Halogen-free Laminates: The technology is there for an emerging market

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Public
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Outline

- Regional importance of commercial halogen free materials
- Recent activities about “halogen free”
- What are “halogen-free” flame retardants?
- Technical requirements to FR system
- Review of halogen-free FR system for base materials
- Review of halogen-free resin chemistries
- Overview of commercially available X-free CCL
- Summary

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Regional importance of commercial halogen free materials

- "Green electronics" are currently limited to Consumer Electronics items e.g. TV-Sets, DVD-Player, Personal Computers etc.
- Automotive OEM interested in, but no innovation pull, would rather switch once technology is mature.
- Although Consumer Electronics are global markets, strong differences can be observed:

- Japan:	>15% halogen-free base materials (growing)
- Europe:	3-5% (stable)
- USA:	<1% (growing)
- Taiwan/China:	>6% (driven by export)
- Korea:	no data available, but probably a few%

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Recent activities about "halogen free"

- US EPA: toxicological and environmental assessment of TBBP-A and non halogenated alternatives (started 2006)
- identify and characterize Flame retardants
- from their environmental, health and safety fate aspects
- focus on areas of life cycle with greatest exposure (e.g. chemical exposure during manufacture, accidental fires, disposal, landfill, recycling)
- include "commercially available FRs", but will not exclude those limited due to their current cost position.

Interested parties may contact: Vokes.Kathleen@epa.gov

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Recent activities about "halogen free"

- Industry consortium iNEMI: "Halogen-free initiative"

- aims to promote standards and test guidelines for halogen-free materials, based on the requirements of the different market segments and their technical, commercial and functional viability
- will exclude toxicological & environmental aspects, as dealt within EPA study.

Contact bpfahl@nemi.org or mark_d_newton@dell.com

- High Density Packaging User Group (HdPUG)

- Update of the report on environmental assessment of halogen-free PWB (phase II report dated January 2004)

Contact: ruben.bergman@hdpug.se or fonga@ibm.com

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Recent activities about "halogen free"

- These activities are motivated by:

- business opportunities

  The development of the halogen-free market is no longer linked to potential restrictions on TBBP-A. but is driven by its own dynamic (market demand). Driving forces are OEM´s requirements as well as Green Procurement (ecolabels to a lesser degree)

- the necessity to update past knowledge on "halogen-free", due to further technical improvements (materials of 2nd or 3rd generation) and the multiplication of commercially available materials

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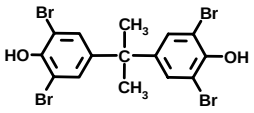
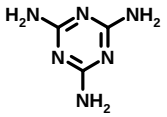
What are "halogen-free" materials?

- The term "halogen-free" is often used as if it would be a class of materials having the same profile and properties.
- This generally applies to halogen-free FR chemicals as well as halogen-free base materials.
- This is in both cases not true and extremely misleading

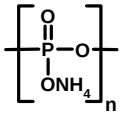


^{35}Cl

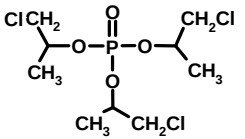


^{31}P

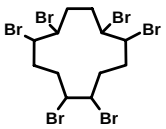
^{27}Al



^{80}Br



^{14}N



^{24}Mg

$Al(OH)_3$

^{11}B

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What are "halogen-free" FRs?

- As far as FR as concerned, 3 chemical classes can be distinguished, that differ by FR mechanisms and intrinsic properties:

- **phosphorus** compounds

- **nitrogen** based compounds

- **mineral FR** (ATH, MDH, borates)

- Big differences also exist within the same product family: e.g. **inorganic** vs. **organic** phosphorus compounds, **liquid** vs. **powders** etc.

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Technical requirements to FR system

- Overall requirements and aspects that may be affected by additives:
  - No blisters or delamination after PCT
  - No decomposition or delamination during soldering (TTD at 260°C/288°C up to 300°C!)
  - Chemical resistance against acid, alkali and oxidative substances
  - No or low water uptake
  - No migration (critical for CAF testing)
  - No or little impact on mechanical properties, CTE as low as possible
  - No or little impact on Tg
  - No or little impact on electrical properties (Dk, Df)
  - No or little impact on resin-glass or resin-copper interface
  - No impact on resin flow of prepregs for press process
  - Optical aspect: no agglomerate for quality inspection

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Technical challenge

- From the >50 different halogen-free FRs, not all are technically suitable for use in electronics applications.
- Usually, a combination of different compounds is necessary to match the requested properties.

