

# *Halogen free laminates: worldwide trends, driving forces and state of play*

EIPC Summer Conference 2005, Stockholm  
10-June-2005



Adrian Beard



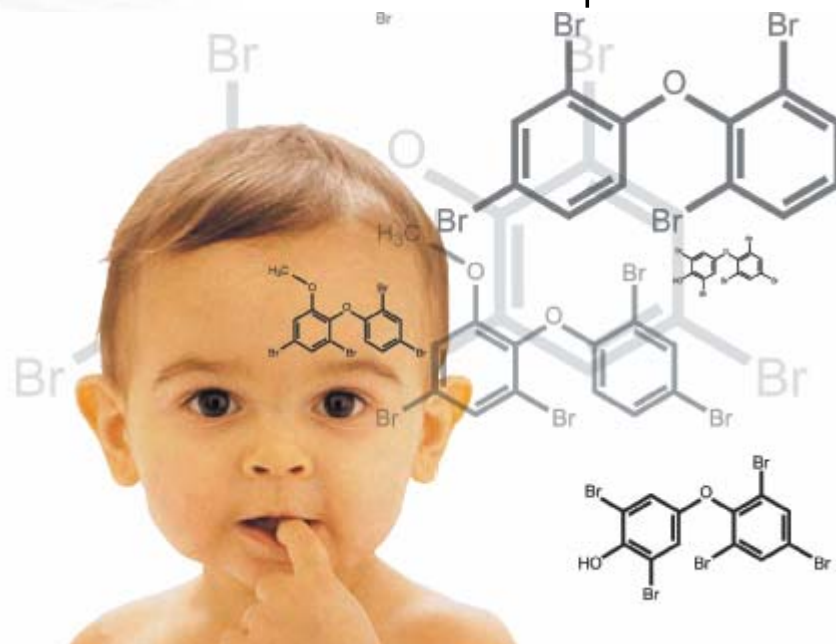
Jérôme De Boysère

# Halogenated FRs between myth and reality

"Green Monster?"



or a matter of sustainable development?



Various and diverging opinions and perceptions...

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Exactly your chemistry.

## *Outline*

- the FR market
- environmental concerns about FRs and electronic waste
- political and legal reactions to concerns
- OEM strategies
- effects on supply chain
- regional trends
- the future

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Exactly your chemistry.

## *Why use Flame Retardants?*



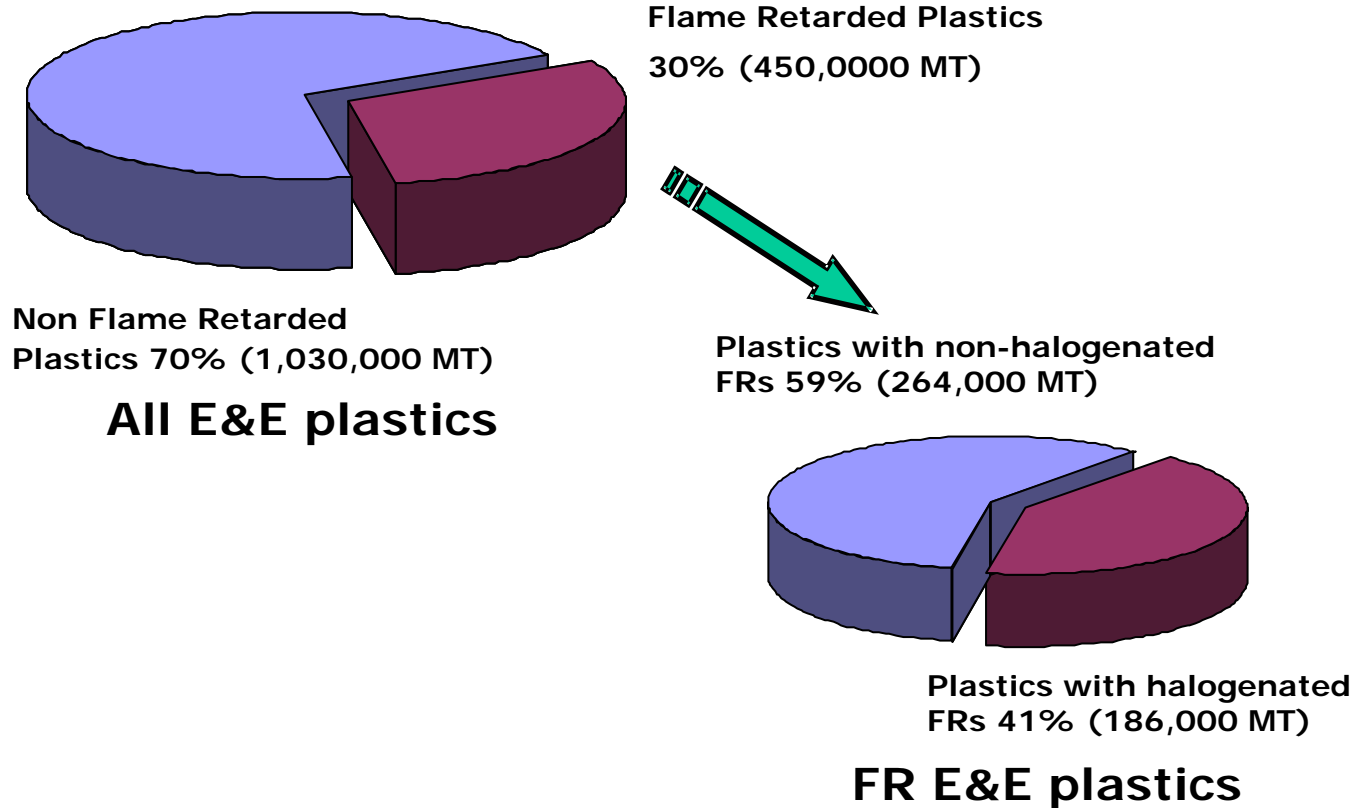
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## The Use of FR Plastics in E&E Consumption in W.Europe - 2000



