93 000 tons of polymer compounds in 2005 (source: AMI Consulting, UK).

Over the past decade, the fate of electronic waste and the contained hazardous materials have gained increasing political attention and have led to the WEEE[8] and RoHS[9] Directives in Europe: The aim of these regulations is that electronic waste shall be properly recovered and recycled; new equipment shall not contain problematic substances. Flame retardants are affected, because according to the WEEE directive, plastics containing brominated flame retardants have to be separated before further treatment of the waste. Under RoHS, certain brominated flame retardants[10] are no longer allowed in new electronic equipment since July 2006.

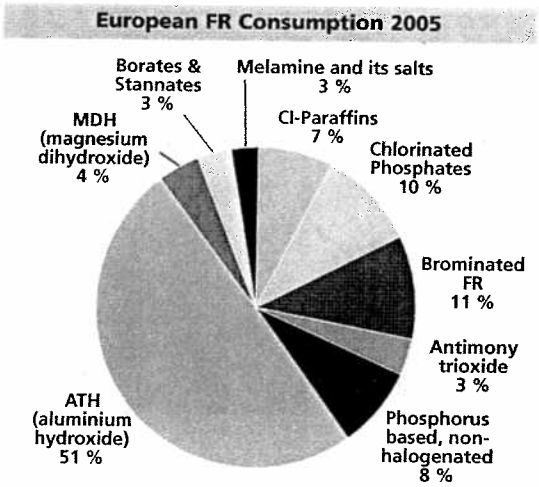


Figure 2: The current consumption of flame retardants in Europe, which amounts to a total of 463 800 metric tons (source: EFRA). Halogen-free FRs are shown in different shades of blue.

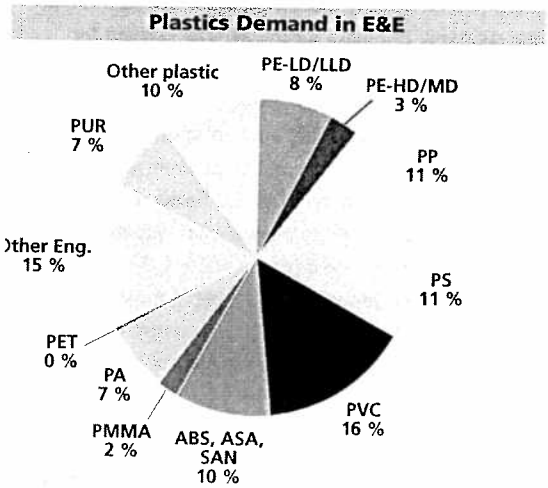
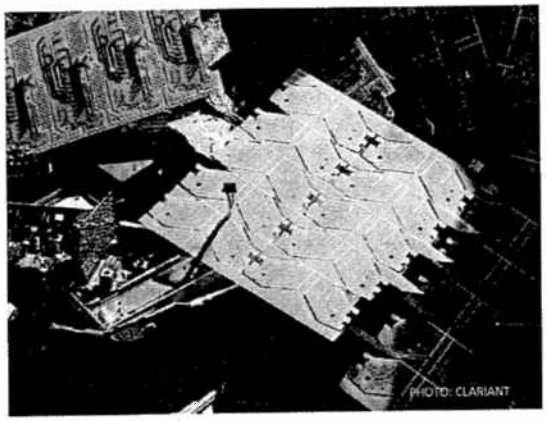


Figure 3: Plastics demand for electrical and electronics applications in Western Europe in 2004 (total of 3.2 million tons; source: PlasticsEurope)

8 *Directive 2002/96/EC on Waste of Electric and Electronic Equipment*

9 *Directive 2002/95/EC on Restriction of certain hazardous Substances in Electric and Electronic Equipment*

10 *Banned BFRs: Polybrominated biphenlys (PBB) and polybrominated diphenylethers (PBDE); for Deca-BDE an exemption was granted by 2005/717/EC*



Other regions of the world are about to follow with similar legislation. These activities increased the interest in halogen-free flame retardants, not only in engineering plastics but also in thermoset resins and printed wiring boards. In addition to legal requirements, ecolabels have been introduced since the 1970ies as voluntary measures in order to promote environmentally friendly products. The idea is that the consumer can make a conscientious decision for such products, if they are labelled according to an accepted and respected scheme. Worldwide, today, there are about 25 ecolabel organizations and schemes (see: *http://www.gen.gr.jp)*. Even in Europe there are several national labels in addition to the EU flower. Ecolabels are specifically designed to go beyond legal requirements like RoHS, because they are meant to endorse the "best in class" and advance environmental benchmarks. Traditionally, many ecolabel systems have prohibited the use of halogenated flame retardants in their criteria for electronic products (e.g. EU label, Blue Angel in Germany, Nordic Swan in Scandinavia, TCO in Sweden). Often, the flame retardants which are used in products need to be declared to the ecolabelling organization. Ecolabels are also relevant for green public procurement, because e.g. in Europe ecolabel criteria can be included in public calls for tender.

Due to this regulatory and environmental pressure, a number of original equipment manufacturers (OEMs) have developed phase out plans for BFRs, some have even made strong commitments with deadlines e.g.:

- Apple has made the commitment to ban all BFRs by the end of 2008:
  http://www.apple.com/hotnews/agreenerapple/

- Dell's policy states that it intends to move away from chemicals that are persistent, bioaccumulative and toxic. It has also pledged to eliminate all brominated flame retardants and PVC from new product designs by 2009.
  http://www.dell.com/downloads/global/corporate/environ/report07.pdf

- In Nokia's most recent list of restricted substance, BFRs are also no longer permitted for new products:
  http://www.nokia.com/NOKIA_COM_1/Corporate_Responsibility/Environment_/Built_green/Substance_management/NokiaSubstanceList_Version_10.xls

- Sony Ericsson also restricts halogenated flame retardants:
  http://www.sonyericsson.com/images/spgd/CWS31AFW_15308_27_0_4001.pdf

2 Wire & Cable

An overview of the most relevant technologies in HFFR cable compounding

2.1 INTRODUCTION

In the discussion of preventive fire safety, cables hold a position of high attention. The reason is that nowadays, cables can be found everywhere, in buildings, mass-transport and even within your cell phone. In addition to the concerns in regard to the flammability of cables, the actual smoke generation during a fire scenario has gained more and more interest over the last 25 years within the wire and cable requirements, as well as topics such as smoke toxicity and corrosivity.

The excellent performance of so called Halogen-free, flame retardant (HFFR) or low-smoke, zero Halogen (LSFOH) cables versus traditional cable designs especially in regard to smoke density, smoke toxicity and acidity have successfully addressed these concerns with safer and ecologically acceptable cable compounds.

2.2 HISTORY AND STANDARDS DEVELOPMENT IN RESPECT TO DEVELOPMENTS IN THE AREA OF HALOGEN-FREE FLAME RETARDANCY

In the last 30+ years the usage of so called HFFR compounds in Wire & Cable applications have been driven by several major incidents, in which mostly the smoke density and the smoke toxicity in case of a fire in a highly populated area has caused numerous casualties, see Figure 4.

In addition, the awareness of the impact of flame retardant polymers on our environment, especially in case of "end-of-life" scenarios has become an additional aspect of the design of flame retardant cables. Nowadays the conformity of cables and wires with WEEE[11] and RoHS[12] is a further requirement for flame retardant cable compounds.

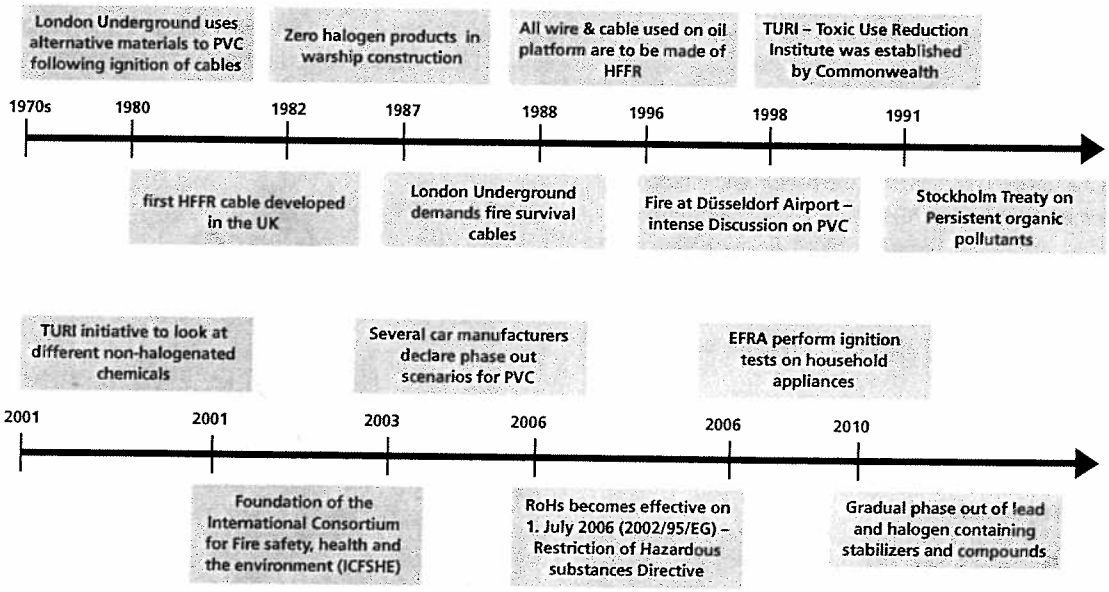


Figure 4: Key events which lead to the development of halogen-free cable development (Nabaltec)

11 *Directive 2002/96/EC on Waste of Electric and Electronic Equipment*

12 *Directive 2002/95/EC on Restriction of certain hazardous Substances in Electric and Electronic Equipment*

2.3 FLAME RETARDANTS USED FOR HFFR COMPOUNDS

The following table gives a general overview of the different flame retardants used in HFFR cable compounds.

