iNEMI HFR-free Program Report

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Abstract

The electronics industry is aggressively pursuing the removal of potentially toxic compounds from their products, including the halogenated flame retardants (HFRs) that were once widely used in electronics housings and cases and are still used extensively in printed circuit boards. Several leading electronics companies have publicly stated their intent to remove brominated and/or halogenated flame retardants from some or all of their products. The International Electronics Manufacturing Initiative (iNEMI), an industry-led consortium, is working with a number of its OEM and supply chain members to assess the feasibility of a broad conversion to HFR-free PCB materials. While IPC and JEDEC are developing halogen-free standard specifications and numerous companies have compliant materials, significant questions remain regarding overall readiness to make a transition to these materials. This paper will discuss results & conclusions from the completed iNEMI HFR-free PCB Materials Project, as well as outline current projects, which include the HFR-free High-Reliability PCB project, the HFR-free Signal Integrity Project and the HFR-free PCB Material Development Project.

Introduction

The European Union's Restriction on the use of certain Hazardous Substances (RoHS) Directive prohibits the use of polybrominated biphenyls (PBBs) and polybrominated diphenyl ethers (PBDEs) in nonexempt electronic equipment. These compounds can be used as flame-retardants and some of these substances have been shown to present unacceptable risks to human health and the environment.

A key requirement that is governed by Underwriters' Laboratory (UL) is the ability to meet the flammability standard of UL 94-V0. In general, thermosetting resins, alone or in combinations with other additives widely used in the electronic industry for PCB laminate applications, meet these requirements only because they contain approximately 30-40% brominated aromatic epoxy components, based on the resin, or approximately 17% to 30% bromine (based on the total resin weight). Although these brominated compounds have excellent flame-retardant properties, they also have some undesirable properties when incomplete burning occurs. The chemical decomposition of aromatic bromine compounds release free bromine radicals and hydrogen bromide, which are highly corrosive.

Non-halogenated alternative fire retardant material systems are being developed and introduced into products today. These systems typically use nitrogen compounds, phosphorus based compounds, or a combination of both. Some of these may be incorporated into the backbone of the polymer as is done with TBBPA in epoxy. These flame retardant systems are currently available for some printed wire boards and engineered plastic applications. It is important to note that the reliability of many alternative flame-retardants has not been fully qualified at the assembly level. Product developers will need to address whether substitutes can meet the same technical and functionality requirements, whether they will decrease product safety or reliability, and what the tradeoffs may be.

Low-Halogen Electronics

The trend toward low-halogen materials in electronic products has created a need for supply chain alignment on the maximum levels of bromine (Br) and chlorine (Cl) allowed in electronic materials and systems that are identified as low halogen (or "halogen-free" and/or "BFR/CFR/PVC-free"). A common definition of maximum halogen levels for low-halogen components and materials will enable the development of compliant material sets. The following definition of Low Halogen ("BFR/CFR/PVC-Free") electronics is supported by iNEMI and its member companies (Dell, HP, Intel, Lenovo, Cisco, Sun, Tyco Electronics etc.).

A **component**[1] must meet all of the following requirements to be Low Halogen ("BFR/CFR/PVC-Free"):

Plastic

Any of a group of synthetic or natural organic compounds produced by polymerization, optionally combined with additives (organic or inorganic fillers, modifiers, etc) into a homogeneous material capable of being molded, extruded, coated, printed or cast into various shapes and films.

PVC copolymer

Copolymers are polymers derived from two or more monomers. Highly chlorinated PVC copolymers, block polymers, and congeners are not considered acceptable alternatives to PVC for low-halogen components.

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[1] Other than those terms listed below, the definitions of terms used in this position statement, such as "component," are in accordance with IPC -T-50 and/or JESD88.

1) All printed board (PB) and substrate laminates shall meet Br and Cl requirements for low halogen as defined in IEC 61249-2-21 and IPC-4101B per 1a below (refer to IEC and IPC standards for actual requirements).

