Electronics Goes Green 2004+
The market trend towards non-halogenated flame retardants continues

By Rüdiger Walz and Elmar Schmitt

At the international **Electronics Goes Green** 2004+ conference in Berlin from 6 – 8 September 2004 more than 500 experts from the electronics industry and their suppliers as well as academia and environmental research institutes gathered. Design for environment (DfE), life cycle analysis (LCA), end of life and recycling issues were discussed in great detail. Recyclability is a parameter that can be in conflict with other environmental aspects, like energy efficiency and miniaturisation, achieved by a mix of customized and diverse materials. Overall, the use phase of electronic products is often the most important from an environmental view point because of the energy consumption[1]. Kei Biu Chan, chairman of the Hongkong Electronics Industries Association, pointed out in his speech[2] that “Green Manufacturing is not necessarily a drain on profits but an opportunity for cost savings, lean production and technology advancement. With Green Manufacturing, an enterprise can differentiate itself from other competitors and establish market leadership.”

Flame retardants were also a topic of interest, especially because of the entry into force of the European directives on waste of electric and electronic (E&E) equipment

(**WEEE**, 2002/96/EC) and restriction of certain hazardous substances (**RoHS**, 2002/95/EC) in such equipment. A number of heavy metals and certain brominated flame retardants are going to be banned (polybrominated biphenyls, PBBs, and polybrominated diphenylethers, PBDEs). Penta- and octabromo diphenylether were already banned in the EU by the directive 2003/11/EC as of August 2004. The European Commission has not taken a decision yet whether to exempt decabromo diphenylether (Deca) from this ban. The WEEE directive demands the separation and separate treatment of plastics containing brominated flame retardants from E&E waste.

Researchers from the Fraunhofer IVV Institute[3] presented chemicals **analyses** of different mixed polymer waste fraction of **WEEE** which showed that levels of up to 2 % of brominated flame retardants are found, including the octabromo diphenylether in excess of the 0.1 % limit now in force in Europe. They also detected around 10 ppb of polybrominated dioxins and furans. Therefore, the researchers conclude that "based on these results the marketability of the mixed plastic fractions does not seem possible according to existing law in Germany without the elimination of dangerous chemicals and reduction below the specified limits.

Currently, large amounts of **WEEE are exported** – sometimes illegally - to countries like China[4] and India where they are dismantled and valuable metals are reclaimed using very primitive technologies. Materials are heated over open flames, acids and other chemicals used without protection. The workers, young children included, are often exposed to hazardous chemicals or degradation by-products like dioxins and furans.

The current **lead based solders** will have to be replaced by lead-free systems. Solders e.g. based on silver are available - however, they require a processing temperature which is about 30 °C higher than lead based solders. Therefore, the resin formulations of halogen free wiring boards and components have to be adapted to withstand these higher temperatures.

The **main concerns** against brominated FRs are their persistence in the environment but mainly their accumulation in living organisms in addition to in some instances steeply increasing concentrations in the environment and biota. They have been found almost every from house dust, foodstuffs to polar bears and human milk. Because of these growing concerns, a number of leading OEMs have committed to phasing out BrFRs or have at least launched strategies to do so. Some examples are

- Hewlett Packard
- Sony
- Hitachi
- Siemens-Fujitsu
- Nokia

A number of **ecolabels** restrict or ban brominated flame retardants in their product criteria, e.g. the Blue Angel in Germany, the Swan in the Nordic countries and TCO which is of particular interest for electronics. IT Eco-declarations of manufacturers as well as the new Global Automotive Declarable Substance List (GADSL) require the declaration of certain halogenated flame retardants.

On the one hand, advanced environmental and material requirement can be a positive business driver: they enhance innovation and create differentiation potential versus commodities or main stream products. On the other hand, the manufacturers of non-halogen flame retardants have experienced that offering a more environmentally friendly product is often not sufficient for market success, even if the price and technical properties are comparable to established flame retardants. Therefore, legally binding requirements together with market pull - manufacturers and consumers of end-use products demanding more environmentally friendly solutions - will encourage the development of alternative non-halogen flame retardants. Once they gain a considerable share of the market, economies of scale can materialise and lower the cost of alternatives.

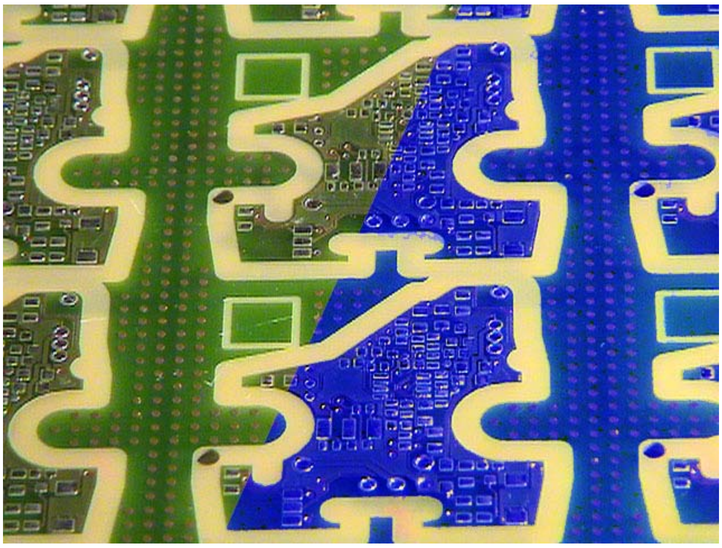
Available halogen-free flame retardant solutions