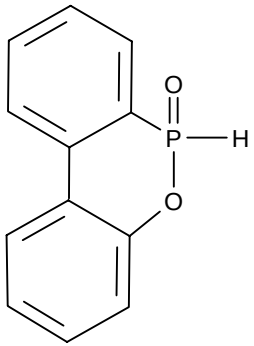
Traditional Varnish composition	Varnish bath (Halogen-free)
Generally a four component system	> 6 components system
– Epoxy Resin (brominated)	– new epoxy resin ?
– Curing Agent	– new curing agent ?
– Accelerator	– new accelerator ?
	– Flame retardants ?
	– Fillers ?
	– Processing additives?
– Solvent (viscosity modifiers)	– Solvent

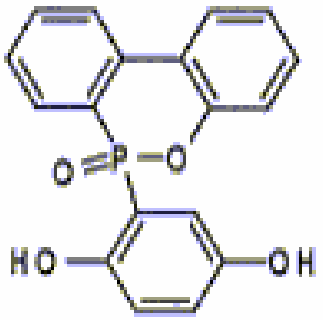
Challenge - the varnish bath must be completely reformulated,
and individual components optimized to customer requirements.
No industry standards - Each customer with own recipe, tests & requirements

Review of halogen-free Flame Retardants

- DOPO (Dihydro oxaphosphaphenantrene)

  Reactive type FR, that, when properly catalyzed, can be grafted to C=C linkages or reacted with epoxy groups.





HCA-HQ

- As it is mono-functional, it is most of the time modified before use. Several modifications are possible (e.g. DOPO-HQ)
- DOPO is the major building block to make phosphorus containing epoxy resins for base laminates (Tg up to 150°C).

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Review of halogen-free Flame Retardants

- Phenylphosphonic acid esters
- Phosphine oxide derivatives

A number of patents (such as US pat. no. 6645631 Dow Chemical Company) describe the reaction of a.m. phosphorus compounds onto the epoxy backbone. Patents and other literature demonstrate acceptable electrical and mechanical properties and suggest possible use in PWB applications.

Market significance can not be assessed, but the raw materials are available from different suppliers, supporting commercial availability.

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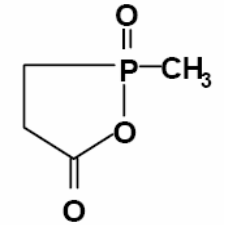
Review of halogen-free Flame Retardants

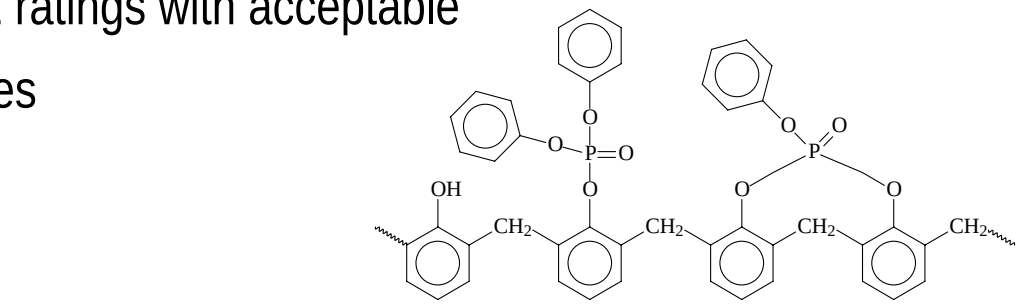
- Organophosphorus anhydrides

  Certain anhydride molecules, such as oxaphospholane (2-methyl-2,5-dioxo-1,2-oxaphospholane e.g. Exolit® PE 110) have the potential to be used as curing agent and/or reactive FR.