1a - Non-halogenated epoxide with a glass transition temperature of 120°C minimum. The maximum total halogens contained in the resin plus reinforcement matrix is 1500 ppm with maximum chlorine of 900 ppm and maximum bromine being 900 ppm.

2) For components other than printed board and substrate laminates:
Each plastic within the component contains < 1000 ppm (0.1%) of bromine [if the Br source is from BFRs] and < 1000 ppm (0.1%) of chlorine [if the Cl source is from CFRs or PVC or PVC copolymers].

iNEMI HFR-Free Project Portfolio

While alternative non-halogenated material systems are being developed and introduced into products, the reliability of many of these alternative flame retardants has not been fully qualified at the assembly level. Data is needed to address whether these substitutes can meet the same technical and functionality requirements as standard products, whether they will decrease product safety or reliability, and what the trade-offs may be.

iNEMI has launched several projects to identify technology readiness, supply chain capability, and reliability characteristics for HFR-Free alternatives to conventional printed circuit board materials and assemblies. The projects are:

- HFR-Free PCB Material Evaluation (completed project)
- HFR-Free High Reliability PCB (active project)
- HFR-Free Leadership Program (new program)
  - HFR-Free PCB Materials
  - HFR-Free Signal Integrity
- PVC Alternative Initiative (new initiative)

HFR-Free PCB Material Evaluation

Working together with the materials supplier base and volunteer printed wiring board manufacturers, this project evaluated the electrical, mechanical and reliability attributes of "halogen-reduced" materials using known designs from IBM and Intel Corporation.

The adoption of the halogen free alternatives requires that the laminates have minimal impact on the electrical, mechanical, electro-migration, chemical resistance, thermal, moisture absorption, and rheological properties. In addition, adhesion to copper, the oxide treatment, and to the laminate itself needs to be sufficient. Processing and assembly performance of the laminate products must meet design requirements.

Upon identification of suitable halogen free PWB laminate materials, a series of tests were performed to evaluate the electrical, thermal, and physical properties of the new commercially available materials. Materials passing the initial screen were then used to build test vehicles to evaluate other material properties. Three test vehicles were adopted in the project.

IBM SMASPP2z Electrical Test Vehicle

This test vehicle design is geared specifically toward the assessment of the dielectric material electrical properties and total loss using the Short Pulse Propagation (SPP) technique [1]. The test vehicle is an 8 layer design, MP1-V2-S3-V4-V5-S6-V7-MP8, with two stripline structure designs, one each on layers 3 and 6, which are used for the material analysis in this effort. See Figure 1. There are also microstrip structures in the test vehicle design on layers 1 and 8 which can be used when those structures are of interest.

The launch structures are designed around a high performance bolt-on SMA connector, rated at 26GHz.

The SMASPP2z test vehicle is approximately 280 x 125 mm [11" x 5"], which allows 6-up on typical panel layout.

The two stripline structures on layers 3 and 6 allow for the assessment of a resin rich and a resin poor design point respectively. This effectively defines the range of dielectric constant and effective loss tangent for any given material.

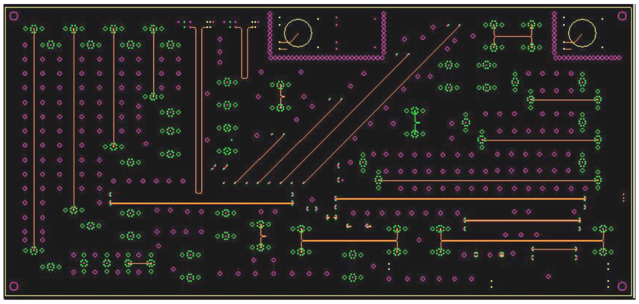


Figure 1 - SMASPP2z Test Vehicle Layout, Showing One Layer of Internal Wiring

HOP31B Test Vehicle:

This test vehicle is specifically geared toward the assessment of the propensity of a given laminate material to exhibit quality issues such as cracks and/or delamination upon exposure to multiple cycles of higher assembly process reflow conditions associated with mixed solder assembly (MSA) and/or full lead free solder assembly processes.

The HOP31B test vehicle is approximately 140 x 100 mm [5.5" x 4"].