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## Where are FRs used in E&E? W.Europe - 2000

Majority of the Br-FR consumption is used in IT & Consumer electronics ( 1000 t per year ).

	ATH	MDH	ATO	BFR	CI	HF P	Hal P	N	Total
<b>Office, data processing &amp; Telecom</b>	1,971		3,858	11,797		6,678			24,304
<b>Brown goods</b>	989		625	4,857		4,307			10,779
<b>Other electrical equipment</b>	7,834	1,260	1,801	3,539	283	140			14,857
<b>Household products</b>	4,500		1,269	348		895			7,012
<b>Industrial electrical equipment</b>	9,510		711	1,572			359	1,230	13,382
<b>TOTAL</b>	24,804	1,260	8,264	22,113	283	12,020	359	1,230	70,334

ATH	Aluminium Trihydrate
ATO	Antimony Trioxide
BFR	Brominated Flame Retardant
CI	Chlorinated flame Retardant
HF-PFR	Halogen Free Phosphorus FR
Hal PFR	Halogen Containing Phosphorus FR
N	Nitrogen based FR
MDH	Magnesium Dihydroxide

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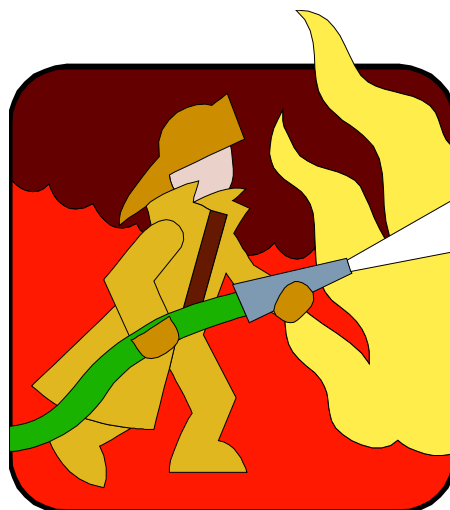
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Source: TN SOFRES Consulting for APME

## *Flame Retardants in the discussion*



- fire safety vs. environment?