- Phosphorylated novolaks

  Limited in use by their phosphate structure, have been reported to give V-1 ratings with acceptable properties

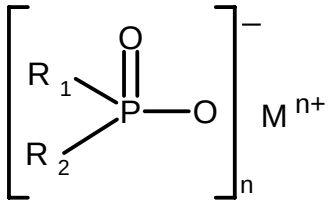


Review of halogen-free Flame Retardants

- Metal phosphinates

  Are a new class of FR developed by Clariant. Primarily designed for thermoplastics, this technology could establish itself in rigid and flexible printed circuit formulation as a synergist to modified resins (epoxy, CE, Benzoxazines, PPO, PPE or their blends)

  Besides its attractive price-performance ratio, one of the main feature is its neutral behavior on electrical properties, having virtually no impact on Dk/Df at higher frequencies.



- Aluminium Trihydrate (ATH)

  ATH is the largest FR by volume worldwide and is priced as a commodity. Main drawback is its low effectiveness, so it can only be used as synergist or for cost reasons. Its commercial use in FR4 material may be threaten by lead-free solder temperature. Possible alternative could be alumina monohydrate (or Boehmite)

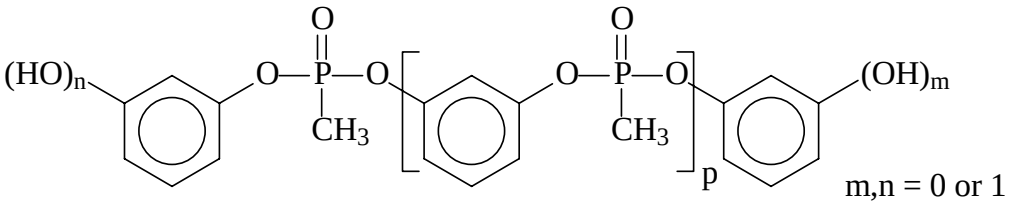
Review of halogen-free Flame Retardants

- Phosphazene compounds

  High purity grades of phosphazene are reported to be exclusively used commercially ín Japan. Several patents tend ot confirm their suitability, but costs (> 5.000 JPY/kg, approx. > 35 €/kg) should remain a brake for wider use.

- Further potential candidates

  Supresta is introducing Fyrol® PMP as reactive FR / curing agent



  Ciba reported potential use of melamine polyphosphate (Melapur® MP 200)

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Review of halogen-free resin chemistries

- The **epoxy chemistry** remains the preferred backbone in CCL applications. Halogen-free systems are usually based on:

- nitrogen modified epoxies
- phosphorus modified epoxies: to date, mainly based on DOPO

In most cases, modifications are limited to a certain extent, as e.g. brittleness and water absorption are affected by the modifications. Modified resins with acceptable properties are usually rating UL 94 V-1 and thus need additional additives (e.g. ATH, Metal phosphinate) to achieve V-0 rating.

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Review of halogen-free resin chemistries

- To achieve different properties or to overcome certain drawbacks, alternative thermosetting polymers can be used, on their own or blended.

- Some of them are already commercially used for years

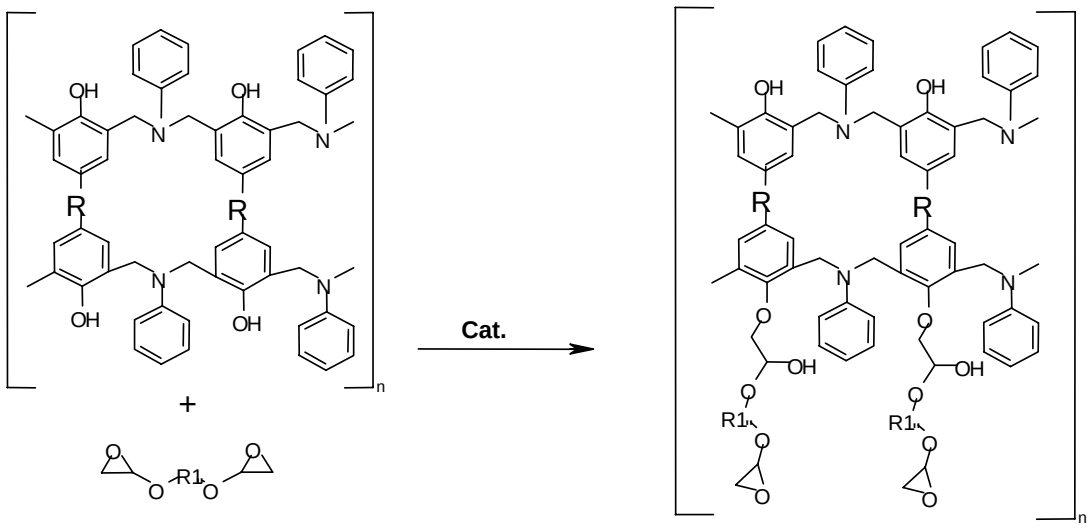
- Cyanate esters (CE)
- Bismaleimide Triazine (BT)
- Thermoset Polyphenylenether (A-PPE)
- Polyphenylenether (PPE) or Polyphenylenoxide (PPO) blended with epoxies e.g. Getek®

