

# Brominated Flame Retardant (BFR) and Polyvinyl Chloride (PVC) Free Material Evaluation Requirements

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## ABSTRACT

Many OEMs have made commitments to eliminate brominated flame retardants (BFRs) and polyvinyl chloride (PVC) from products over the next several years. In order to meet the transition targets, replacement materials must be evaluated based on technical, procurement, and environmental criteria. This paper describes material assessment requirements for various material types and components, with a focus on printed wiring boards (PWBs) and the additional environmental criteria that will be used to help understand whether new materials are better for the environment than the materials they replace.

## INTRODUCTION

Flame retardants and PVC are widely used in electronics to improve product safety by reducing the likelihood of ignition within equipment, and also to reduce the spread of fire beyond a piece of equipment if ignition occurs. An average printed circuit assembly (PCA) might contain as much as 33% polymers and may have several resin types, many of which require added flame retardants to meet fire safety standards.

Although flame retarding agents serve an important function in modern electronics, some commonly used flame retardant compounds have been restricted for environmental reasons, and many more are under scrutiny. It is important that as the industry moves toward alternative materials the replacements not only meet the fire safety goals for electronics, but also have a smaller environmental footprint.

Changing flame retarding additives, or the resin itself in the case of PVC, clearly has a direct impact on the attributes of the polymer, which requires the alternative material to be assessed against many criteria. Beyond functional performance, alternate materials must also meet procurement criteria, and perhaps most importantly, they must meet environmental criteria to ensure that they are in fact better for the environment than the materials they replace.

This paper describes key evaluation criteria for BFR and PVC replacement materials, with an emphasis on PWB laminates.

## DEFINITION OF BFR FREE and PVC FREE

Companies may have slightly different definitions of BFR and PVC free material, however, HP requires that low halogen content PCBs meet Br and Cl levels in IPC-4101B, and that all other materials must meet the following requirements:

- BFRs and CFRs must not be present in concentrations equal to or greater than 0.09% (900 ppm) by weight in any homogeneous material, and
- PVC must not be present in concentrations equal to or greater than 0.09% (900 ppm) by weight in any homogeneous material.

Note that this definition is not an elemental restriction, however, the presence of elemental Br or Cl requires the identification of the Br or Cl compounds to ensure that a BFR, CFR, or PVC is not present.

## TECHNICAL EVALUATION CRITERIA

In the case of PWB laminates, there are several excellent resources containing best-practices, guides, and checklists for evaluating and qualifying new materials.<sup>1,2</sup> The tests suggested in these resources must be undertaken with new BFR free laminates, just as they would be in qualifying any new material.

This section describes a screening approach, but any final qualification plan must necessarily include validation appropriate to the product. Also, verification of datasheet test results may be needed for certain criteria.

The most basic technical requirement for alternate materials is that they must perform their intended function, which includes the following three goals:

1. Minimize design impact
2. Meet or exceed product reliability requirements
3. Meet or exceed current flammability rating

### Minimize design impact

For most materials, the best way to minimize design impact is to match existing performance criteria. Standard electrical characterizations must be completed on representative constructions, including:

IPC-TM-650 <sup>5</sup>	Test description
2.5.17.1	Volume and surface resistivity
2.5.6	Dielectric breakdown
2.5.5.2	Permittivity (dielectric constant) and loss tangent (dissipation factor)
2.5.5.3	
2.5.5.9	
2.5.6.2	Electric strength
2.5.1	Arc resistance

Another critical way that replacement materials must match existing performance criteria is to have an ease of fabrication sufficient to create all technologies needed in the intended application.

In some cases, newer BFR free laminates may offer performance improvements over existing materials, especially when a BFR free laminate replaces an older material for Pb-free assemblies. However, some of the formula modifications to reduce cost or to meet flammability ratings can negatively impact performance,<sup>4</sup> and there are fewer choices for high performance applications.