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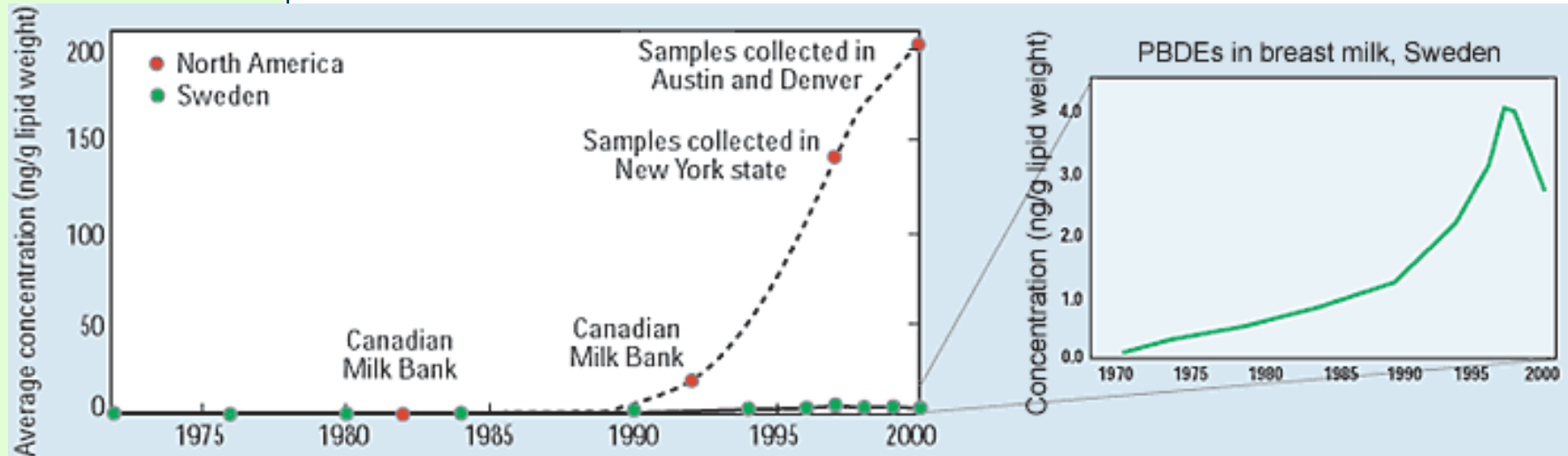
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# *FR and Environmental concerns*

## PBDE Bioaccumulation ./. Persistence in the Environment



Source: Canadian Milk Bank and New York state data: Ryan and Patry; Denver, Colo. and Austin, Tex. data: Pöpke; Swedish data: Norén

published in: Environ. Sci. & Technol.: February 1, 2002 / Volume 36, Issue 3 / pp 50 A-52A

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## German-UBA: Assessment of FRs

I	Phase-out is recommended	Decabromdiphenyl ether Tetrabromo bisphenol A, additive
II	Reduction is expedient, substitution desirable	Tetrabromo bisphenol A, reactive Tris(chloropropyl)phosphate
III	problematic properties; reduction expedient	Hexabromocyclododecane Sodium borate-decahydrate (Borax) Antimony trioxide
IV	No recommendation possible due to gaps in knowledge	Bis(pentabromophenyl)ethane Resorcinol-bis-diphenyl-phosphate Pyrovatex CP new Melamine cyanurate
V	Use is unproblematic	Red Phosphorus Ammonium polyphosphate Aluminium trihydroxide

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Umweltbundesamt (2001), German Agency for the Environment: Evaluation methods for the substitution of environmentally problematic flame retardants. Research report 297 44 542, Band I, II, III.  
<http://www.umweltbundesamt.de>

## *Environmental concerns: what is next?*

- Deca-BDE found in wild life and animals, as well as human milk
- Farm salmon show higher contamination than wild salmon
- Study of way of exposition: food chain ./ air contamination (dust) incl. End of life of FR-products
- Hexabromocyclododecane (HBCD) and Tetrabromobisphenol-A (TBBPA) are increasingly being studied and found.
- Risk Assessment on TBBPA expected by end of 2005

Reclassification as R50/53 appears to be likely?

(Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment.)

## *End-of-life PWB recycling – the theory*

Options for the recycling of PWB material are limited:

- Smelters
  - low waste management costs
  - 80% energy saving for copper recovery
  - but does it comply with WEEE?
  