Flame retardant	*Polymers*	*Applications and effectiveness*
Aluminium-tri-hydroxide **(ATH)** Magnesium-dihydroxide **(MDH)** Boehmite **(AOH)** (aluminium-oxide-hydroxide)	Low density polyethylene Ethyl vinyl acetate Polyolefins	In fire, these mineral FRs decompose, absorbing energy, releasing water (reducing fire intensity and diluting fire gases), and causing charring (fire barrier)
Phosphorus flame retardants	Used in fire resistant coatings for cables	The coatings form a charred foam layer on the cables
Zinc borate	Synergist with ATH	
Red phosphorus	Polyolefins	
Phosphate esters (e.g. Tricresyl Phosphate TCP)	Rubber	Flame inhibition and charring fire resistance properties of phosphorus
Melamine cyanurate, melamine phosphate,	Polyamides Polypropylene	A low dosing between 7–15 % results in polymer decomposing (PA) without flaming
Intumescent products based on Ammoniumpolyphosphate (APP)	Polyolefins, Thermoplastic Elastomers	With loading of 15–30 % new developed products can achieve highest fire safety standards (UL 94 V0) by formation of an insulating fire barrier

Table 1: Overview of the different flame retardants used in HFFR cable compounds.

In the following sections, the mechanism and function of aluminium hydroxide (ATH), aluminium-oxide-hydroxide (AOH), magnesium hydroxide (MDH) and nanocomposites will be discussed, as these flame retardants are by far the most important ones in regard to HFFR cable compounds by volume and variety of application within the cable industry.

2.3.1 THE MECHANISM OF METAL HYDROXIDES AS FLAME RETARDANT

Metal hydroxides are

- Halogen-free
- Environmentally friendly
- Non-toxic
- Not volatile

→ Substantial reduction of smoke
→ No corrosive or toxic decomposition products
→ Reduction of subsequent damages

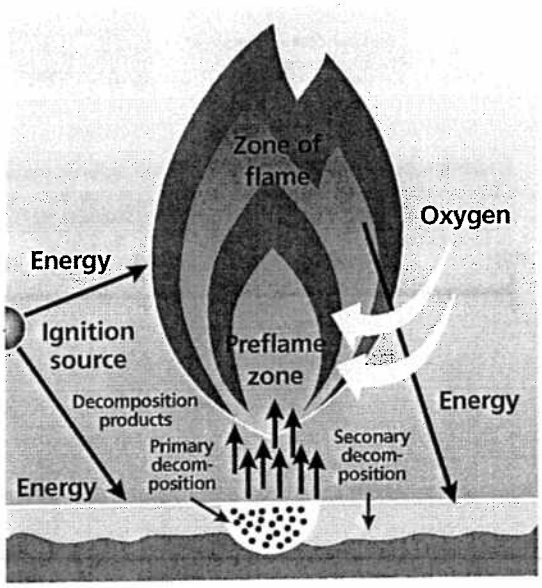


Figure 5: Flame retardancy mechanism of metal hydroxide (Nabaltec)

The function of metal hydrates as flame retardants is based on physical and chemical processes. The schematic drawing shows the involved processes of a metal hydroxide filled polymer in case of a fire. In the presence of an ignition source – a flame or a hot object – the thermal decomposition of the metal hydroxide into metal oxide and water according to the reactions A to C takes place:

(A) 2 $Al(OH)_3$ + 1075 kJ/kg → $Al_2O_3 + 3H_2O$

(B) 2 AlOOH + 700 kJ/kg → $Al_2O_3 + H_2O$

(C) $Mg(OH)_2$ + 1220 kJ/kg → $MgO + H_2O$

During this process, energy is detracted from the ignition source, as the decomposition is an endothermic reaction. At the same time, the released water vapour cools the surface of the polymer and particularly dilutes the concentration of burnable gases in the surrounding area. The remaining metal oxide residue has a high internal surface where sooty particles, respectively polycyclic aromatic hydrocarbons are absorbed. Additionally, the oxide residue acts as a barrier, disabling the further release of low molecular weight decomposition products as well as a heat barrier protecting the polymer against further decomposition. Depending on the decomposition temperature of the metal hydroxide, the usage as flame retardant filler in cable compounds is restricted (see Figure 6). The maximum processing temperatures range from 200 °C (ATH) to 320 °C for MDH and 340 °C for AOH.

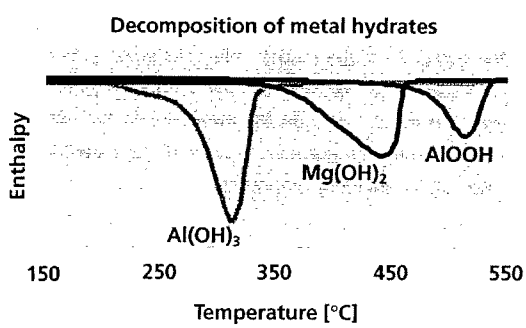


Figure 6: Decomposition of metal hydroxides versus temperature (Nabaltec).

2.3.2 HOW TO ACHIEVE FLAME RETARDANCY WITH METAL HYDROXIDES

The most commonly used test to describe the flammability of a cable compound is still the Limiting Oxygen Index (LOI) in accordance with ISO 4589. This test describes the minimum concentration of oxygen in an oxygen/nitrogen mixture which is just sufficient to support the combustion of a vertically oriented specimen. At a lower oxygen concentration, the flame is extinguished. High LOI values thus indicate high flame retardancy or low flammability. Figure 7 shows the LOI values for EVA (Poly-ethyl-co-vinyl acetate) with varying wt% concentrations of Aluminium hydroxide (ATH), Aluminium-oxide-hydrate (AOH) and Magnesium hydroxide (MDH)

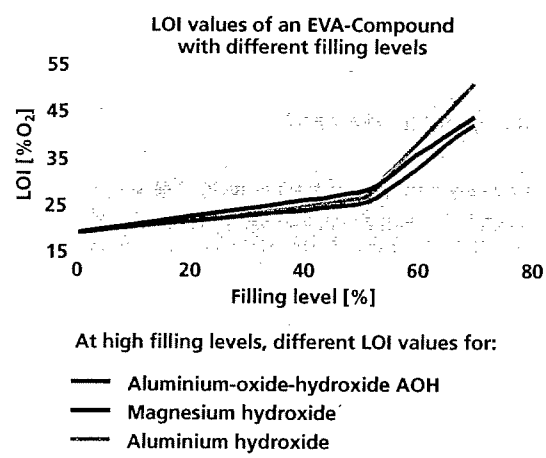


Figure 7: LOI values of an EVA compound with different filling levels (Nabaltec).

Experience shows that LOI values of at least 30 % oxygen are necessary to fulfil the basic flame retardancy requirements in a wide range of applications. In the example given here this corresponds to a filling level of around 55 % by weight in EVA. For more stringent standards far higher values are required. The initially very flat curves illustrate that the physical mechanism requires a minimum concentration of flame retardant agent which is higher than for products with specific chemical reactions such as phosphorus containing flame retardants.

2.4 CURRENT DEVELOPMENTS IN THE AREA OF METAL HYDROXIDES

2.4.1 PROCESSABILITY

One downside of the use of metal hydroxides is the high filling level which is required to achieve a basic flame retardancy for a cable compound. Therefore a lot of work has been spent on the improvement of either the efficiency of metal hydroxides as flame retardants and on the processability of such compounds by adjusting the metal hydroxide properties such as particle size distribution, bulk density or oil absorption. The major goal of these developments has been and still is to improve the extrusion behaviour of such metal hydroxide based compounds, thus manufacturing cost both in compounding and cable extrusion can be reduced. To achieve this goal, basically three different options are investigated:

2.4.2 SURFACE TREATMENT

Historically, the usage of surface treated fillers is a well known technology to improve the incorporation of a mineral filler into a polymer matrix. Due to the improved interaction between coated filler and polymer, not only the mechanical properties of the compound improved but also the compound viscosity can be reduced. This improves the processing behaviour during compounding and cable extrusion.

Whereas for magnesium hydroxide the usage of surface coated grades is essential for the mixing behaviour of the magnesium hydroxide and the achievable compound properties, the usage of surface treated aluminium hydroxide and boehmite is getting less and less common.

In addition to the extra cost of surface treating metal hydroxides, one has to be careful in regard to the selection of the proper surface treatment, e.g. vinyl silane versus amino silane, as the nature of the surface treatment may also have an impact on the long-term mechanical properties of the compound as well as the electrical properties, especially the water absorption can become problematic.