### Meet or exceed product reliability requirements

New materials must also meet or exceed the product reliability requirements. In the case of PWBs, the following minimum characterizations should be completed on representative constructions:

IPC-TM-650 <sup>5</sup>	Test description
2.4.24C	T <sub>g</sub> and Z-axis CTE by TMA
2.4.25C	T <sub>g</sub> by DSC (midpoint)
2.3.40	Decomposition temperature (1%, 2% 5% weight loss)
2.4.24.1	Time to delamination (at 260°C, 288°C, and 300°C)
2.6.2.1A	Water absorption
2.4.8C	Copper peel strength (Conditions A and B)
2.6.8E	Thermal stress, PTH, Condition A
2.4.13.1	Thermal stress (288°C)
2.6.25	Conductive anodic filament (CAF) resistance
2.6.26	DC current induced thermal cycling test (IST) to failure

New PWB laminate materials must also be able to routinely meet acceptability criteria, such as IPC-A-600

Acceptability of Printed Boards,<sup>6</sup> when in high volume production.

Other mechanical and electrical polymeric materials will have their own complement of appropriate tests.

It should be noted that from a reliability perspective, red phosphorous is generally not an appropriate replacement technology for BFRs or PVC in most electronics applications.<sup>7</sup>

### Meet or exceed current flammability rating

The substitution of non-halogenated flame retarding compounds into polymers, including PWBs, necessarily changes the flammability behavior. One key requirement for new PWB laminate materials is that they should maintain or exceed the current rating for any application. In most PWB applications, this will mean meeting the UL-94 flame rating of V-0.<sup>8</sup>

It is important to specify and verify the flammability rating because the BFR free laminate slash sheets in IPC-4101B only require a V-1 flammability rating. Self-reported V-0 values should be validated.

### PROCUREMENT EVALUATION CRITERIA

Compared to the technical requirements, procurement requirements are generally more straightforward. New materials must:

1. Meet cost targets
2. Be widely available in sufficiently high volumes to meet product demands
3. Be sufficiently manufacturable to not negatively impact cost

### Meet cost targets

Cost is perhaps the most obvious, simplest, and most likely criteria to be enforced in the evaluation of replacement materials. Obviously, the goal for all replacement technologies is to be less expensive than existing BFR and PVC solutions. In some cases, it may take time and effort to achieve this goal, and in others, the inherent technologies may not support parity or below. However, as volumes increase and BFR and PVC free materials are widely adopted, it is expected that prices will decrease, which is critical to adoption of BFR and PVC free materials in a wider range of products.

### Widely available in sufficiently high volumes

Fortunately, BFR free PWB laminates have been developed and used for several years. These materials are some of the most readily available BFR free technologies, but they are only now being ramped up for high volume

production sufficient to support the product transitions anticipated in 2009. The selection criteria for volume availability will vary from product to product, but multiple approved materials from multiple sources will probably be critical for assurance of supply and meeting product introduction schedules. Given the significant differences in chemistry and performance, selecting interchangeable materials may be a challenge in the short term.

#### **Sufficient manufacturability to not increase price**

High PWB price may include cost contributions from manufacturability issues. OEMs often rely on PWB fabricators for assessing and managing manufacturability, and may not always directly assess this aspect of performance. However, when manufacturability is the underlying cause of an otherwise acceptable material not meeting price targets, manufacturing issues quickly gain visibility. The notable concern with BFR free laminates is the negative impact of inorganic filler loading on drilling.<sup>9</sup> PWB fabricators will certainly keep pressure on laminate vendors to improve performance against manufacturability criteria, but cost will probably be the proxy criteria used by OEMs and other end users to account for ease of processing.

#### **ENVIRONMENTAL EVALUATION CRITERIA**

One of the disadvantages of the current industry approach to chemical restriction is that all unrestricted solutions are treated as equal. However, some replacement chemistries are already being targeted for future restriction, and they should not be selected to replace BFRs or PVC in order to avoid multiple transitions. These materials include bisphenol A diphosphate (BAPP or BPADP), antimony compounds, chlorinated flame retardants, and perhaps resorcinol bis(diphenylphosphate) (RDP). The best way to avoid the negative impacts of future restrictions is to continually select into less hazardous materials.