- Incineration
  - handling in municipal waste incinerators
  - PBDD/F emission within limits for state of the art incinerators

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Source: BSEF

## *PWB recycling - the reality*

- In practice, consumer electronics and IT-equipments are rarely taken back, dismantled and appropriately recycled.
- Significant amounts of e-Waste are exported to countries like India and China (sometimes illegally)
- 21st Century Waste recycled with 19th Century techniques



## *E-Waste and public awareness*

- Several presentations at Electronic Goes Green conference (Berlin, September 2004) – Ex. Greenpeace China

### What is happening in GuiYu now?

---Discovered by Greenpeace China in early 2004



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## *E-Waste and public awareness*

- Several presentations at Electronic Goes Green conference (Berlin, September 2004) – Ex. Swiss EMPA

### **PWB acid washing / burning**



Step 0

Inspecting raw material: PWB (Printed Wiring Boards) with varnish or multilayer

Step 1

remove varnish manually with spate and water. Residues washed away!



Step 2

PWBs submerged in sulphuric acid to remove Cu layer (12hrs)

Step 3

pouring acid to stainless steel tub and boil of the water (firing with PWBs!). Remove Cu-Sulphate crystals for selling.



Step 4

remaining acid solution is poured into plastic drums and iron scrap (for instance Fe wires) is added to fallout Cu.

Step 5

the solution is poured in drums for settling. Cu sludge is recovered. Solution is thrown. Cu is sold.



Step 6

glass fiber residues are stocked (further use unclear). Some cleaning / rinsing processes take place here. water hose runs constantly and dilutes effluents

Step 7

behind the factory wall are rice paddies and vegetable gardens. Effluents end up here.



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## *Impact of environmental discussions*

- European Directives on
  - WEEE: waste electric and electronic equipment (2002/96/EC)
  - RoHS: restriction of hazardous substances in E&E (2002/95/EC)
- Polybrominated Diphenylethers (PBDE)
  - banned according to the RoHS directive as of 2006. **Penta- and octa-BDE** already removed from the market, **however:**
- Deca-BDE positively concluded the RA
  - consequently, ban on Deca-BDE *should* be lifted, **but:**
  - EC proposal to exempt Deca from the RoHS-directive did not achieve the qualified majority (April 2005)



# WEEE

- WEEE (2002/96/EC)
  - separation requirements for plastics containing brominated flame retardants of any kind (incl. TBBPA)
  - collection & recycling targets
- Impact is not clear
  - go halogen free?
  - OEM (consortia) take back and recycle their products?



## *WEEE – Recycling Options*

### ■ Thermoplastics

- many FR thermoplastics can be recycled/reused while maintaining good mechanical properties and keeping the FR performance.
- bromine recovery possible (but economical viability?)
- halogen free alternatives are available for many polymers at an acceptable price-performance ratio

### ■ Thermosets incl. Printed Wiring Boards

- price penalty for halogen free alternatives
- recycling possibilities limited

## *Further developments at political level*

- How the situation will evolve is difficult to forecast
- Discussions are driven by a mix of scientific and emotional behaviors
- Discussions are highly controversial
  - contradictory studies with different results on the same topic
  - case of Deca-BDE
  - Reality is not black or white, but grey in different shades

**Realistically, the pressure on FR should last as long as FR chemicals are found in humans, animals and in the nature.**

- Examples of controversial topics:
  - PWB recycling?
  - benefits of brominated ./.. Halogen free boards?



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## Benefits of halogen free PWB

- study on "Environmental and economic implications of a shift to halogen free printed wiring boards"
  - presented at EGG2004+ by Bergendahl et al.

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### Analysis of brominated flame retardants in circuit boards shows benefit for brominated flame retardant systems

by  
Feb 28, 2005

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#### [Printed Circuit Board Fab](#)

FR-4, Rogers,  
Aluminum PCB  
Protos to Volume

*A study by the Swedish IVF institute(1) compared the costs and environmental implications of halogen-free flame retardants used in the manufacture of printed wiring boards (PWB) to using bromine-based fire safety systems. It concluded that the move to halogen-free flame retardants resulted in initial cost increases of 10-50%. Whilst some material costs would fall if there was widespread uptake of halogen-free flame retardants, overall cost increases related to PWB panel drilling and desmearing would remain.*

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<http://www.emsnow.com/newsarchives/archivedetails.cfm?ID=7887>

Also available at IPC website [www.halogenfree.org](http://www.halogenfree.org)

## *Benefits of halogen free PWB*

The study itself states:

- “the potential improvements [...] with respect to **toxicity is not modelled** due to lack of data.
- “Due to a lack of experience of volume production with halogen-free laminates and a lack of data **it was not possible to assess the environmental and economic effect of the shift or the full product life cycle and the toxicological effects**”.
- “With increasing use the materials cost for halogen-free laminates is expected to decrease and **cost should not restrict the use.**”
- “The findings presented in this paper are based on **one single case study**. [...] The conclusions drawn are only valid for this specific case study and further studies are needed to attain more comprehensive insight [...]”