2.4.3 NANOCOMPOSITES

A good deal of research work is being carried out on nanoparticles and their contribution in the field of plastics. Polymers reinforced with as little as 2 % to 5 % of these particles via melt compounding or in-situ polymerization exhibit dramatic improvements in thermo-mechanical properties, barrier properties and flame retardancy. They also can outperform standard fillers and fibres in raising heat resistance, dimensional stability and electrical conductivity.

The two types of nano-fillers that have been most widely discussed and the first to break into commercial use are nanoclays and carbon nanotubes. Both must be chemically modified with surface treatments in order to achieve the fine dispersion and resin coupling required to derive maximum benefit. Both of these nano-fillers have demonstrated improvements in structural, thermal, barrier and flame retardant properties of plastics. Carbon nanotubes also enhance electrical conductivity.

For HFFR cable compounds, nanocomposites based on so called modified nanoclays (organoclays) are the most commonly used ones. In these organoclays the layered silica (montmorillonite or hectorite) has been modified with organic salts such as tetra-alkylammonium salts to improve the compatibility with polymers in order to generate polymer-layered silicate nanocomposites.

For wire and cable applications organoclays are normally used in combination with traditional flame retardants such as ATH and MDH because compounds containing only organoclays are not fulfilling the required flame retardancy. So far the usage of organoclays is nearly entirely within EVA based cable compounds, with filling levels in the range of 3–5 %. The content of the traditional flame retardant in these compounds can be reduced down to 50 % versus 60–65 % in absence of the organoclay.

The function of the organoclay as flame retardant is basically to form a stable and strong char (barrier) on the polymer surface in case of a fire. This barrier prevents the exposure of further low molecular decomposition products, thus stopping the „refueling" of the fire and works as a thermal insulation preventing further polymer degradation.

2.4.4 *IMPROVED MORPHOLOGY OF THE METAL HYDROXIDE*

Whereas the two previous technologies require the usage of an additional ingredient to improve the processability of the metal hydroxide as such and/or the HFFR compound, most recently a lot of work has been carried out to adjust the particle morphology of the metal hydroxide to obtain better performance. The basic principle behind this work has been to produce a metal hydroxide with much lower oil absorption and more consistent bulk density. The lower oil absorption reduces the compound viscosity, thus extrusion processes can be run substantially faster. Compound viscosities can be reduced by 30 to 50 % [13].

Although the specific gravity of Metal hydroxides used in HFFR Cable compounds is in the area of ~2.5 g/cm^2, bulk densities of the used hydroxides is much lower. These low bulk densities in combination with strong attractive forces between the fine inorganic filler particles lead to poor flow properties and bridge building in the feeding process which limits output rates of continuous compounding processes. Low bulk densities also slow down the filler uptake by the polymer melt and the air, which is entrapped by the melt, has to be removed by vacuum degassing [14]. As shown in Figure 9 a metal hydroxide with more consistent bulk density also gives up to 20 % lower screw speeds in a gravimetric dosing unit commonly used in continuous compounding lines. This difference in screw speed of up to 20 % clearly demonstrates the improved feeding characteristics which consequently enhance the space for further improvements in the entire production process.

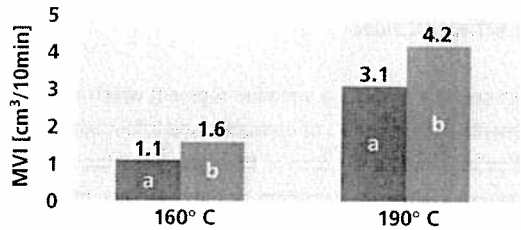


Figure 8: Melt volume rate for EVA (19 % VA) compound filled with 60 wt% ATH, Aminosilane coupled; a) standard ATH, b) improved ATH (Nabaltec)

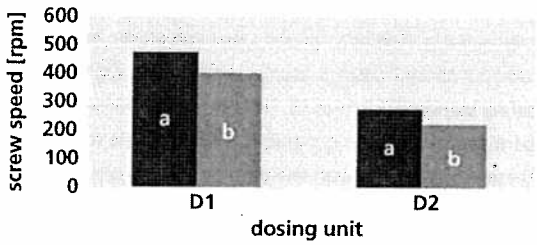


Figure 9: Screw speed of a gravimetric dosing unit with constant mass flow; a) regular ATH, b) improved ATH (Nabaltec)

13 *R. Sauerwein: New generation of aluminium hydroxide flame retardant filler for the wire and cable industry, Cables 2003, Cologne, Germany, March 2003*

14 *R. Sauerwein, M. Klimes: Process Optimized Fine Precipitated Aluminium hydroxide offering outstanding Compound Properties, 53rd IWCS/Focus Philadelphia, PA, USA, 14-17 November 2004*

3 Electric Enclosures

3.1 INTRODUCTION

Electronic enclosures are a market segment which includes primarily the enclosures of consumer and information technology equipment such as televisions, desktop or notebook computers, monitors, printers, copiers, household appliances, etc. These housings are made of different types of polymer resins such as high impact polystyrene (HIPS), acrylonitrile butadiene styrene copolymers (ABS), polycarbonate / ABS blends (PC/ABS) and polyphenylene ether / HIPS blends (PPE/HIPS).

International standards provide that the plastic materials used for these housings usually should meet high fire safety standards such as UL 94 V or similar flame retardant specification. In general, it is not possible to meet these requirements with the pure polymer resins. Therefore, flame retardants are added to the polymer compound. Halogen-free phosphates based flame retardants are of growing importance in this electronic enclosures segment, because the electronics industry tends to move to more sustainable flame retardants. In addition to the required level of fire safety, the used polymer resins have to meet additional criteria such as:

1. **Processability**
   Important for a good processability is a high melt flow, which allows a high throughput
2. **Thermal stability**
   Especially a high Heat Deflection Temperature (HDT) is required
3. **Mechanical properties**
   In particular a high impact strength is requested
4. **Hydrolytic stability**
   A high resistance against degradation caused by moisture is stipulated
5. **Recyclability**
   The used polymer resins must be suitable for easy separation and they should be recyclable with standard processes.
6. **RoHS and WEEE directives**
   The polymer resins have to comply with the RoHS[15] and WEEE[16] directives.

The combination of requirements can be fulfilled by using phosphorus based flame retardants, especially the aromatic phosphate esters presented in Table 2.

Properties	TPP	RDP	BDP
Chemical name	Triphenyl Phosphate	Resorcinol Bis-(Diphenyl Phosphate)	Bisphenol A Bis-(Diphenyl Phosphate)
CAS number	115-86-6	57583-54-7	181028-79-5
Appearance	Solid	Liquid	Liquid
Phosphorus content [%]	9.5	10.8	8.9
Density at 25 °C [g/cm^3]	–	1.31	1.26
Viscosity at 25 °C [mPa·s]	Melting point 49°C	600	13000

Table 2: Halogen-free flame retardants for electronic enclosures

15 *Directive 2002/95/EC on Restriction of certain hazardous Substances in Electric and Electronic Equipment*

16 *Directive 2002/96/EC on Waste of Electric and Electronic Equipment*

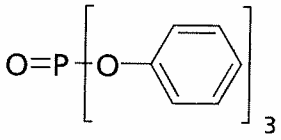
These three phosphorus compounds are halogen-free and are based on aromatic phosphate esters. All three phosphorus compounds can be used in PC/ABS blends as well as in PPE/HIPS blends.

Wt. Loss	2 %	5 %	10 %
TPP	202	220	235
RDP	288	325	360
BDP	273	327	393

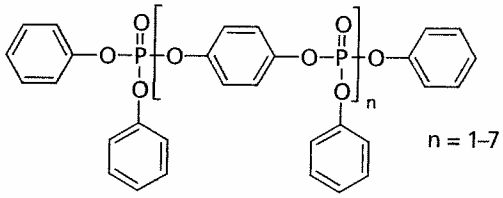
*10 °C /minute ramp rate in Nitrogen

Table 3: Thermogravimetric analysis (TGA) of phosphate esters: The values in the table indicate the temperatures at which a certain weight loss is reached.

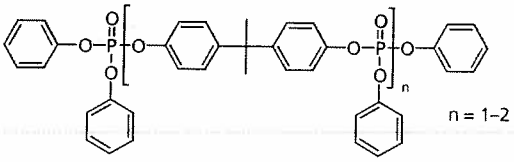
Tri-phenyl phosphate (TPP)

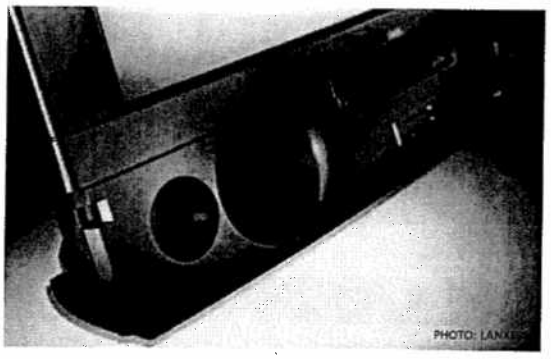


Resorcinol bis (diphenyl phosphate) (RDP)



Bis-phenol A bis(diphenyl phosphate) (BDP)





3.2 PC/ABS BLENDS

TPP, RDP and BDP are suitable halogen-free flame retardants for PC/ABS blends. The required loadings depend on the ratio of PC and ABS in the blend. In commercial PC/ABS blends where the ABS content normally does not exceed 25 % it is possible to achieve a UL 94 V0 rating with these products at 8–15 wt% loading in combination with a co-additive. The co-additive usually retards the dripping. A common anti-dripping agent is PTFE with loadings up to 0,5 wt%.

