

**Ninth meeting of the Persistent Organic Pollutants Review  
Committee (POPRC 9)**

**Rome, Italy, 14 to 18 October 2013**



**Frame of the Publication  
“POPs in Articles and Phasing-Out  
Opportunities”**

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# Objective of the publication

- To add understanding on POPs in articles & products.
- To help parties to get a simple overview on POPs free/POPs alternatives linking to the available materials developed by POP reviewing committee, activities of parties, regional centers, industry, NGOs and the research community.
- To update on alternatives where POPRC is not updating information (e.g. on alternatives POP-PBDEs).
- To allow an easy update on POPs free/POPs alternatives information.

*Only an electronic version of the publication will be developed containing links to the reports and resource materials with the option of an easy update when substantial new information e.g. by POPRC is developed.*

# Outline/Scope of the publication

## Content/main chapters of the publication

- 1) Introduction
- 2) Snapshot of information on each chemical in articles and products (PFOS, POP-PBDEs, Lindane, Endosulfane, DDT, PCB and HBCD)
- 3) Current status/case studies POPs free/POPs alternative
- 4) How can we add more understanding on the use and alternatives of POPs in articles
- 5) Conclusions and recommendations

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# Snapshot of information on the chemicals

## Perfluorooctane sulfonic acid (PFOS), its salts and perfluorooctane sulfonyl fluoride (PFOS-F)

Listed under Annex B with acceptable purposes and specific exemptions

Risk profile [Ar](#), [Cn](#), [Fr](#), [En](#), [Ru](#), [Sp](#)

Risk management evaluation (RME) [Ar](#), [Cn](#), [Fr](#), [En](#), [Ru](#), [Sp](#), addendum to RME [Ar](#), [Cn](#), [Fr](#), [En](#), [Ru](#), [Sp](#),

Perfluorooctane sulfonate (PFOS) is a fully fluorinated anion which is used as such in some applications or incorporated into larger polymers. It is also commonly used as a salt. PFOS and its related substances, referred to as “PFOS precursors” which can transform or degrade into PFOS, are members of the large family of perfluoroalkyl sulfonate substances.

Chemical identity and properties

POPRC recommendations

Articles and products

POPs characteristics of PFOS

Alternatives

Guidance (Drafts)

Useful links

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### 3) Case studies/current status for the individual POPs

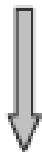
- Information on alternatives from POPRC (PFOS, PBDEs, Endosulfan, Lindane, DDT)
- Information on alternatives and approaches of assessment of alternative other than POPRC (UN organisations, parties; research community, industry, NGOs).
- Case studies might include e.g. chemical alternatives, alternative materials, or alternative processes.

# PBDE - Alternatives and POPs free

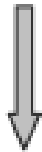
- PentaBDE alternatives document has been developed within the POPRC Process (UNEP/POPS/COP.4/INF/24).
- SC PBDE BAT/BEP guidance has a paragraph on alternatives  
⇒ UN documents are available to refer to.

## OctaBDE/DecaBDE substitution strategies in EEE plastic.

Substance



Material



Product

HIPS resins using *decabromodiphenylethane* instead of decaBDE

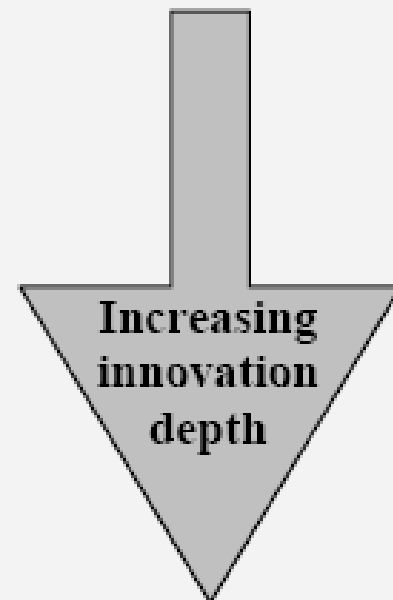
HIPS and PPO blend with phosphorus-based FR