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## *Ecolabels and Green procurement*

- various national schemes
  - since the late 1970ies, e.g.
- Blue Angel in Germany:
  - restricts halogenated FRs in a number of products, some exceptions for parts < 25 g and recycling
- EU Flower
  - uses risk phrases from classification of chemicals
  - only few FRs are explicitly blacklisted (e.g. PBDEs)
- **TCO Development**
  - wide-spread acceptance in the business electronics sector
  - restricts halogenated FRs
  - manufacturers have to submit environmental and tox data



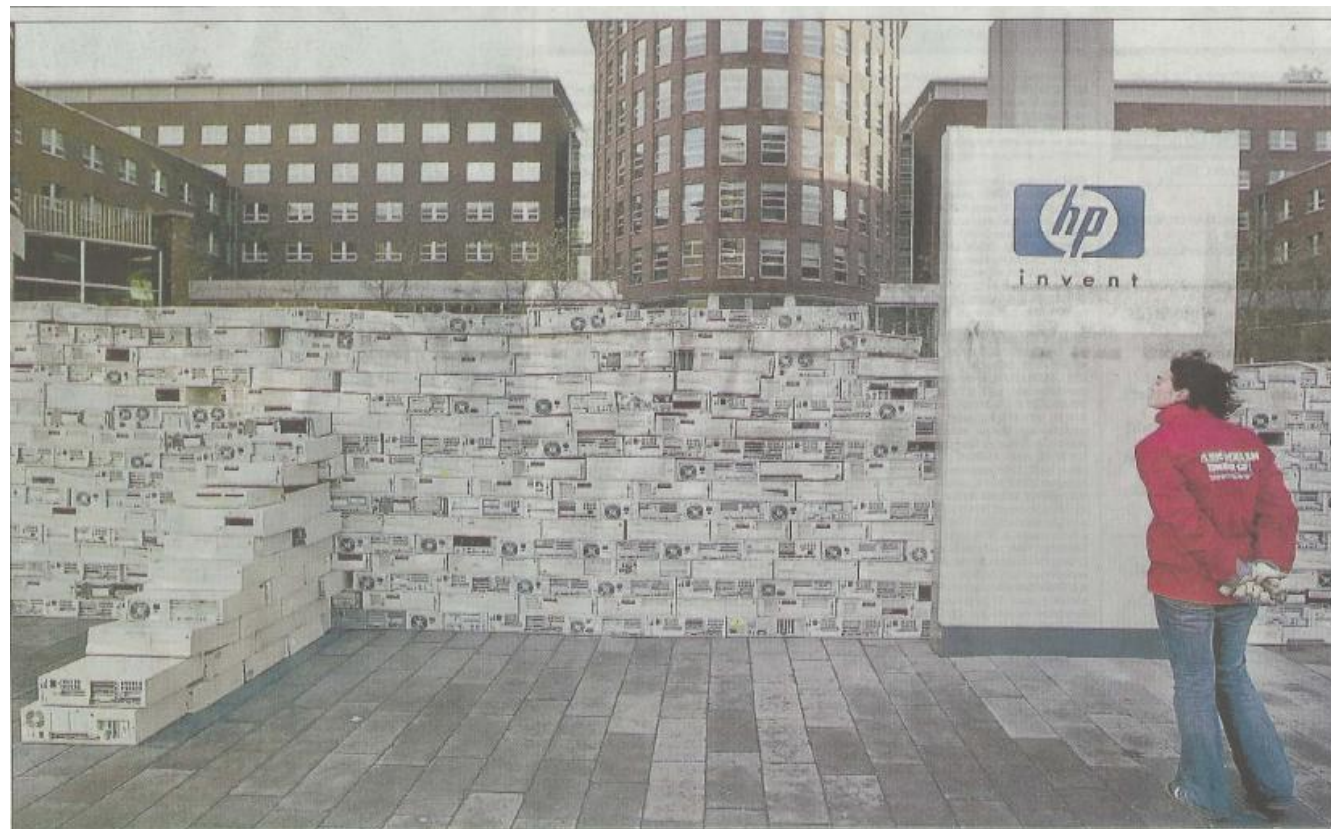


Exactly your chemistry.