Various results about TPP, RDP and BDP in PC/ABS blends are presented in Table 4 to Table 6.

PC/ABS 4/1	% FR Additive	UL 94* (1.6 mm)
RDP	9.0	V0 (1.5)
BDP	12.3	V0 (1.5)
TPP	14.0	V0 (1.7)

* avg. flame time

Table 4: UL 94 flammability in FR-PC/ABS (4/1)

R-PC/ABS – V0	Additive	MFI
Composites	Level	g/10 min.
	[%]	260°/2.16 kg
BDP	12.3	26.9
RDP	9	18.7

Table 5: Melt viscosities of V0 rated FR-PC/ABS composites

PC/ABS (4/1)	FR Level	Tensile Strength	Flexural		HDT	Notched Izod Impact
			Modulus	Strength	1,80 MPa	
Flame Retardant	[%]	[N/mm^2]	[MPa]	[N/mm^2]	[°C]	[J/m^2]
RDP	9	53.3	1586	81.4	83.3	651
BDP	12.3	55.6	1655	84.8	81.4	496
TPP	14	46.0	2620	82.7	67.8	123

Table 6: Physical properties of UL 94 V0 rated FR-PC/ABS

3.3 RECYCLABILITY OF FR-PC/ABS COMPOSITES USING NON-HALOGEN FLAME RETARDANTS

The European WEEE (Waste Electrical and Electronic Equipment, 2002/96/EC) Directive is an example of regulations which force producers to consider the full life-cycle of manufactured goods. Plastic components not recycled directly are stripped of hardware, washed, granulated and recycled back into the market for use in a similar or completely different application. The WEEE directive bans recycling of composites containing hazardous heavy metals and brominated flame retardants back into the feed stream. Current waste technology prefers not to have halogenated additives in this feed stream as it may limit or "poison" the subsequent generation of products. Although the U.S. and other regional markets do not have similar regulations, many manufacturers/fabricators are global producers and prefer to standardize their products using similarly sourced materials. By de facto, these companies force these regulations and the practice of recycling components becomes a design consideration in the life-cycle of products.

With a new public consciousness over the life cycle of plastics, manufacturers are designing products with the intent to recycle. This is especially true with computer and office equipment manufacturers where both industry and consumers rely on a desktop, laptop and/or a PDA to organize their day to day lives. Because of the fast pace of innovation in this market, hardware becomes outdated very quickly and is replaced with products that are faster, cheaper and smaller but with greater capability than its predecessor. And more mobile: in May 2005, for the first time laptop computers outsold desktop units claiming 53 % of all computer sales[17]. It is these units that are particularly vulnerable to flammability because they carry their own power (and ignition) source. PC/ABS composites are used extensively for housing components in these applications and as a result, are becoming more significant in the plastic waste stream. For many of these systems, some form of flame retardancy either through system design or component materials is used. Due to environmental concerns, many of these systems use non-halogen flame retardants such as triaryl phosphate flame retardants (TPP, RDP or BDP). For current non-halogen options for FR-PC/ABS, Table 7 to Table 9 present properties which are relevant for performance in a realistic recycling program using techniques common to the industry. Because phosphate esters are known to be susceptible to hydrolysis, this study also considers composites utilizing additives found useful as stabilizers.

Additive(s)	RDP	BDP
Cycle 1	V0	V0
Avg. flame time	1	1.1
Cycle 5	V0	V0
Avg. flame time	0.9	1.1

Table 7: Flammability of recycled FR-PC/ABS according to UL 94 flammability (1.6 mm)

17 *"The End of the Computer as we Know it", Wall Street Secrets Plus Newsletter, Vol. 2, No. 58, July 22, 2005*

[J/m]		Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5
BDP	B1	491	491	512	512	532
RDP	R2	619	534	619	534	577

Table 8: Izod impact (3.2 mm) of recycled FR- PC/ABS

ASTM-1238, 260 °C/2 kg.	BDP
	g/10 minutes
Initial BDP	19.0
Recycle 1	20.5
Recycle 3	22.1
Recycle 5	20.9
	RDP
Initial RDP	14.5
Recycle 1	16.3
Recycle 3	17.2
Recycle 5	16.8

Table 9: Recycling influence on melt flow

Hydrolytic Stability: FR-PC/ABS

- Polycarbonate is sensitive to acidic conditions.
- Different phosphate esters have different hydrolytic stabilities.
  - All phosphate esters decompose to acid species especially after exposure to high heat and humidity.
  - Bis-phenol A bridged phosphate FRs are less susceptible to hydrolysis but will show PC polymer degradation eventually.
  - RDP analogs displayed instability earlier in the testing exposure regime but with the addition of stabilizers, substantial improvements are seen.

Summary recyclability:

- Used at typical recycling rates (20 % recyclate), all bis-phosphate FRs used in this study meet industry standards.
  - Retention of flammability
  - Retention of impact properties
  - Stable melt viscosity
- Where hydrolytic stability is an issue, stabilizers can be used.

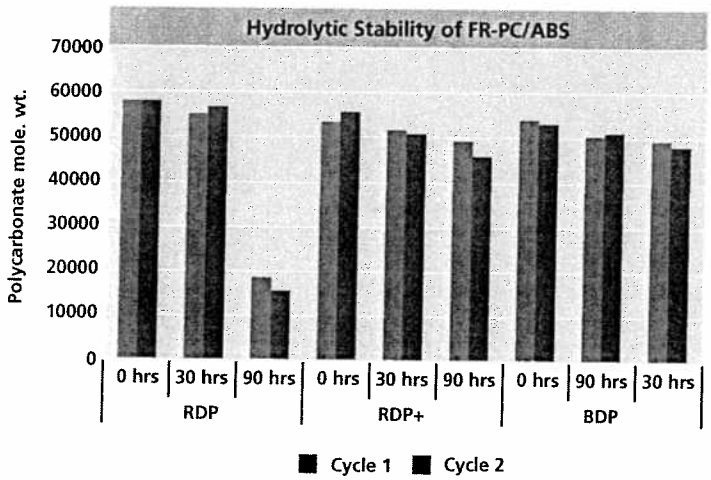


Figure 10: Hydrolytic stability of FR-PC/ABS

3.4 PPO/HIPS

PPO/HIPS blends can be flame retarded with the aromatic phosphates TPP, RDP and BDP. Typical levels of PPE used to achieve a UL 94 V0 rating are 30–70 %; these blends also contain 10–20 % of TPP, RDP or BDP.

Physical property	HIPS	HIPS + Deca + Sb_2O_3	PPO/ RDP	PPO/ RDP
Loading, [wt%[		20	40	35
UL 94 (3.2 mm)		V0	V0	V1
Tensile strength, [N/mm^2]	21.8	20.7	25.2	31.7
Izod [J/m]	80.1	64.1	64.1	69.4
Tg [°C]	88	86	64	84

Table 10: Combustion and physical properties of phosphorus based flame retardants in HIPS

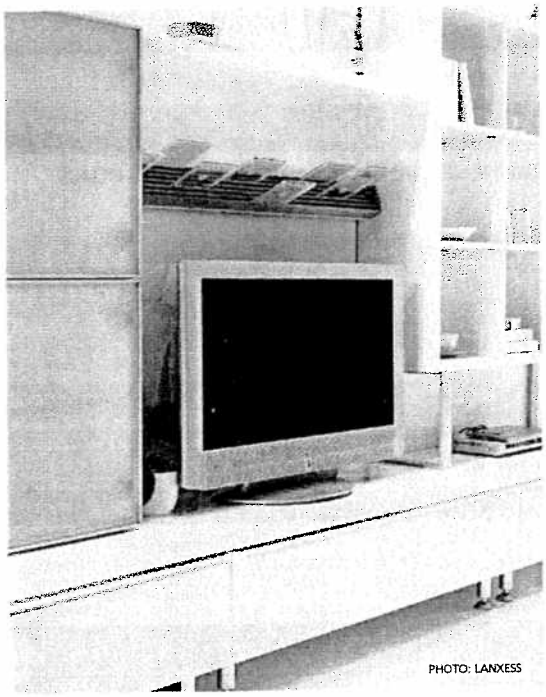


PHOTO: LANXESS

4 Electric Installations and Components

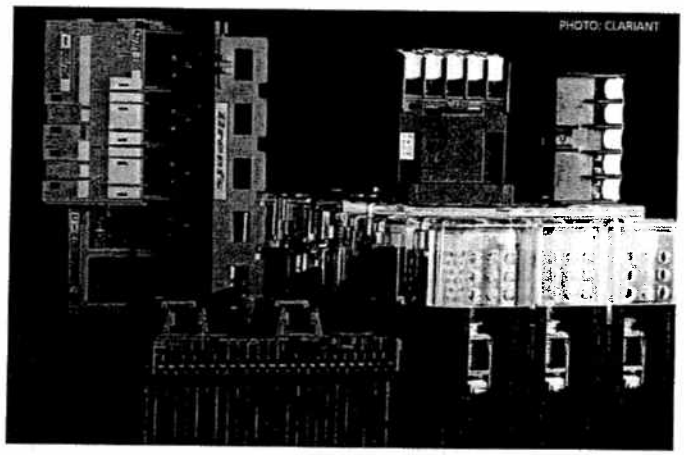
4.1 SCOPE AND MATERIAL REQUIREMENTS FOR ELECTRICAL COMPONENTS

Connectors and switches play an essential role in every electrical component, from the point where electricity enters the home or office to the actual electrical appliance or (industrial) equipment. Whether it is in dish washers, laptop computers, coffee makers, TV sets or in car electrical systems, trains, planes, you find them everywhere where electricity is used.