PC/ABS blend with phosphorus-based FR

Separation of high/low voltage

**Green/Sustainable Design!**

Reduce operating voltage





# PBDE – Alternatives

## (Substance substitution; Level 1)

Main use area of POP-PBDEs	Alternative BFR or CFR	Non-halogenated alternatives
Casings of EEE (c-OctaBDE)	c-DecaBDE and decabromodiphenyl Ethane (DBDPE) or tris(tribromophenyl)cyanurate (for ABS and HIPS); HBCD (for HIPS); TBBPA (for ABS); brominated polymers	Phosphorous based halogen-free flame retardants: bisphenol A-bis(diphenylphosphate) resorcinol-bis(diphenylphosphate) (for PC, PC/ABS, and PPE/HIPS)
Small components in EEE (c-OctaBDE)	DecaBDE and DBDPE (for PBT, PET, and PA); brominated polymers	Microencapsulated red phosphorus, magnesium hydroxide, melamine, metal phosphinate (for PA), and Metal phosphinate (for PBT and PET)
Printed circuit boards (c-PentaBDE)	Reactive TBBPA (for epoxy resin); Additive TBBPA (for phenol resin)	Phosphorus based halogen-free flame retardants: dihydrooxaphosphaphenanthrene (DOPO)/ aluminium hydroxide (for epoxy resin); Metal phosphinate/ DOPO/ silica dioxide (for epoxy resin); Polymer phosphonate (for epoxy resin); Flame-resistant thermosets Flame-resistant thermoplastics (under development)
Textile coatings (c-PentaBDE)	DecaBDE (for various fibres); HBCD (for various fibres); Halogenated phosphor organic flame retardants	Inherently flame-resistant synthetic fibres with integrated flame retardants (for PP and PE); Flame-resistant synthetic fibres (for polyaramide); glass fibres; Long-term integration of phosphonium compounds (for cellulose); Intumescent systems (for various fibres)
Polyurethane foam (c-PentaBDE)	Firemaster 550 and 600; Halogenated phosphor organic flame retardants	Various barrier technologies; Substitution of PUR foam in certain applications

Main use areas of c-PentaBDE and c-OctaBDE and some alternative halogenated and non-halogenated flame retardants (Stockholm Convention PBDE BAT/BEP Guidance 2012).



# Paxymer – polymer meeting flammability standards without the use of flame retardants

Was included in 1. POPs Free project (No PBDEs, HBB, HBCD).

- No persistent, bio-accumulating or toxic characteristics (PBT).
- No carcinogenic, mutagenic or reprotoxic characteristics.
- Improved burning performance and elimination of HBr/Smoke.
- Improved recyclability of the product (sustainable production).

(information from CPRAC SC Barcelona)

**THE BURNING PROCESS:**  
Paxymer material vs.  
a brominated material



Paxymer material



Brominated material



# HBCD - Alternatives and POPs free

- Three case studies on HBCD alternatives:
  - “Chemicals in products - Alternatives to the use of flame retarded EPS in buildings” (Norwegian EPA for POPRC).
  - USEPA activities under the „Design for the environment“ framework <http://www.epa.gov/dfe/pubs/projects/hbcd/about.htm>
  - EU-funded SUBSPORT project report „Specific Substances Alternatives Assessment – Hexabromocyclododecane”.
- Other relevant new information will be integrated (e.g. POPRC9).



# PFOS – Alternatives and POPs free

## Reference to the the work of POPRC:

- Guidance on alternatives to perfluorooctane sulfonic acid, its salts, perfluorooctane sulfonyl fluoride and their related chemicals (ongoing work).
- Alternatives for PFOS in open applications (2013).

Based on POPRC recommendation on certain applications COP 6 request parties and observers to provide information on use of PFOS or its alternatives and on quantities of PFOS used for:

- (i) Aviation hydraulic fluid;
- (ii) Chemically driven oil production;
- (iii) Electric and electronic parts for some colour printers and colour copy machines.

The publication can be easily updated with information coming from this process or add reference to POPRC document.

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## 4) How can we add more understanding on the use and alternatives of POPs in articles ?

- **Currently lack of data on POPs in articles:**
    - No/scarce data on PFOS in carpets, aviation hydraulic etc.
    - On the presence of PBDE in waste/recycling flow.
  - **Challenge on monitoring** of POPs in articles to conclude in an “accredited” manner on POPs content and on “POPs free”:
    - Global lack of standards to measure POPs in articles.
    - Lack of monitoring capacity in developing countries/countries with economies in transition.
- ⇒ Challenge/need to develop monitoring (optimizing resources).  
(Involvement of regional centers in monitoring in regions?)
- **Other monitoring approaches** (custom approaches, industry approaches).

# Referencing to Guidance on screening of newly listed POPs in products and articles (Draft)

Paragraph in publication referencing to the monitoring guidance highlighting some key features of the monitoring guidance:

- Provide guidance and monitoring strategies on screening of the POPs content in articles and products in use and in the recycling streams for those POPs listed in 2009 and 2011.
- Where available, best practice case studies for key articles/products possibly containing POPs listed in 2009 and 2011 were referenced in the respective chapters. A selection of these case studies on monitoring POPs in articles can also be referred in the publication (e.g. the screening of PFOS in articles by SCC China).