## *Impact on OEM strategies*

“the Biggest risk any company faces is the loss of its good name, and you cannot insure against that”

OECD, 2003: Emerging Systemic Risks in the 21st Century



### GREENPEACE BOUWT COMPUTERMUUR TEGEN HEWLETT PACKARD

Militanten van de milieuorganisatie Greenpeace blokkeerden gisteren met een muur van duizend oude computers de hoofdingang van de Nederlands vestiging van Hewlett Packard (HP) in Utrecht. Ze protesteerden tegen het gebruik van de mogelijk giftige stof broom in vlamvertragers. (Foto: W1)

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## *Impact on OEM strategies*

- Product safety is important
  - fire safety
  - chemical safety
  - consumer organisations
- “poisoning” of workers and customers
- It takes years to build up a good image in the public -  
But you can loose it overnight.

## *Impact on OEM strategies*

- The majority of OEM's has responded by globally committing to regional regulations, like RoHS and WEEE.
- Japanese companies (JVC, NEC, Sony) were pioneers, started in 2001

Ex: Sony



**Sony SLV-SE820**

(Halogen free PWB & Housing)



**KV 29 FX 66 (intr. 2001)**

Halogen free housing  
Lead reduced  
Reduced stand-by consumption  
Packaging 100% recycled material



**DCR-TRV30**

Halogen free PWB & Housing  
Printing ink from vegetal oil  
Packaging 100% recycled material  
Lead free solders



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## *Pro-active OEM consider halogen free*



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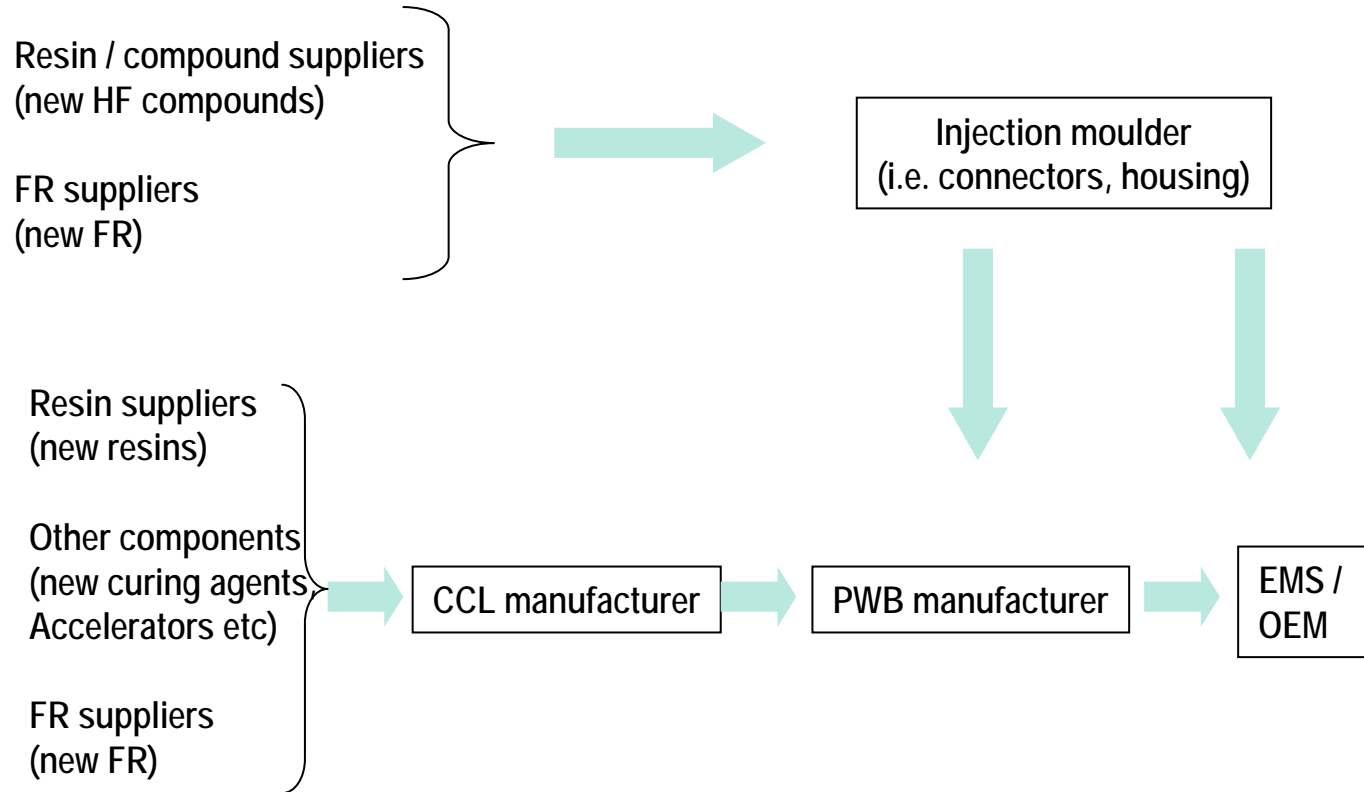
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Non exhaustive list of OEM having an halogen free roadmap