Types of connectors	Switches and switchgear
Terminal blocks	Low Voltage Switchgear
Crimp-on terminals	Light switches
Insulation displacement connectors	Rotary switches
Plug and socket connectors	
Component and device connectors	
PCB connectors	

Over the years plastics have become ever more important in the development and innovation of electrical equipment. Besides the obvious benefit of offering electrical and thermal insulation, plastics allow designers to develop smaller and lighter parts.

Because of the very broad array of application areas, and the increasing number of different international requirements each of these applications need to meet, it does not come as a surprise that there are many different plastics in use today that are tailored to meet these very different national and international standards. Which plastic is ultimately chosen to design a specific part or component depends very much on the performance of a plastic with respect to mechanical, electrical and fire properties.



4.1.1 MECHANICAL PROPERTIES

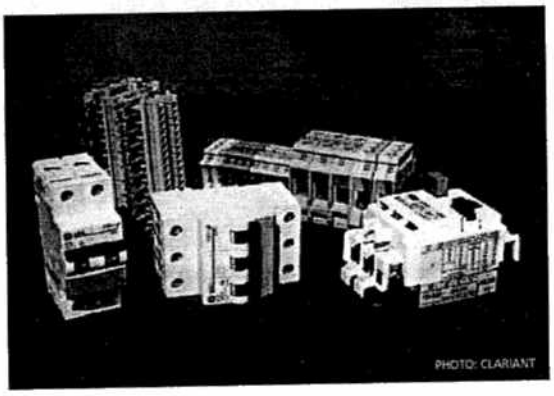
Polyamides for example are often chosen because of their good toughness and rigidity. In connectors this enables the design of so called "living hinges" that need to be opened and closed easily without breaking, whereas toughness is particularly important in snap fits for terminal blocks to allow easy assembly. Polyamides typically also perform well regarding heat ageing, which is important because of the increasing temperatures due to miniaturization of electrical components. PBT on the other hand offers the benefit of good dimensional and hydrolytic stability

4.1.2 ELECTRICAL PROPERTIES

An important electric requirement relates to the insulation efficiency which is expressed as the dielectric constant for alternating currents and signals. The closer this value is to one the better the insulating effect. The other important parameter is the Comparative Tracking Index or CTI (expressed in Volts) which specifies the electrical breakdown (tracking) properties of an insulating material. Tracking is an electrical breakdown on the surface of an insulating material. A large voltage difference gradually creates a conductive leakage path across the surface of the material by forming a carbonized track. The higher the value, the better performing the material is. With some halogen-free FRs the CTI of polymers remains as for the neat polymer.

4.1.3 FIRE RESISTANCE

Most plastics are derived from fossil fuels. As a result plastics have a tendency to easily ignite when exposed to heat or a flame. Therefore fire safety is particularly important for plastics used in components that (potentially) generate heat due to the use of electricity, or in case of malfunctions.



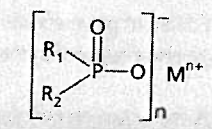
In Europe the fire safety requirements for connectors and switches are determined by technical standards from the International Electrotechnical Commission (IEC). Some of the most important standards include IEC 60898 for circuit breakers, IEC 60947 for industrial control equipment and IEC 60335 for the area of domestic appliances. Besides the IEC standards many of the requirements from the American Underwriters Laboratories (UL) have been adopted in Europe and Asia as well. UL 94 V0 for example, is probably the most commonly used flammability requirement anywhere in the world.

Depending on the end application, for IEC standards approval is based on either material testing or on testing the finished component, whereas under UL tests are always performed on the material only. Despite the differences between these test methods one common denominator in all tests is the specified ignition source and the way a sample is exposed to the ignition source.

Ultimatley choosing the right polymer for an electrical connector or switch evolves around finding the right balance between fire safety on one hand and mechanical and electrical properties on the other hand. A variety of halogen-free flame retardants are available today, that allow compounders to optimize their formulations.

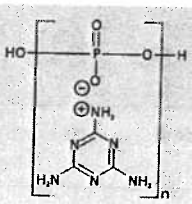
4.2 OVERVIEW OF HALOGEN-FREE FRS FOR ELECTRICAL INSTALLATIONS

Metal phosphinates: These are well suited for glass fibre reinforced polyamides and polyesters and are added at levels of about 20 % – often combined with N-synergists. Key aspects are a high phosphorus content (> 23 %), no affinity to water and a good thermal stability (up to 320 °C) which make them compatible with lead-free soldering operations.



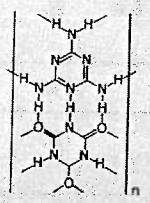
General structure of phosphinates

Melamine Polyphosphate (MPP) is especially suited for glass fibre reinforced polyamide 6,6, where it is added at ca. 25 % for UL 94 V0 performance. It has a good thermal stability (ca. 300 °C). MPP is often used as synergist in combination with phosphorus FRs.



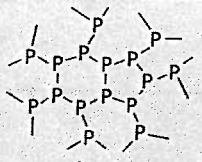
Structure of melamine polyphosphate

Melamine cyanurate (MC) is especially suited for unfilled and mineral filled polyamides. UL 94 V0 can be achieved with 10 to 15 % in unfilled PA and up to 20 % for UL 94 V2 in low glass filled PA 6. MC is often used as synergist in combination with phosphorus FRs.



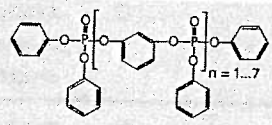
Melamincyanurat

Red phosphorus is a polymeric form of elemental phosphorus. It is used mainly in glass fibre reinforced PA 6,6 at 5 to 8 % addition level. Due to its inherent colour, compounds are limited to red or black colours. In addition, precautions against degradation have to be taken.



Structure of red phosphours

Aryl phosphates and phosphonates: their main use is styrenic blends at 10 to 20 % addition level for UL 94 V0. They are often used as co-components in FR-formulation. Their limitations are possible plastisicing effects and a certain volatility at high processing temperatures. Blooming can have a negative influence on electrical properties.

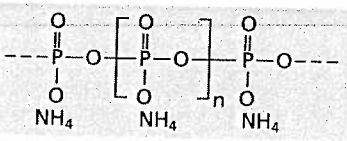


e.g. RDP

Magnesium hydroxide (MDH): high filler levels of about 45 to 50 % are necessary to reach UL 94 V0. Because of its limited temperature stability, it is mainly used in low glass fibre PA 6.

$Mg(OH)_2$

Ammonium polyphosphate in combination with nitrogen synergists can be used in polyolefins at addition levels of ca. 20 % to 30 %.



4.3 POLYMERS USED IN ELECTRICAL COMPONENTS AND SUITABLE FR SYSTEMS

The following table presents an overview of typical technical properties which can be achieved with halogen-free flame retardants in different polymers and with different glass fibre contents. The values are meant for orientation only, because the exact properties depend on the specific polymer used, additive packages and processing conditions.

	glass fiber [%]	halogen-free FR	tensile strength [N/mm²]	notched impact [kJ/m²]	CTI [V]	GWIT [°C]	UL 94
Polyamide 6	0	melamine cyanurate	~ 75	~ 4	600	> 775	V0
	30	metal phosphinate + N-synergist	~ 160	~ 15	600	750–775	V0
Polyamide 6,6	30	metal phosphinate + N-synergist	~ 150	~ 14	600	750–775	V0
	30	red phosphorus	~ 160	~ 18	600	675–775	V0
	30	melamine polyphosphate	~ 140	~ 12	400	675	V0
HTN	30	metal phosphinate	~ 140	~ 8	600	775	V0
PBT	0	metal phosphinate + N-synergist e.g. melamine phosphate	~ 45	~ 3	600	700–775	V0
	30	metal phosphinate + N-synergist e.g. melamine phosphate	~ 110	~ 7	500	750–800	V0
PET	0	metal phosphinate + N-synergist e.g. melamine phosphate	–	–	–	–	V0
	30	metal phosphinate + N-synergist e.g. melamine phosphate	–	–	–	775	V0
Polyolefines	0	intumescent system	10–30	–	600	775	V0
Polyolefines	30	intumescent system	20–60	–	500	775	V0

5 Printed Wiring Boards

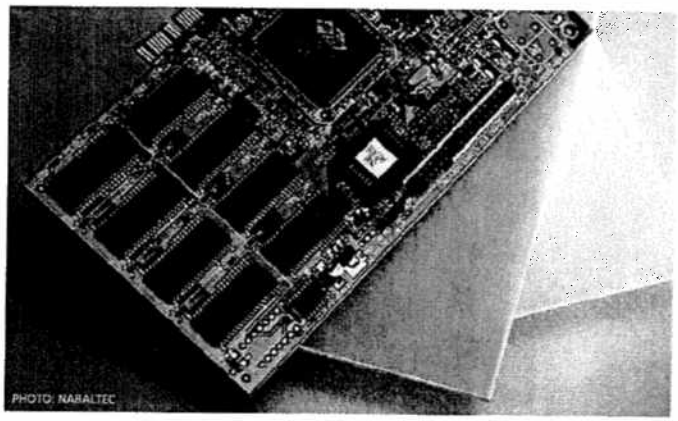
5.1 MARKET ENVIRONMENT AND TRENDS

Electronic devices play an increasing role in our daily life and virtually all electronic items contain a printed wiring board (PWB). For safety reasons, there are requirements for the fire resistance of PWBs, the UL 94 V0 classification being the most widely used specification. Many common PWB materials need a flame retarding system to achieve this classification.