Currently, halogen-free solutions exist for printed circuit boards as well as for plastics for housings, connectors and other E&E materials. Four papers dealt with flame retardants specifically:

New environmentally friendly Phosphorus based Flame Retardants for Printed Circuit Boards as well as Polyamides and Polyesters in E&E Applications[5]

Elmar Schmitt and coworkers from Clariant Corporation discussed the properties of a newly developed class of phosphinate flame retardants (Exolit OP series) for engineering thermoplastics like polyamides and polyesters. Different polyamides, especially glass fibre reinforced grades, can be effectively fire retarded with these new halogen-free products based on phosphinates. The required dosage for a UL 94 V-0 performance is lower than for other flame retardant formulations apart from red phosphorus. In engineering thermoplastics, the new formulations based on Exolit OP 1311 / 1312 allow a high CTI (Comparative Tracking Index) of 600 Volt and a low compound density. Mechanical properties are at the same level as for halogenated compounds. Particular advantages of the new formulations are also the good flow properties and the fact that they flame retarded plastics can be coloured with any pigments. The established bromine and red phosphorus based flame retardants in this sector suffer from technical drawbacks like limited electrical properties, high density or limited colour range.

Exolit OP 930 is the phosphinate designed for printed circuit boards based on epoxy resin (high Tg of 170 °C, FR-4 laminates). Unlike most other phosphorus containing compounds, Exolit OP 930 is not hygroscopic (no water pick-up after pressure cooker test), has no plasticizing effect, is not soluble in organic solvents, has verly low solubility in water and does not hydrolyse in the presence of water. Furthermore, Exolit OP 930 has an excellent thermo stability, showing a start of decomposition around 330°C, making it suitable for the next generation of lead-free solders. The temperature of 330°C is also the range in which most of the epoxy resins will decompose, making Exolit OP 930 a very effective flame retardant in this type of polymer.



"To be blue or not to be blue, that's the question …" Shakespeare would have posed: Currently, green is the common colour of printed wiring boards containing brominated flame retardants, whereas blue is used for materials with non-halogenated flame retardants.

Highly Efficient Flame Retardant Curing Agent for Epoxy Resins[6]

Cefn Blundell from Akzo Nobel Chemicals, now Supresta, presented results on physical properties and combustion performance of a new polymeric organo-phosphorus curing agent, specially designed for electronic thermoset resins. The new flame retardant has quite promising properties like higher glass transition temperature and lower thermal expansion, however, at the time it was not available in commercial quantities nor was its chemical nature disclosed.

Sustainability Concerns For Flame Retarded Plastics Used in Electrical and Electronic Equipment Applications[7]

Raymond Dawson and Susan Landry from Albemarle Corporation highlighted the fire safety provided by flame retardants, but mainly looked at the currently available end-of-life options for plastics containing flame retardants. The main conclusion is that flame retardants are not in the way of any recycling or treatment option which is currently technically feasible, e.g. plastic parts can be mechanically recycled and retain their material and fire safety properties, although various polymers and flame retardants differ in suitability. Also, waste-to-energy recovery by incineration is not a problem, provided state-of-the-art technology is applied. However, the same limitations apply as to all plastic materials: for mechanical and feedstock recycling continuous streams of input materials of defined composition are necessary. Therefore, these routes are currently only applied in either closed loop recycling systems or by polymer processors who recycle their process waste.

Comparison of brominated versus halogen-free printed wiring boards

A research consortium from Sweden and Germany[8] presented a paper on "Environmental and economic implications of a shift to halogen free printed wiring boards" at the conference. They come to the conclusion:

> "PWBs have been manufactured with halogen-free laminates for more than five years. However, manufacturing volumes and production experience are still limited. Thus there is an uncertainty in analysing manufacturing costs. 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 for 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. Therefore, the findings should only be considered as indications of the economical and environmental implications associated with the shift in PWB material. The conclusions drawn are only valid for this specific case study and further studies are needed to attain more comprehensive insight into the implications associated with the material shift."

As the main difference, the study finds a higher energy consumption for drilling of the non-halogenated wiring boards, probably because inorganic filler materials were applied (like aluminium hydroxide or silicium oxide) as flame retardants. Whereas the bromine industry promotes this paper as proof that brominated flame retardants are environmentally more friendly than non-halogenated flame retardants, this quote clearly shows the limitations of this study. Environmental and toxicological effects like bioaccumulation were not even covered.

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Links and References:

http://egg2004.izm.fraunhofer.de/

Proceedings of the conference (the indexed references below refer to the proceedings volume):

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