There is currently no widely accepted environmental assessment method for BFR and PVC replacements for electronics materials, so developing criteria for this aspect of material selection is challenging. Full life cycle analysis and risk assessment of every option would be ideal. It is beyond the scope of any single company to satisfactorily complete such an analysis for every possible combination of materials, however, there are three screening activities that may help identify environmentally preferable choices:

1. Hazard assessment of neat chemicals
2. Chemical analysis of laminates
3. Chemical analysis of pyrolysis byproducts

#### **Hazard assessment of neat chemicals**

Assessing the hazard of the neat chemicals used as replacements for BFRs and PVC potentially enables the selection of substances that are inherently safer for human health and the environment, thereby reducing the risk from any type of exposure and also reducing the business risk of selecting a replacement that will be restricted in the future. Screening may be especially helpful in differentiating between different phosphorous-based BFR replacements as there is a wide range of behaviors observed in phosphorous compounds.

There are several schemes for assessing chemical hazard, including proprietary ones such as SC Johnson's Greenlist™<sup>10</sup> and the McDonough Braungart Design Chemistry (MBDC) Cradle to Cradle Design Protocol. Unfortunately, these tools are not freely available in the public domain. Also, a company-specific, proprietary system may lack the transparency and peer review needed to ensure general acceptance beyond the company that created it.

There are other categorization and assessment schemes in the public sector, including the criteria developed by the Canadian government to create their Domestic Substances List<sup>11</sup> as well as the U.S. Environmental Protection Agency's P2 framework and Design for the Environment Program (DfE) method for assessing chemical alternatives to certain flame retardants.<sup>12</sup> Although the DfE method is a step forward in providing information on chemicals, it is still difficult to make material selection decisions without guidance on how to interpret and apply the information.

Ideally, procurement staff with no background in chemistry or toxicology would have a way to easily compare materials options, and be able to confidently identify and select better materials for the environment. What is needed is a widely accepted, industry standard, transparent, peer reviewed, data driven, predictive assessment approach that could yield easy-to-understand ratings for competing materials options.

One promising comparative assessment tool available for public use and dissemination is the Green Screen for Safer Chemicals, developed by Clean Production Action.<sup>13</sup> This method has been used to compare flame retardants for TV enclosures and is being adapted for use in the US EPA's DfE partnership on flame retardants in printed circuit boards. The tool is still being refined, but this approach may be able to serve as the prototype for an industry standard approach for assessing the relative human health and environmental impacts of new materials and provide information to support the ongoing preferential selection of less hazardous materials.

## Chemical analysis of laminates

Even if the hazard of the new neat chemicals has been assessed, analysis of the final material or product may be required to know which chemistries are present and also to assess the combustion or pyrolysis byproducts.

Information regarding chemical makeup of materials and components is usually needed, and MSDS information is in most cases insufficient for the purpose of identifying the chemicals present for the purposes of human health and environmental assessment. Although it is possible to analytically determine the chemical composition of a material, it is much more effective and efficient to get this information directly from the formulator. Well-crafted disclosures by formulators also protect intellectual property much better than having customers fully reverse engineer substances to determine chemical composition.

When formulation information is not available, however, a range of analytical techniques can be used to categorize the replacement technologies into broad categories. It is possible to confirm basic chemistry analytically with tests such as X-ray photo-electron spectroscopy (XPS or ESCA) or X-ray fluorescence (XRF). Initial XPS or XRF tests are often performed to screen for certain restricted substances already, so it is possible to use the elemental scans to determine appropriate additional tests on BFR and PVC replacements. Although XPS is a surface technique and only analyzes approximately 70Å deep, most additives and fillers migrate to the top surface as a result of structural and density factors and are easily detectable.

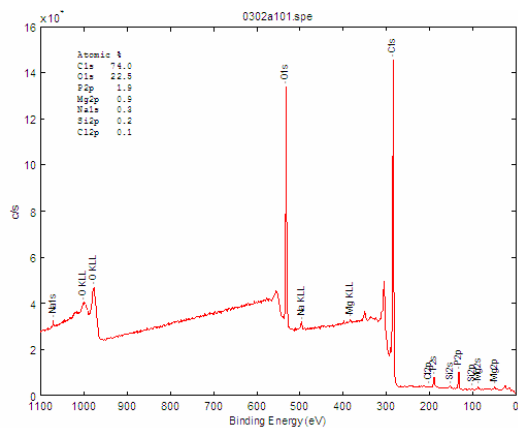


Figure 1: Example XPS scan of PCB laminate

As noted above, HP requires low halogen content PCBs to meet elemental Br and Cl restrictions as described in IPC-4101B, but all other materials must meet these substance restrictions:

- BFRs and CFRs must not be present in concentrations equal to or greater than 0.09% (900 ppm) by weight in any homogeneous material, and
- PVC must not be present in concentrations equal to or greater than 0.09% (900 ppm) by weight in any homogeneous material.