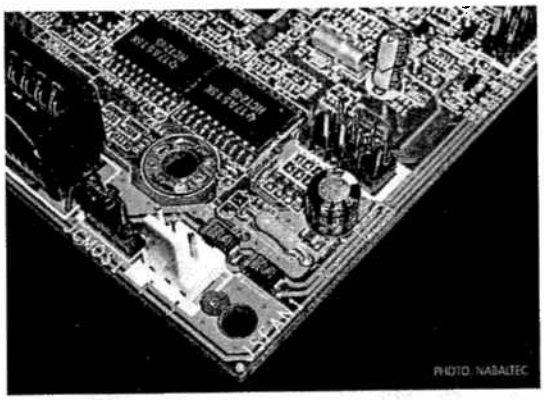
Epoxy resins are widely used as resin backbone for PWB base materials. The European Directive on Restriction of certain Hazardous Substances in E&E (RoHS, 2002/95/EC) has stimulated a change in the base material market, because it bans products that contain lead (Pb) since July 2006, unless the use is specifically exempted. Due to the higher process temperatures for lead-free soldering materials, base materials with higher thermal stability have to be used. For halogen-free base materials with higher glass transition temperature (Tg > 165 °C) epoxy-novolac resins are often employed. These epoxy-novolac resins need less flame retardants in comparison to the normally used diglycidyl ether of bisphenol-A (DGEBA) resins, which makes it easier to achieve the technical requirements with halogen-free flame retardants. The transition to base materials with higher thermal resistance makes it necessary to reformulate base material recipes. Many manufacturers have taken this opportunity to investigate halogen-free FRs when developing new materials.

5.2 TECHNICAL REQUIREMENTS TO FR-4 PRINTED WIRING BOARDS

There are several National Electrical Manufacturers Association (NEMA) classes of fire retardant laminate materials used for PWBs. For example FR-2 is made from a phenolic resin with paper reinforcement. These PWBs traditionally contain triphenyl phosphate as a halogen-free flame retardant. FR-3 boards (paper-epoxy system) are still in use for simple applications. Flexible Printed Circuits (FPC) are used for computer peripherals and mobile devices like cell phones. They are made from epoxy, polyurethane, polyimide, polyester or acrylic resins and usually contain brominated epoxy or phenoxy resins. PWBs of the FR-4 classification are made from epoxy resins with glass fibre reinforcement. They are most commonly used in the electronics industry (about 80 %) and have to fulfil a number of requirements:



- No blisters or delamination after pressure cooker test (PCT)
- No decomposition or delamination during lead free soldering
- Chemical resistance against acid, alkaline and oxidative substances
- No or low water uptake
- Resistance against inner laminate electro migration (CAF)
- Small coefficient of thermal expansion (CTE)
- No or little impact on Tg
- No or little impact on electrical properties in particular Dk and Df
- No or little impact on copper peel strength and inner laminate adhesion
- No impact on resin flow of prepregs for press process
- Optical aspect, no agglomerate for quality inspection



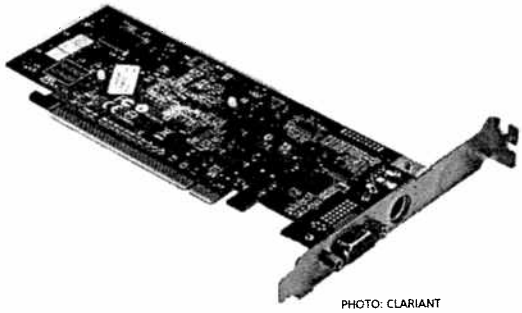


PHOTO: CLARIANT

5.3 NON-REACTIVE FILLERS

5.3.1 METAL HYDROXIDES

These minerals are useful flame retardants, whether used on their own or in synergy with other flame retardants. They act by consuming energy during thermal decomposition, releasing water and forming an oxide layer. Thereby they cool the polymer, dilute the combustion gasses, and shield the resin substrate by the formed oxide layer. Furthermore, this oxide layer adsorbs soot particles leading to low smoke levels. A big advantage of these mineral Flame retardants is their effect to reduce the CTE down to very low values (< 40 ppm are possible).

Aluminium Trihydroxide (ATH)

$Al(OH)_3$

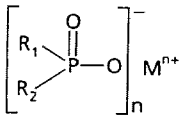
Although concerns can be raised due to the moderate thermal stability (regular ATH starts to decompose at approx. 200 °C), ATH is still used in halogen-free formulations. Rather high loadings are necessary to achieve the necessary fire performance. Therefore, the combination with other FR's is common.

Alumina monohydrate

AlOOH

The transition to lead-free solders with significantly higher temperatures is certainly a challenge for ATH. It may be replaced by alumina monohydrate (Boehmite), which excels in a high temperature stability up to 340 °C. Thus, absolutely no decomposition and water release (water can catalyse conductive anodic filaments, CAF) appears during lead free soldering. Consequently, laminates produced with boehmites feature very high temperature stabilities resulting in very reliable products which are suitable for long term usage as well as usage under elevated temperatures, e.g. in automotive applications ("under the hood"). Due to the lower flame retarding efficiency in comparison to ATH a combination with other halogen-free FR or novolac based epoxy systems is recommended.

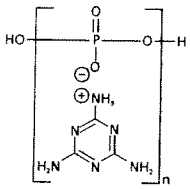
5.3.2 METAL PHOSPHINATES AND POLYPHOSPHATES



Metal phosphinates are a new class of non-halogenated flame retardants which can be used for rigid as well as flexible PWB or other applications around this area. Unlike most other phosphorus containing compounds, the metal phosphinate is not hygroscopic, not toxic, has an extremely low solubility in water and common solvents and does not hydrolyse in the presence of water. The latter point is especially crucial, since the release of phosphoric acid is a not tolerable in E&E applications. Further key aspects are the high phosphorus content (> 23 %) and its good thermal stability (> 300 °C) which makes it compatible with lead-free soldering operations. Electrical properties show virtually no impact on Dk / Df even at frequencies well above one GHz. However, the metal phosphinate can not be used alone to achieve a UL 94 V0 classification, therefore it is usually combined with N- synergist such as Melamine polyphosphate, with modified (phosphorus or nitrogen containing) epoxy resins or blends with other polymers (cyanate esters, benzoxazines, PPE or others).

To obtain a UL 94 V0 rating for laminate thicknesses between 1.6 mm to 0.05 mm, the addition of 15 to 20 wt% metal phosphinate in a varnish formulation are a good starting point. But in every case the dosage of the metal phosphinate depends on the chemical nature of the varnish backbone. For example, in a combination with a phosphorus modified epoxy resin 15-20 phr (parts per hundred resin) of metal phosphinate are recommended. Metal phosphinates are also suitable for flexible printed circuit boards (FPC).

Melamine Polyphosphate has been suggested in combination with other FRs (e.g. phosphinates, minerals). It has a good thermal stability and low influence on Tg.

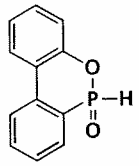


Structure of melamine polyphosphate

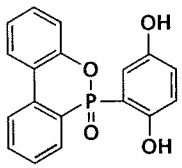
5.4 REACTIVE FLAME RETARDANTS

Reactive FRs are chemically bound to the polymer. This solves most of the migration problems, e. g. vaporisation.

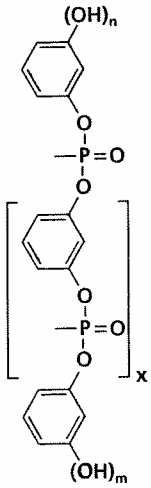
DOPO (Dihydrooxaphosphaphenantrene) is a cyclic hydrogenphosphinate containing a P-H bond. It is mono-functional, but several modifications are possible, which, when properly catalyzed, can be grafted to C=C linkage or reacted with epoxy groups.



Today, DOPO can be regarded as the major building block used to make phosphorus containing epoxy resins (Tg up to 150 °C). DOPO is commercially available from different suppliers and global capacities have consequently increased over the past 2 years to respond to the increasing market demand from PCB.



Poly(1,3-phenylene methylphosphonate): Due to its hydroxyl groups it can react into the polymer and act as a curing agent for epoxies. It is recommended in combination with ATH or AOH. High temperature stability is reported (high Tg, pressure cooker test).



m, n = 0 or 1

5.5 AMOUNT OF FLAME RETARDANT NECESSARY FOR UL 94 V0 CLASSIFICATION

The following tables show the necessary flame retardant levels in order to achieve a UL 94 V0 classification. The experiments were performed with resins without glass fiber reinforcement. Therefore, these values only indicate the range in a final commercial FR 4 material.