## Guidance on Sampling, Screening and Analysis of Persistent Organic Pollutants in Products and Articles

Relevant to the substances listed in Annexes A, B and C  
to the Stockholm Convention on Persistent Organic Pollutants  
in 2009 and 2011



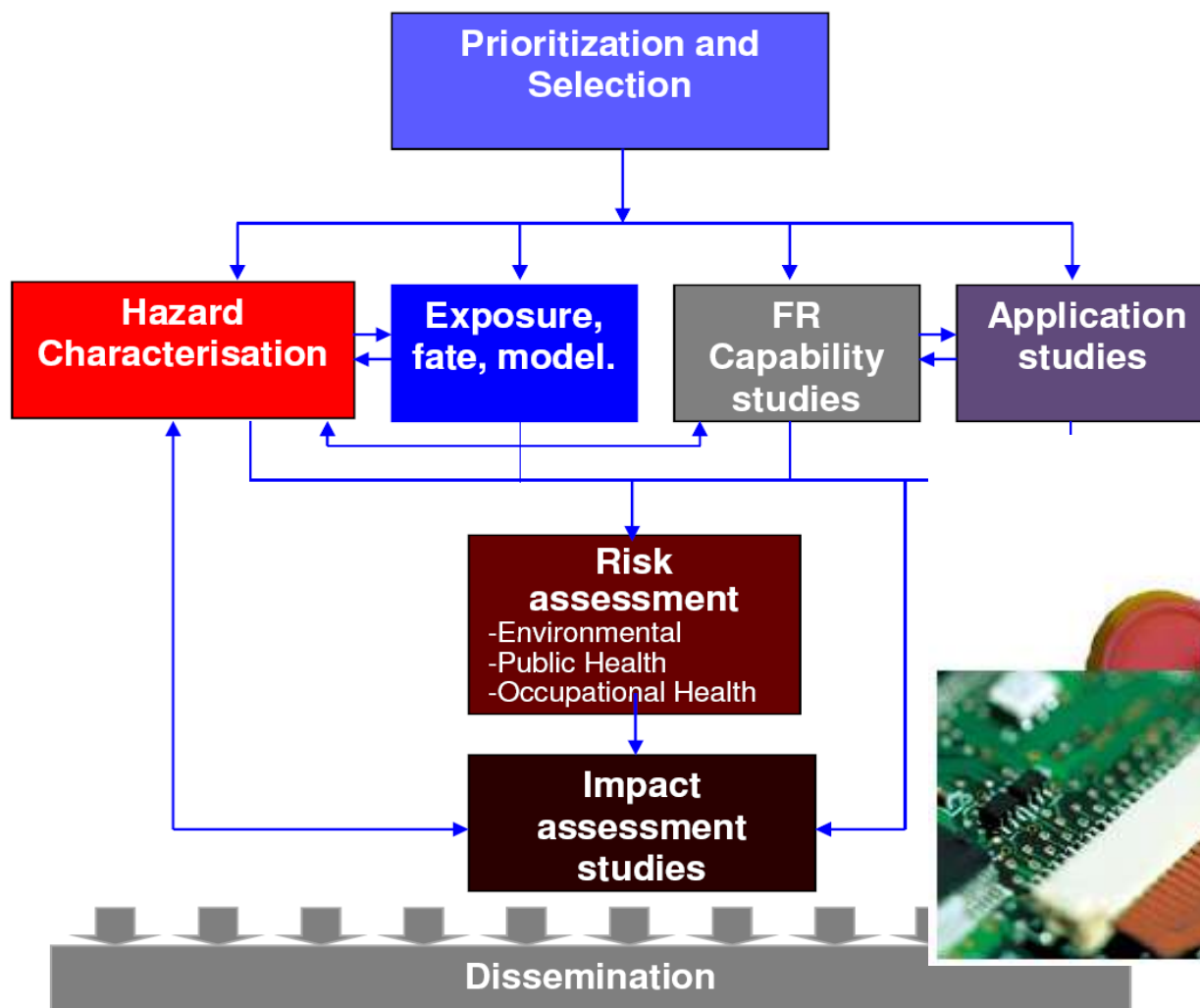
## 4) How can we add more understanding on the use and alternatives of POPs in articles

Approaches of assessment of alternative (in addition to POPRC). There are a range of activities of parties/governments, research community and NGOs on alternative assessment. Examples with relevance/link to POPs alternatives will be considered e.g.:

- **Green Screen approach** US EPA (was used by SCC China for assessment of alternatives to PFOS in insecticide use).
- **SUBSPORT** Internet portal supporting practical substitution. Certain POPs alternatives are addressed (e.g. HBCD; PFOS).
- **ENFIRO project**: European Commission-funded project offers a prototypical case study on substitution options for PBDE/BFR considering Life Cycle Assessment approach.