Review of halogen-free resin chemistries

- More recently, Huntsman Advanced Materials launched Azyral® resins based on benzoxazine chemistry

- can be homo-polymerized: High Tg (200°C), V-0 without additives, but expensive, brittle and potentially water uptake issue.

- however, can react with epoxies, offering a balanced price-performance profile, but typically need FR booster



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Halogen-Free CCL

- Commercially available halogen-free materials (only FR-4, non exhaustive list) and some more to come!

NanYa	NPG-R, NPG-TL, NPG-170TL *
Hitachi	BE-67G(H), E-679FG*
Elite Materials Co	EM280
Isola (incl. Polyclad range)	DE 156, IS500 *, HF 541, HF 551,HF 571*
Nelco	4000-7EF *
LG Chemical	LG-E(B) 481
Doosan	DS 7402, DS 7402H*
Sumitomo Bakelite	ELC-4784GF, ELC-4782GH
TUC	TU-642
ITEQ	IT 140G, IT155G, IT 170G*
Mitsubishi Gas	CCL-EL150
Panasonic / MEW	R1566, R1515*
Guangdong Shengyi	S1155, SL 65*
Ventec	VT44
Grace	GA-HF-14, GA-HFR/GA-HFTL*

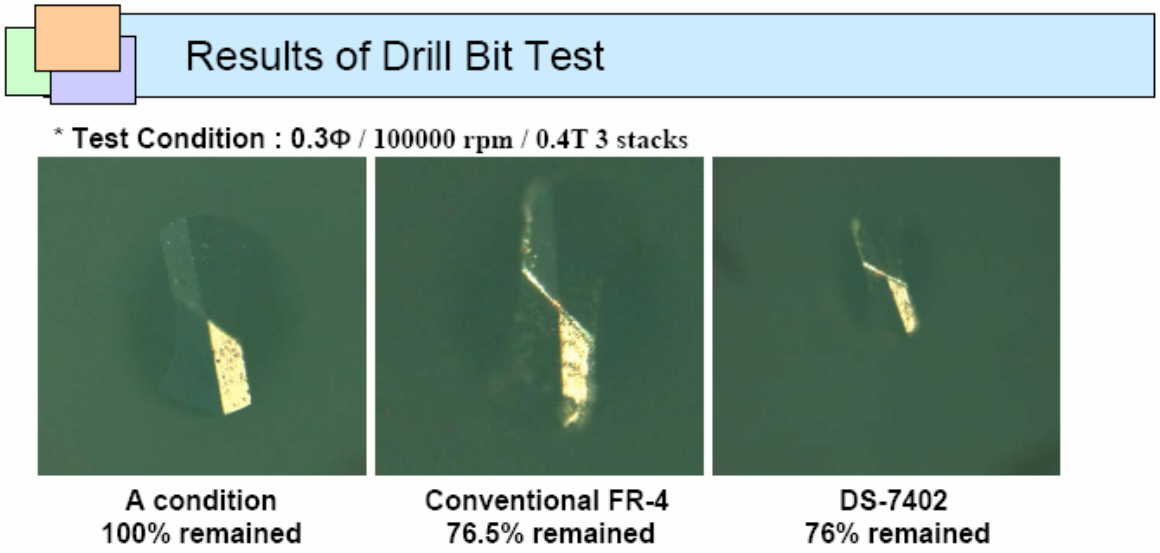
* High Tg materials

Concerns about halogen-free materials

- Processing / drilling

  A number of problems have been reported concerning bad processing of halogen-free materials: lower number cycles for drilling bit and increased energy consumption.