Resin hardened with DICY / Fenuron				
Flame Retardant	Phosphorus-content [%]	FR-content [%]	UL 94 (4 mm)	Tg (DSC) [%]
Metal phosphinate	3.2	16.7	V0	167
Poly(1,3-phenylene Methyl-phosphonate)	3.2	23.5	V0	165
DOPO-HQ	1.4	17.0	V0	161
DOPO	0.93	6.5	V0	158
DOPO + 30 % Boehmite	0.42	2.9	V0	168

Table 11: DOW DEN 438 resin hardened with DICY / Fenuron (no glass fibre): Amount of Flame Retardant necessary for UL 94 V0 classification

Resin hardened with phenol novolak / NMI				
Flame Retardant	Phosphorus-content [%]	FR-content [%]	UL 94 (4 mm)	Tg (DSC) [%]
Metal phosphinate	0.6	3.0	V0	172
Poly(1,3-phenylene Methyl-phosphonate)	0.7	4.9	V0	174
DOPO-HQ	0.7	7.4	V0	169

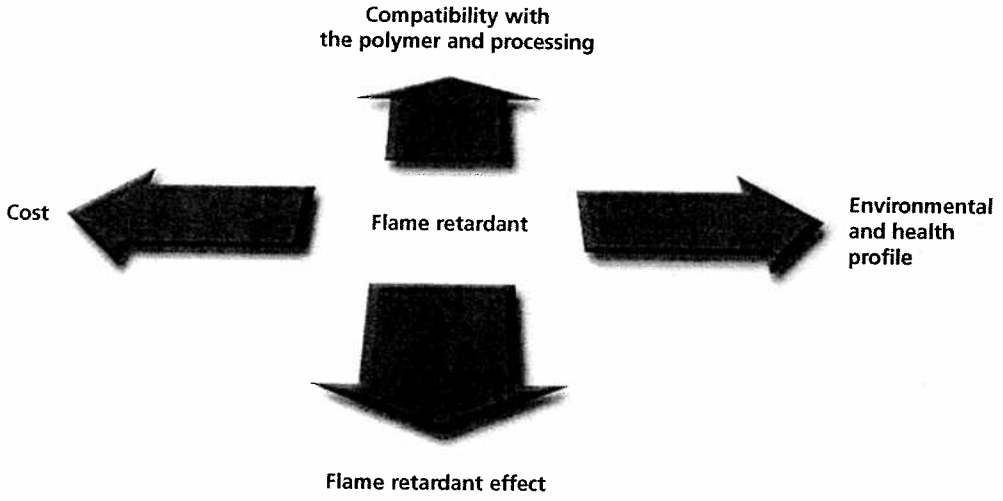
Table 12: DOW DEN 438 resin hardened with phenol novolak / NMI (no glass fibre): Amount of FR necessary for UL 94 V0 classification

6 Future Trends and Innovation

In recent years, halogen-free flame retardants increasingly replaced conventional halogenated flame retardants in plastics used in the E&E sector. This was due to a growing environmental awareness of the population, legal regulations, and an equal ranking of both types of flame retardants in terms of cost and technology.

Costs of brominated flame retardants have increased drastically, and novel, mainly phosphorus-organic flame retardants have been developed and introduced for various materials in E&E applications. As mentioned in the previous chapters, three types of phosphorus-organic compounds were conceived for epoxy resins to be used in printed-circuit boards. Additionally, electric cast resins and coatings were developed to replace the traditional tetrabromobisphenol A, also when using existing technologies. In glass fibre reinforced polyamides and polyesters of electric components on the market, decabromodiphenylether was replaced by halogen-free alternatives based on aluminium phosphinates and melamine salts. New oligomer phosphoric acid esters were developed and are presently applied for electric enclosures. Phosphorus-organic flame retardants have been introduced, as the mode of action of these phosphorus-organic derivatives in both the condensed and the gas phase is increasingly understood. All these halogen-free flame retardants are reactive systems that become part of the polymer network or represent salts or polymer species in the form of additive flame retardants. By reaction or by these low-volatile additives, migration of the flame retardants and, hence, loss of flame retardancy are prevented. At the same time, these additives have a sufficient thermal stability for them to be incorporated easily in the polymers mentioned.

Based on these findings, further development work is being pursued. It is aimed at creating synergistic systems with these substances and other additives like aluminium and magnesium hydroxides, nitrogen compounds, silicon or sulfur compounds. Next to the further improvement of the processability of mineral flame retardants by means of morphology alteration or surface treatments, the synergistic use of classical mineral FRs in sub-micron to nano size is examined and commercialized. Such synergistic systems should require smaller amounts of flame retardants, while the remaining material properties are hardly affected. Furthermore, major efforts are dedicated to developing halogen-free flame retardants for polystyrene based plastics. Examples are HIPS, ABS, SAN, and others. First work relating to HIPS is presented in this brochure (chapter 3).



In principle, all newly developed flame retardants must have a sufficient thermal stability and chemical neutrality for an easy incorporation in polymers and, at the same time, exhibit no tendency to migrate out of the polymer. By adding small amounts of the additive, a high flame-retarding effect should be achieved, while other material properties should not be affected. Two trends can be observed in the development of novel phosphorus-containing flame retardants: More sterically complex groups are incorporated mainly in arylphosphates to enhance the hydrolysis stability of the flame retardants. Another focus lies on the development of nitrogen-containing phosphorus compounds, e.g. phosphamides and phosphacenes, which require less flame retardants due to potential synergistic effects. This trend applies to both polymer enclosures and glass fiber-reinforced materials. For pure polycarbonates, alkali sulfonates and siloxanes are being developed. Already small amounts of these substances result in an excellent flame-retarding effect. In the area of epoxy resins, solutions are being developed for the transport sector based on the halogen-free flame retardants for printed-circuit boards referred to above. The aim is to find efficient flame retardants for epoxy resins that can be processed easily and which are suitable for carbon fiber composites. Phosphorus compounds that primarily act via the gas phase are preferred for this purpose. Innovations are regularly discussed at dedicated international conferences, e. g.:

- International conference on Flame Retardants in London, biannual, next in 2008 *(http://www.intercomm.dial.pipex.com)*
- European Meeting on Fire Retardant Polymeric Materials (FRPM), biannual, next in 2009 *(http://www.frpm07.com/)*
- Fire and Materials Conference, biannual, next in 2009, USA, *(http://www.intercomm.dial.pipex.com)*
- Annual BCC Conference on Flame Retardancy, Stamford, CT, USA *(http://www.bccresearch.com/conferences.htm)*

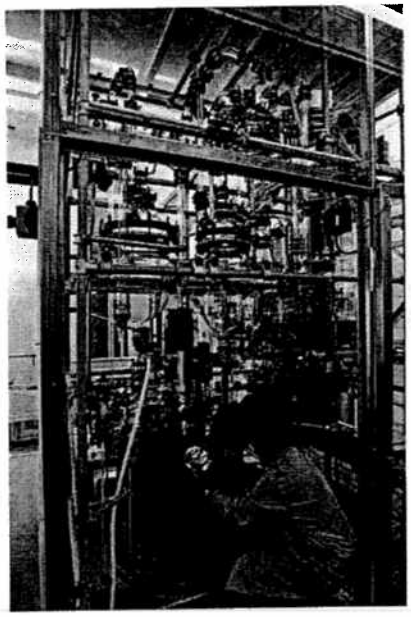


PHOTO: KARLSRUHE RESEARCH CENTRE

REBEKA facility for the synthesis of flame-retarding, halogen-free polymer additives

7 Environmental and Toxicological Properties of Halogen-free Flame Retardants

Whereas the previous chapters focussed on the technical properties of halogen-free flame retardants in various application areas, this chapter discusses their environmental and toxicological properties. It has often been claimed that not enough toxicological and environmental data exist to justify a switch from currently used flame retardants to halogen-free materials. It is true that a wealth of information and studies exists on halogenated high volume products, but this is mainly a consequence of the concerns regarding health and environment and of risk assessment activities. For halogen-free flame retardants, no official European risk assessments have been carried out, because they did not make it onto the so called priority lists for high volume chemicals, which were the basis for carrying out risk assessments in Europe.

Most halogen-free flame retardants have an environmentally friendly profile, which means that they pose no harm to the environment and do not bio-accumulate in biota. In addition they have a low (eco)toxicity profile and will eventually mineralize in nature. Due to these characteristics, none of the halogen-free flame retardants are considered to be PBT or vPvB. For the purpose of this brochure the environmental and toxicological properties for a number of flame retardants have been summarized in fact sheets. The data in the sheets are typical hazard oriented data and should not be used as such to deduce risks. The sheets are divided into a Health and Environmental chapter, and also include an overall PBT / vPvB analysis to indicate the regulatory status. The fact sheets can be downloaded from *http://www.halogenfree-flameretardants.com*.

Manufacturers of flame retardants have started to identify data gaps and commission the necessary tests and studies, because these will also be required by the new European chemicals legislation, REACH (1907/2006/EC). Under REACH not only hazard data, but also data concerning emissions, uses and end of life will be gathered. One company has already commissioned a life cycle emission study[18].