# European research project ENFIRO: “Study of Environment-Compatible Flame Retardants”

Assessment of PBDE/HBCD/BFR alternatives in selected applications with life cycle assessment for a prototypical approach.



Selected applications:

- Printed circuit boards
- Electronic components
- Injection moulded product
- Textile coatings
- Intumescent paints



<http://www.enfiro.eu/>

# ENFIRO: Assessment of toxicity of BFR alternative flame retardant applications

In parallel to ENFIRO project, toxicological information on halogen free flame retardants have been compiled in a scientific review.

## Persistence, Bioaccumulation, and Toxicity of Halogen-Free Flame Retardants

Susanne L. Waaijers, Deguo Kong, Hester S. Hendriks, Cyntia T. Cousins, Remco H.S. Westerink, Pim E.G. Leonards, Michiel H.S. Kraak, Wim Admiraal, Pim de Voogt, and John		5	Organophosphorus Flame Retardant Compounds and Their Salts .....
1	Introduction .....		5.1 Triphenylphosphate.....
2	Selected HFFRs .....		5.2 Resorcinol Bis(diphenylphosphate).....
3	Characteristics of the Selected HFFR .....		5.3 Bisphenol-A Bis(diphenylphosphate).....
3.1	Physical–Chemical Properties .....		5.4 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide .....
3.2	Environmental Presence and Production Volumes .....		5.5 Aluminum Diethylphosphinate.....
3.3	Persistence .....		A Nitrogen-Based Organic Flame Retardant: Melamine Polyphosphate
3.4	Bioaccumulation .....		6.1 Physical–Chemical Properties .....
3.5	Toxicity .....		6.2 Persistence .....
3.6	Classification.....		6.3 Bioaccumulation .....
4	Inorganic Flame Retardants and Synergists .....		6.4 Toxicity .....
4.1	Aluminum Trihydroxide .....		An Intumescent System: Pentaerythritol.....
4.2	Magnesium Hydroxide, Mg(OH) <sub>2</sub> .....		7.1 Physical–Chemical Properties .....
4.3	Ammonium Polyphosphate.....		7.2 Persistence .....
4.4	Zinc Borate (ZB).....		7.3 Bioaccumulation .....
4.5	Zinc Hydroxystannate.....		7.4 Toxicity .....
4.6	Zinc Stannate .....		Discussion .....
			8.1 Data Availability .....
			8.2 Inconsistency of Data.....
			8.3 Persistence, Bioaccumulation, and Toxicity of the Selected HFFR

Source: Waaijers et al., Reviews of Environmental Contamination and Toxicology 222 (2013)

# First feedback from stakeholders

A comment from the first exchange on the outline of the publication with some regional centers:

- Suggestion to include a paragraph on unintentionally POPs.

This issue will now be considered by referring to case studies available from UN documents:

- Japan government input on HCB in certain pigments (COP 4/5): Suggestion on BAT-levels for HCB in certain pigments.
- Stockholm Convention Dioxin Toolkit BAT category for 2,4-Dichlorophenoxyacetic Acid (2,4-D) and Derivatives with BAT-level for Dioxin content.

Question: At what level is an article/product “POPs free”?

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## 5) Conclusions and recommendations

- Recommendations which have been developed by the POPRC in respect to alternatives to POPs. E.g. on PFOS:
  - Recommendation on specific Applications;
  - Recommendation regarding Information Gaps;
  - Recommendation on Future Work.
- Recommendations/conclusions from the workshop POPs free/alternative WS 23/24. August SC/BCRC China. E.g.:
  - Need of monitoring of POPs in articles in developing country;
  - Assessment of the recycling flows of products and related risks (RiskCycle).
  - More research studies on the life cycle of POPs and the alternatives;
- Elements for consideration from exchange with stakeholders that will be compiled in the frame of developing the publication.