→ This mainly relates to fillers (like SiO_2) used to reduce CTE and sometimes to reduce costs. This does not directly relate to the FR



→ Filler-type FR like ATH or Exolit® OP 930 (metal phosphinate) are not very abrasive

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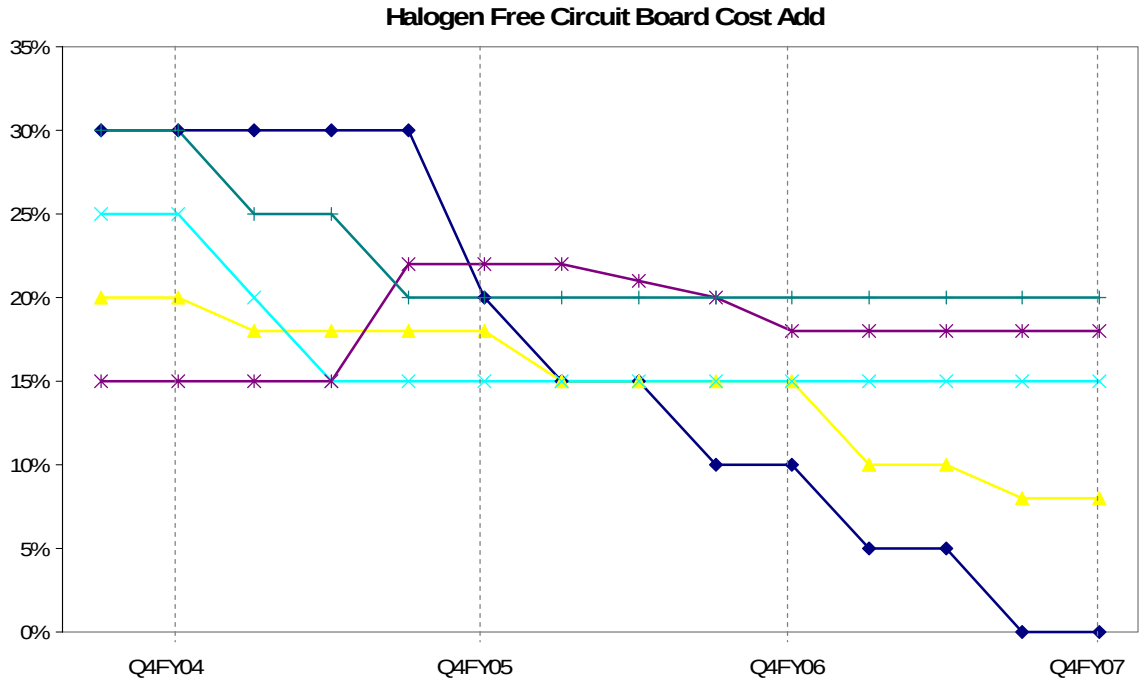
Concerns about halogen-free materials

- Cost

  FR account for a minor part of the total value.

