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White Paper

Bromide-Free Options for Printed Circuit Boards

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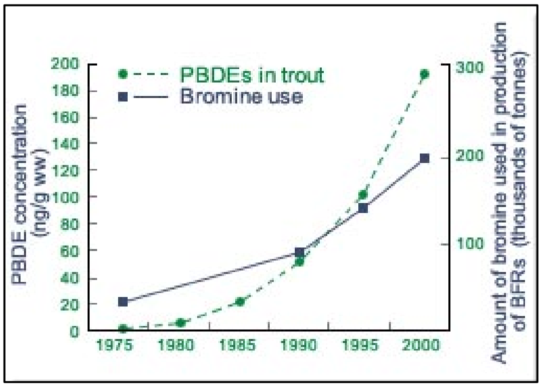
Flame retardants have been around since the Egyptians and Romans used alum to reduce the flammability of wood. Brominated flame retardants (BFRs) first experienced use after World War II as the substitution of wood and metal for plastics and foams resulted in materials that were much more flammable. The widespread use of BFRs initiated in the 1970s with the explosion of electronics and electrical equipment and housings. For the US market, all of these products must conform to the UL 94 flammability testing specifications. In fact, the most common printed circuit board (PCB) in the electronics industry, FR-4, is defined by its structure (glass fiber in an epoxy matrix) and its compliance to UL 94 V0 standard.

However, at the same time BFRs saw increasing use, scientists began to detect increasing concentrations of these substances in the environment, food chain, and wildlife[1]. Additional research has expressed concern over the potential toxicity of BFRs and their potential for endocrine disruption. As a result, industries using these BFRs, including the textile and electronics industries, have been looking for alternatives to satisfy current (and in anticipation of new) bans and regulations controlling their use.



To date, researchers and environmentalists have identified several suspect BFRs, including poly-brominated biphenhyls (PBBs), penta-polybrominated diphenyl ethers, octa- polybrominated diphenyl ethers, and deca-polybrominated diphenyl ethers (PBDEs). These BFRs are mostly irrelevant for the electronics industry as printed circuit boards (PCBs) and component moldings primarily use tetrabromobisphenol-A (TBBPA), with TBBPA accounting for 95-97% of all flame retardants in PCBs. The difference between TBBPA and the other BFRs is that TBBPA is reacted into the polymer backbone as opposed to being physically added. As such, studies and organizations such as the World Health Organization (WHO) have concluded that TBBPA poses a negligible risk to the general population. The chemical is currently not banned in any country and is not included in the European Union's Restriction of Hazardous Substances (RoHS).

However, several governments, organizations, and the general public do not differentiate among the many BFRs and have requested an overall elimination of these chemical compounds. There is even indication that in some countries and industries, OEMs who still use BFRs are losing market share[2].

In response, the electronics industry has begun to offer alternatives. These alternatives, which can be divided into three classes, are often described as halogen-free:

- Inorganic compounds
- Phosphorous compounds
- Nitrogen compounds

[1] Mehran Alaee, Flame Retardants: A Threat to the Environment? http://www.nwri.ca/sande/may_jun_2002-2-e.html
[2] Tisdale and Krabbenhoft, iNEMI Halogen-Free Project: Phase 1 Review, SMTA 2006, http://thor.inemi.org/webdownload/newsroom/Presentations/SMTAI_2006/H-free.pdf

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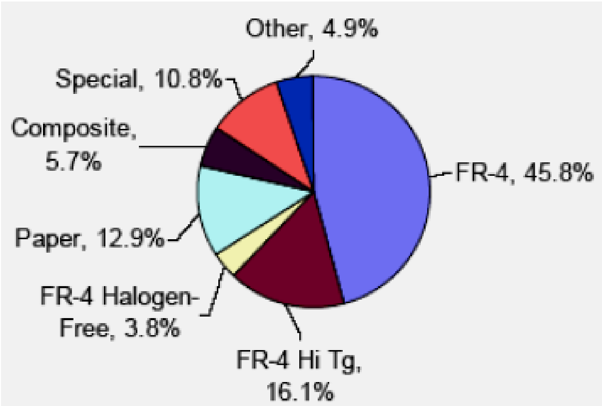
The inorganic substances include aluminum and magnesium hydroxide, antimony trioxide, zinc borate, and red phosphorous (one allotrope of elemental phosphorous). Phosphorous compounds include phosphate esters and phosphonates. The nitrogen compounds include polyamides and melamine and its salts. Mixtures of different flame retardants can also be used to meet the UL 94 V0 standard.

All major suppliers of encapsulants (Sumitomo Bakelite, Henkel, etc.) and FR-4 laminate (Matsushita, Isola, Hitachi, Nanya, ParkNelco) now offer halogen-free options, but performance and reliability concerns still exist. And the reality is that very few companies are ordering halogen-free in high volumes (less than 5% of the marketplace), primarily because of concerns with processing margins and material performance.



Several organizations are now proceeding to perform research into the properties of these halogen-free materials. iNEMI has identified 30 specific laminate offerings from 15 different laminate manufacturers, see below, and is assessing a variety of electrical parameters, material behaviors, and reliability performance (dissipation factor, CAF, SIR, IST, etc.). HDPUG and EPA are also conducting research in various areas.

Laminate Supplier	Material	Country of Manufacture
NanYa	NPG-R	Taiwan / China
	NPG-TL / NPG-170TL *	
Hitachi	BE-67G(H)	Japan / Hong Kong / China
	E-679FG *	Japan
	EX-77G	? Japan ?
Elite Materials Co	EM280	China
Isola	IS500 *	Italy
	DE156	Germany, Taiwan
	HF571 (formally Polyclad) *	Germany, Taiwan
Nelco	4000-7EF *	Singapore
LG Chemical	LG-E(B) 481	Korea

Laminate Supplier	Material	Country of Manufacture
TUC	TU-642	Taiwan
ITEQ	IT155G	Taiwan
	IT140G	Taiwan
	IT170G * (??)	
Mitsubishi	CCL-EL150	Japan
Panasonic / MEW	R1566	Japan/Taiwan/China
	R1515T *	Japan
	R1515B	
Ventec	VT44	China
Grace	GAHF14 / GAHFR / GAHFTL *	China
Doosan	DS7402 (H) *	South Korea
	DS7402	South Korea
Guangdong Shengyi	S1165 *	China
Sumitomo Bakelite	ELC-4785GS / ELC-6785GS / ELC-4765GF	Japan

In the meantime, as common with any introduction of new technology into a cost-sensitive, low-margin business, the customers are the guinea pigs. Problems reported to DfR include failure to meet UL 94V-0 requirements (both components and boards), failure to meet NEBS flame tests, excessive deformation after reflow (components), failure under high temperature / humidity testing (components), and an increase in drilling defects (printed boards).

And remember, not all halogen-free materials are labeled as such ('form-fit-function') and some companies are going the cheap route – simply reducing the percentage of bromine in the material.

There are multiple concerns regarding the introduction of these materials, including

- Are they environmentally safer than TBBPA?
- Is electrical performance maintained?
- Do they pass industry standard flame retardant tests?
- Do they maintain flame retardancy over time?
- Are they manufacturable?
- Are they susceptible to long-term degradation (CAF, SIR, etc.)?

However, the biggest and most unspoken question is:

Has the industry learned from red phosphorus?

Unfortunately, from our perspective, the answer seems to be no. The same narrow focus on test to spec, failure to select representative samples, and avoidance of any failures during test, almost guarantees that more than one OEM will experience substantial pain during the transition to halogen-free.