# Thank you for your attention – Questions ?



Stockholm Convention  
on persistent organic  
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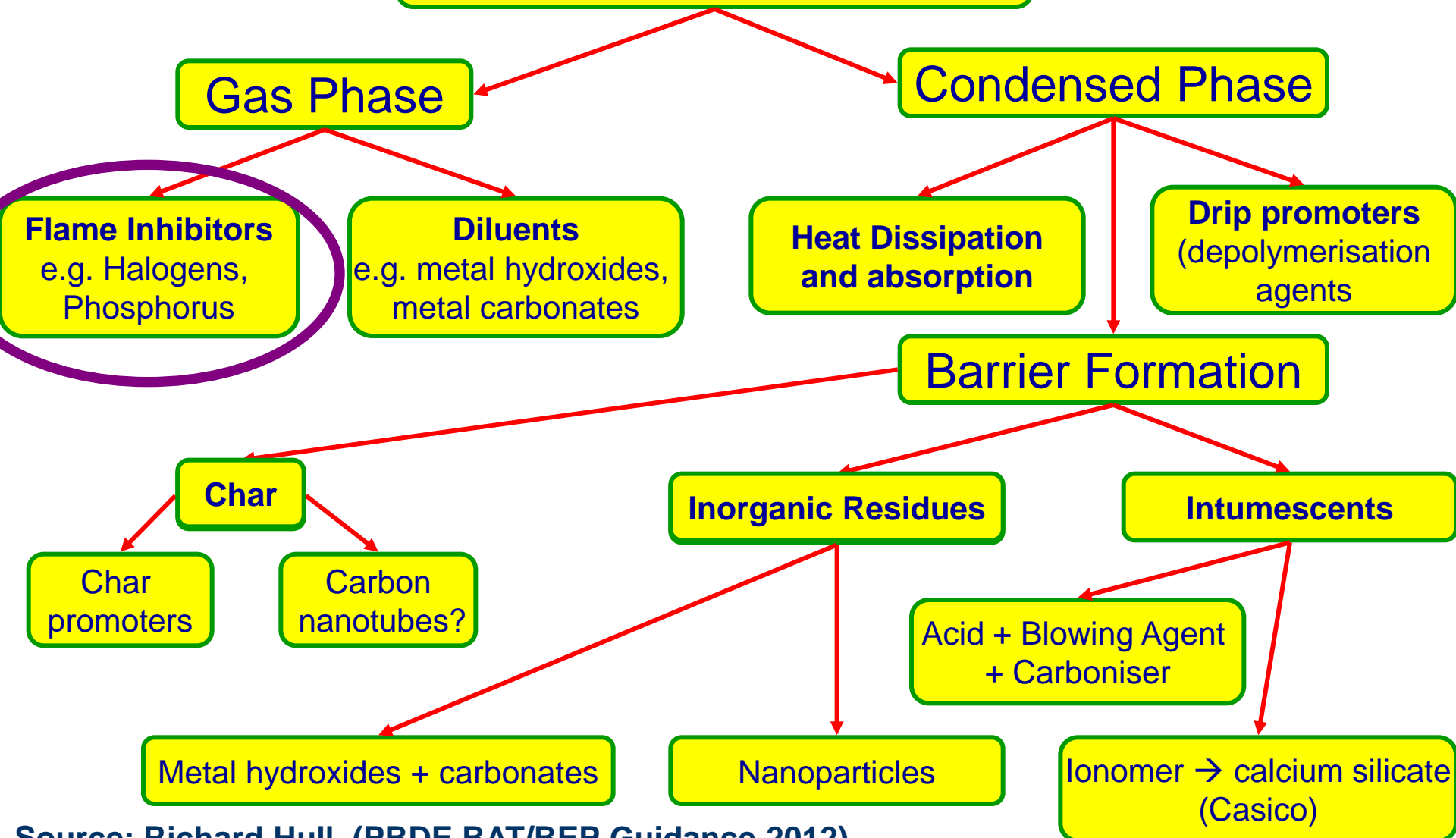
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<http://www.pops.int>  
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# PBDE - Alternatives and POPs free Level 1&2 – Substance & material substitution

## Fire Retardants





# Snapshot of information on the chemicals

## Technical endosulfan and related isomers

Listed under Annex A with specific exemptions

Risk profile [Ar](#), [Cn](#), [Fr](#), [En](#), [Ru](#), [Sp](#)

Risk management evaluation (RME) [Ar](#), [Cn](#), [Fr](#), [En](#), [Ru](#), [Sp](#),

Endosulfan is an insecticide that has been used since the 1950s to control crop pests, tsetse flies and ectoparasites of cattle and as a wood preservative. As a broad-spectrum insecticide, endosulfan is still used to control a wide range of pests on a variety of crops including coffee, cotton. It has been listed with crop-pest list of exemptions.

Chemical identity and properties

POPs characteristics of Endosulfan

Alternatives

Guidance

Useful links