In addition, there have also been various independent, third party evaluations of halogen-free flame retardants as part of environmental programmes initiated by authorities, agencies or NGO's. The majority of these studies specifically assess alternatives to major brominated flame retardants. These reports sometimes come to different conclusions on the same products, because of different criteria used and because not all authors had the same information available. In various studies the data generated by the manufacturers have not been included. Examples are:

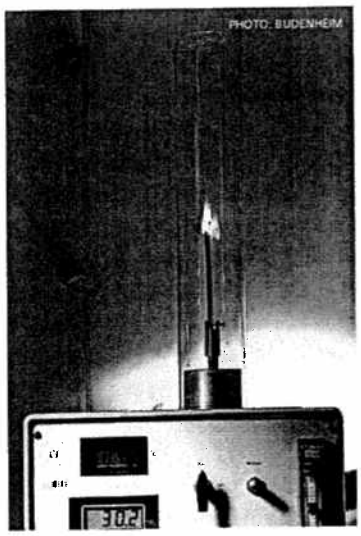
- German UBA 2001: Substituting Environmentally Relevant Flame Retardants: Assessment Fundamentals Volume I: Results and summary overview - *http://www.umweltbundesamt.de/uba-info-medien/dateien/1988.htm*
- Danish EPA: Environmental Project no. 1141, 2007, Deca-BDE and Alternatives in Electrical and Electronic Equipment *http://www2.mst.dk/Udgiv/publications/2007/978-87-7052-349-3/pdf/978-87-7052-350-9.pdf*
- An Overview of Alternatives to Tetrabromobisphenol A (TBBPA) and Hexabromocyclododecane (HBCD). March, 2006 Prepared for: The Jennifer Altman Foundation, By Gregory Morose *http://sustainableproduction.org/downloads/AternativestoTBBPAandHBCD.pdf*
- Illinois Report: "Report on Alternatives to the Flame Retardant DecaBDE: Evaluation of Toxicity, Availability, Affordability, and Fire Safety Issues", Illinois Environmental Protection Agency, March 2007 *http://www.epa.state.il.us/reports/decabde-study/index.html*
- European Chemicals Bureau (2007): Review on production processes of decabromodiphenyl ether (Deca-BDE) used in polymeric applications in electrical and electronic equipment, and assessment of the availability of potential alternatives to Deca-BDE. *http://ecb.jrc.it/documents/Existing-Chemicals/Review_on_production_process_of_decaBDE.pdf*

18 *Marzi T, Beard A (2006): The ecological footprint of flame retardants over their life cycle- A case study on the environmental profile of new phosphorus based flame retardants. Flame Retardants 2006 Conference. Interscience. ISBN 0954121678. pp. 21-30*

8 Common Fire Tests for E&E Materials

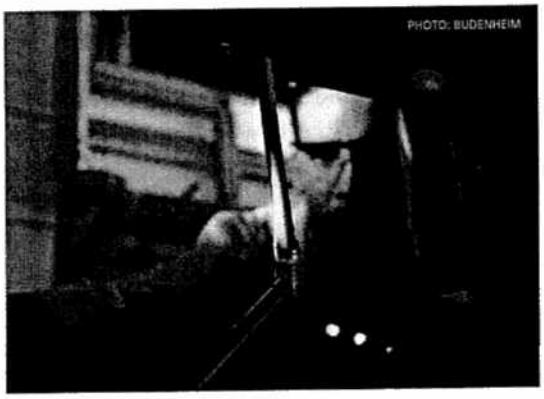
Limiting Oxygen Index (LOI)

In this vertical burn test the specimen is mounted in a cylinder which is supplied with an oxygen and nitrogen mixture from the bottom. The LOI value is the lowest oxygen concentration which will sustain burning of the specimen. A pilot flame from the top is used for ignition. In contrast to other vertical tests, the specimen burns downwards. The LOI value gives a approximate indication how well a material burns, e.g. LOI of around 20 (the natural concentration of oxygen in air is 21 %) and below indicate easily ignitable materials. These standards define the LOI method:
ASTM D 2863,
BS ISO 4589-2,
NES 714.



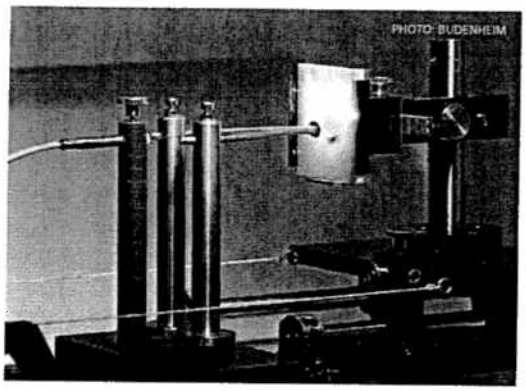
UL 94

The UL 94 test is the most commonly referenced test in the E&E sector. It is a good measure of flammability of materials by a small ignition source like a match, a candle or similar – the pilot flame has an energy output of 50 W. The sample can be oriented horizontally or vertically, the latter being the more challenging test. The classification result depends on how long the specimen continues to burn after removal of the pilot flame and whether a cotton piece below is ignited by flaming droplets. The test is defined in these standards:
Underwriters' Laboratories (UL) 94,
ASTM D 3801,
IEC 60695-11-10,
IEC 60707,
ISO 1210.



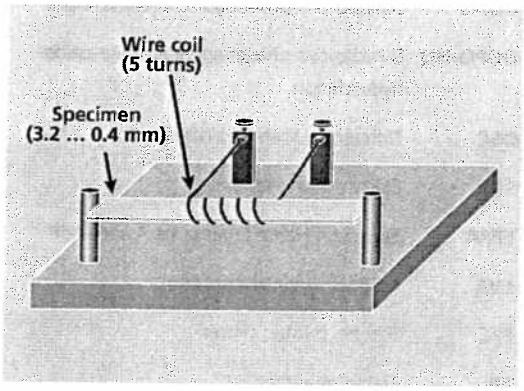
GWT

The glow wire test (GWT) uses a heated resistance wire which is pressed against the specimen for 30 sec, then withdrawn. For a given glow wire temperature, the test criterion is whether the specimen ignites on contact (or in the 30 sec after withdrawal) and whether droplets can ignite a filter paper below the specimen. The glow wire ignition temperature (GWIT) relates to the ignition of the sample where only a flame of very short duration is permitted (< 5 sec). The glow wire flammability index (GWFI) indicates the temperature where the occurrence of flames is less than 30 sec. The test is specified in these standards:
IEC 60695-2-10 ... 13.



Hot wire index (UL 746C)

The hot-wire ignition performance is expressed as the mean number of seconds needed to either ignite standard specimens or burn through the specimens without ignition. The specimens are wrapped with resistance wire that dissipates a specified level of electrical energy. Performance level categories (PLC) from 0 to 5 are defined depending on the time to ignition (> 120 sec to < 7 sec).
http://www.ul.com/plastics/746C.html



Definition of UL 94 Vertical test categories:				
Class	V0	V1	V2	n.r.
Afterflame time	< 10 s	< 30 s	< 30 s	> 30 s
Afterflame time, sum for 10 applications of flame	< 50 s	< 250 s	< 250 s	> 250 s
Ignition of cotton	No	No	Yes	Yes

9 List of Abbreviations

ABS	Acrylonitrile butadiene styrene copolymers
AOH	Aluminium-oxide-hydroxide
ATH	Aluminium-tri-hydroxide
BDP	Bis-phenol A bis(diphenyl phosphate)
BFR	Brominated flame retardant
CAF	Conductive anodic filament
CTE	Coefficient of thermal expansion
CTI	Comparative tracking index
Df	Dissipation factor
DGEBA	Diglycidyl ether of bisphenol-A
DICY	Dicyandiamide
Dk	Dielectric constant
DOPO	Dihydro-oxa-phosphaphenantrene-oxide
DOPO-HQ	Dihydro-oxa-phosphaphenantrene-oxide-hydrochinon
DSC	Differential scanning calorimetry
E&E	Electric and electronic
EFRA	European Flame Retardants Association
EVA	Poly-ethyl-co-vinyl acetate
FPC	Flexible printed circuit
FR	Flame retardant
GWFI	Glow wire flammability index
GWIT	Glow wire ignition temperature
GWT	Glow wire test
HDT	Heat deflection temperature
HFFR	Halogen-free flame retardant
HIPS	High impact polystyrene
HTN	High temperature nylon
IEC	International electrotechnical commission
LOI	Limiting oxygen index
LSF0H	Low smoke – flame retardant – zero halogen
MC	Melamine cyanurate
MDH	Magnesium-dihydroxide
MPP	Melamine polyphosphate
NEMA	National electrical manufacturers association
NGO	Non-governmental organization
NMI	N-methylimidazole
OEM	Original equipment manufacturer
PBT	Persistent, bioaccumulative, and toxic or (different meaning) Polybutyleneterephthalat
PC	Polycarbonate
PCT	Pressure cooker test
PET	Polyethyleneterephthalat
PPO	Polypheneylene oxide
PWB	Printed wiring board (synonymous to printed circuit board)
RDP	Resorcinol bis (diphenyl phosphate)
REACH	Registration, evaluation and authorisation of chemicals
RoHS	Restriction of certain hazardous substances in electric and electronic equipment
SAN	Poly-styrene-acrylnitrile copolymer
Tg	Glass transition temperature
TGA	Thermogravimetric analysis
TPP	Tri-phenyl phosphate
UL	Underwriters Laboratories
vPvB	Very persistent, very bioaccumulative
WEEE	Waste of electric and electronic equipment

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