## *Impact on the supply chain*



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## *New halogen free raw materials*

- Halogen free Flame Retardants
  - Clariant Exolit OP range
  - Chemtura (former Great Lakes CC)
  - Supresta (former Akzo Nobel)
  - ...
- New halogen free FR resins
  - Huntsman
  - Dow
  - Bakelite
  - Tohto Kasei
  - Nan Ya
  - Japan Epoxy Resin
  - ...

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## *Halogen free capacities are expanding*

- Matsushita Electric Works will double its halogen-free production from 10 to 20% in 2006.
- Tohto Kasei (Japan) increasing its capacity of halogen-free epoxy resin (phosphorus type) for CCL to 3 000 tons per year
- Park Electrochemical Corp.
  - introduction of its new N4000-7 EF halogen-free, 165 degrees C Tg substrate
  - lead-free compatible, excellent thermal and moisture resistance
  - CAF resistance and UL 94 V-0
  - exceeds the electrical attributes of a brominated FR-4 system



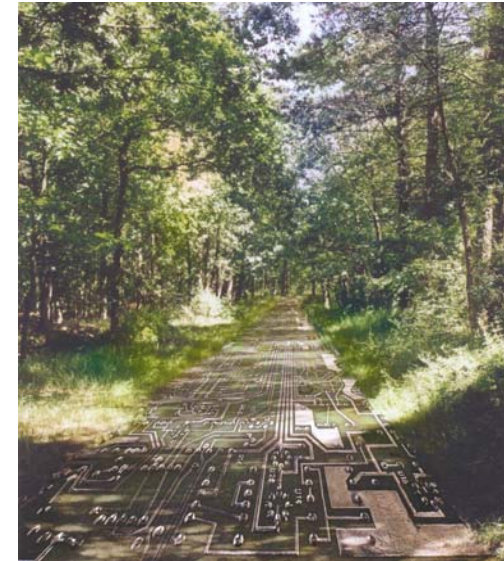
## *Halogen free: Asia and USA*

### ■ Asia

- Asian companies early identified “halogen free” as a business opportunity (Green procurement)
- R&D accomplished and already commercial production
- Technical and cost leadership
- 15-20% of Chinese PWB export already halogen free?

### ■ US:

- only observing activities in Asia in the past
- recently started to consider halogen free products as a market





## *Halogen free: Europe*

- Europe:
  - designed to be a major market for the final products
  - worked for many years on HF technologies but no real commercial business
  - today: little activities.
  - R&D and production shift to Asia/US.



## *Halogen free: perspectives*

- “Halogen free” is no longer simply a marketing term, as recognized by IPC. It has become a market.
- Halogen free PWB should represent a market share of 3-4 % in 2005 vs. 0 % in 2001 (Clariant estimate)
- Further growth no longer linked to decision based on “good science” or “bad science” (re. TBBPA), but driven by market demand.
- End market seems limited to Consumer electronics at the time. Possible boom in the mid term if automotive OEM move to halogen free (under evaluation).

## *More Information*

- [www.exolit.com](http://www.exolit.com)
- [www.flameretardants-online.com](http://www.flameretardants-online.com)
- [www.cefic-efra.com](http://www.cefic-efra.com)

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