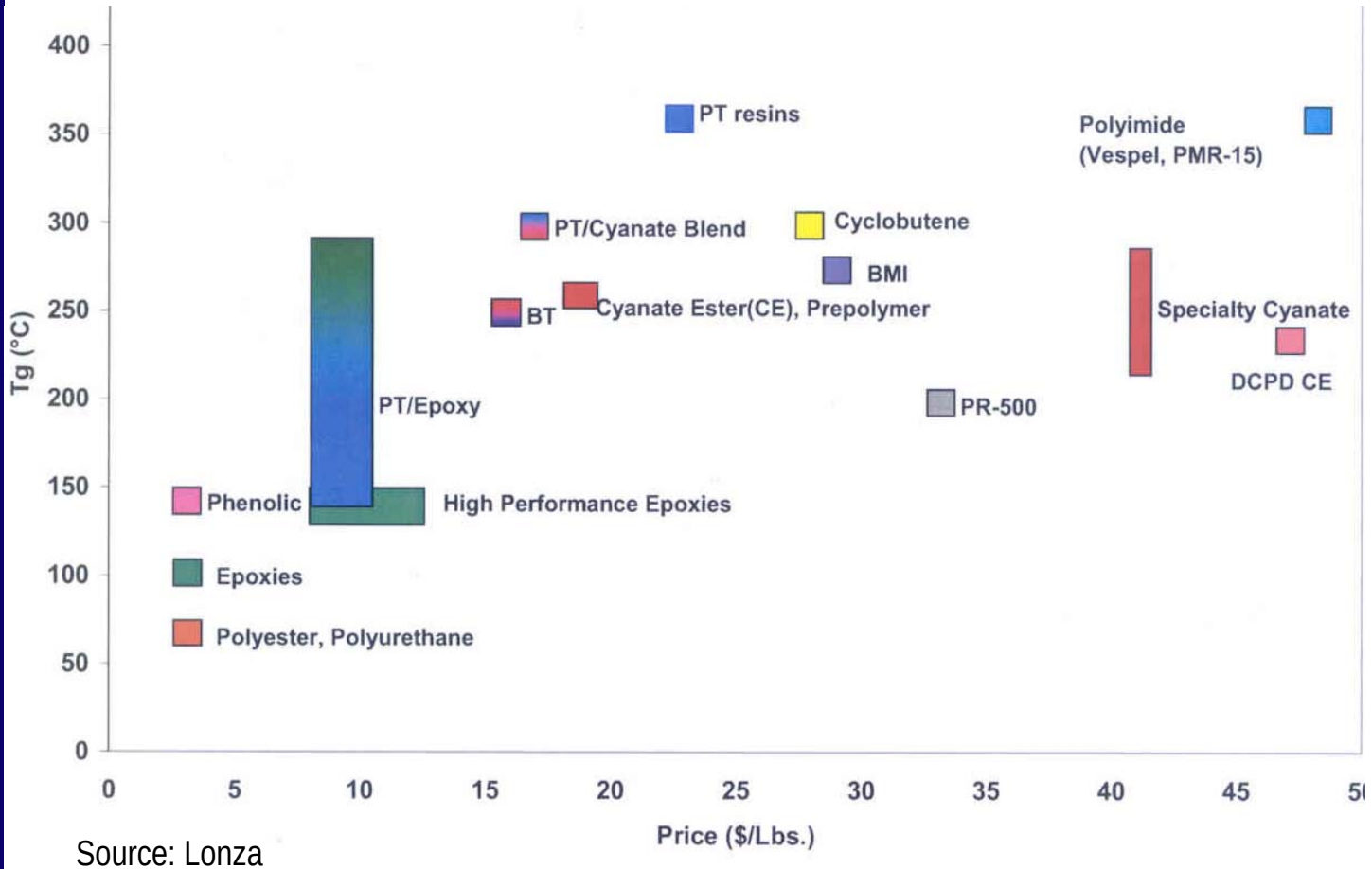
- additional costs in a range (10)20-50% relative to a laminate
- add. cost of approx. 0,10-0,15 US$ relative to a 100 $ motherboard
- Costs expected to decrease by increasing volumes. However, price-performance of TBBP-A still difficult (impossible?) to match.



Source: iNEMI

Concerns about halogen-free materials

- Other cost factors include resin type, resin content (high vs low fill), reinforcement type (glass, aramid, kevlar, carbon), fabric style (thick, thin, plies no.), copper foil (type, thickness)



Source: Lonza

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Summary

- A wide range of materials of halogen-free technologies are currently available and further research is expected to result into new raw materials
- This include FR additives, as well as resin backbones
- All have different mechanical and electrical properties and different impact on cost.
- To a certain extent, costs are expected to decrease with volumes.
- This offers an increasing wide range of CCL properties, which makes it easier to find suitable halogen-free alternatives for different applications and markets segments.

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Feel free to contact us for detailed information

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Thank you!

Any Question? Visit us at Table Top corner or check our websites:

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