This definition is not an elemental restriction, however, XPS or XRF detection of elemental Br or Cl may require substance disclosure or additional analytical testing, such as liquid chromatography (LC), gas chromatography-mass spectrometry (GC/MS), or Fourier transform infrared spectroscopy (FTIR), to identify the specific Br or Cl compounds in the material to ensure that BFRs, CFRs, and PVC are not present

Beyond establishing that BFRs, CFRs, and PVC are not present, knowing the basic chemistry of the replacement technology makes it easier to interpret pyrolysis test results, as described in the next section. Again, it is usually best to rely on well-crafted materials disclosures than to fully reverse engineer chemical composition. In the case of PWB laminates, it is sometimes possible to use general knowledge about the common chemistries to interpret screening and pyrolysis data. In the case of laminates, one common replacement chemistry is 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) and derivatives with inorganics, such as alumina trihydrate (ATH), magnesium hydroxide or silica.<sup>14</sup> These compounds can be identified with a variety of analytical techniques.

Materials other than PWB epoxies may require additional tests to identify the chemical constituents.

## Chemical analysis of thermal byproducts

The concerns about BFRs, CFRs, and PVC are strongly linked to their end of life fate in uncontrolled burning, which means that as replacements are evaluated, it is important to look at thermal byproducts in addition to the toxicology of the base chemicals.

Some additional analyses that may help determine potential thermal byproducts are to analyze samples by TGA and FTIR, and also by pyrolysis followed by GC/MS to identify the compounds that form during thermal excursions. The data from these tests can be compiled to form a chemigram, showing the compounds released as the temperature increases. An example is shown in Figure 3.

One limitation of pyrolysis with GC/MS is that the sample size is very small, which means that it does not have sufficient mass to generate detectable amounts of certain compounds of interest (such as dioxins and

furans); however, it is still useful to know the major constituents when comparing materials.

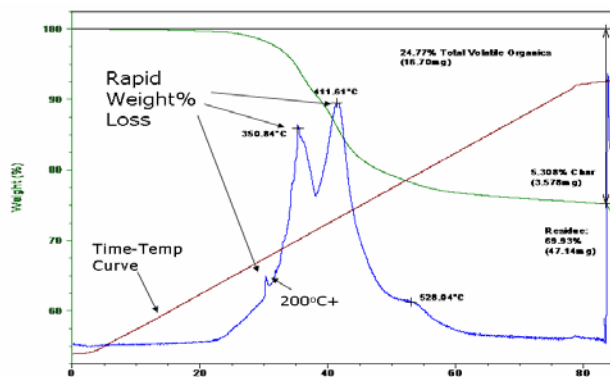


Figure 2: Example TGA (nitrogen)

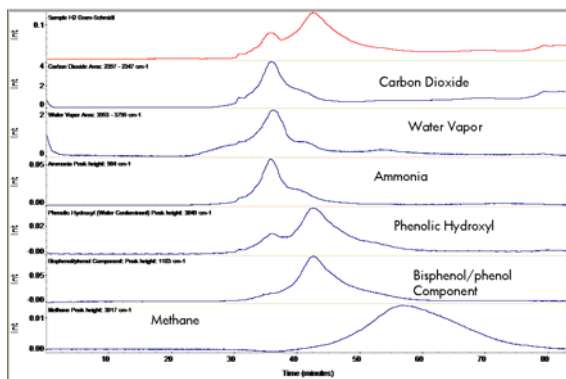


Figure 3: Example chemigram aligned to TGA results

## CONCLUSIONS

Evaluations of replacement technologies for BFRs and PVC must include assessments against technical, procurement, and environmental criteria. Technical and procurement assessments are relatively straightforward, and are comparable to qualifying any new material. Human health and environmental assessments are more complex because there are no standard assessment methods. Hazard assessment and chemical analysis are important components of ensuring that replacement materials meet the requirement to have a better human health profile and a smaller environmental footprint than the materials they replace.

## REFERENCES

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