The HOP31B test vehicle contains various size PTH arrays, all of which consist of 0.2mm [0.008"] PTHs on a 0.8mm [0.031"] pitch. See Figure 2. These PTH arrays have been shown to be sensitive to the laminate properties for which the test vehicle was designed to screen.

The HOP31B test vehicle shares the same 10 layer cross section definitions with the MEBII test vehicle, which is described in a latter portion of this paper. As with the MEBII test vehicle, two varieties of the HOP31B test vehicle were constructed, targeting a 40 mil thickness and 80 mil thickness, respectively.

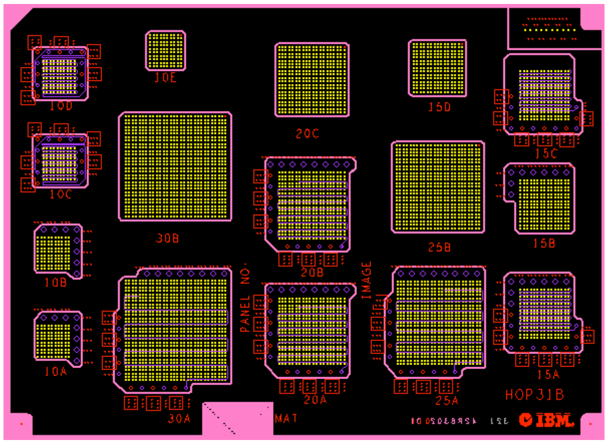


Figure 2 - HOP31B Test Vehicle Layout

Process Simulation Conditions:

The test vehicles were exposed to a specific set of assembly process conditions as follows:

SMASPP2z: The SMASPP2z test vehicles were exposed to an overnight moisture removal bake at 125°C, along with 3x, 245°C IR reflow processes.

The bake was implemented to put all laminates on a more level playing field with regards to potential impact of moisture content on the test results.

NOTE: The SMASPP2z test vehicles were inadvertently exposed to a 165°C overnight bake instead of the defined 125 °C bake.

Immersion Ag was used as the surface finish whenever possible. This was done to reduce the impact (on probing) of Cu oxide formation during reflow process simulation.

HOP31B: The HOP31B test vehicles were exposed to a matrix of conditions, all of which were preceded by an overnight moisture removal bake at 125°C. **NOTE:** The 40 mil test vehicles were inadvertently exposed to a 165°C overnight bake.

The bake was implemented to put all laminates on a more level playing field with regards to potential impact of moisture content on the test results.

The 4 cell matrix of assembly process simulations consisted of the following conditions, emulating mixed solder assembly (MSA, 245 °C) and full Pb-free (260 °C) reflow process conditions.

- 3x, 245 °C peak temperature
- 5x, 245 °C peak temperature
- 3x, 260 °C peak temperature
- 5x, 260 °C peak temperature

MEB II Evaluation

The Material Evaluation Board II (MEB II) is Intel's 2nd generation multifunctional test vehicle which contains test structures for the electrical, thermal, and mechanical performance evaluation. The test vehicle is designed to evaluate performance across a full working panel used at the PCB fabrication facility. The design is modular and can be broken into 4 quadrants for ease of testing and handling after fabrication. The test structures contained on the MEB II include: 1) Registration coupons for soldermask, drill to innerlayer and drill to outerlayer copper structures in the 4 corners of the working panel, 2) All laminate and copper plane/laminate coupon structures for flexural modulus and thermo-mechanical testing (TMA, DMA, DSC), 3) Through via, buried via, and microvia IST coupons, 4) Through via, buried via, and microvia in-line daisy chain structures for tight pitch CAF testing, 5) Trace and space capability coupons for all copper layers, 6) Hi Pot/Capacitance coupons, 7) Performance network analyzer electrical structures with GSG micro-probe contact points, 8) Moisture diffusivity coupons with SMA connection structures, and 9) BGA pad structures for Cold Ball Pull test evaluation.

The MEB II was constructed as a 10 layer board at 2 different thicknesses (40 and 80 mils or 1 and 2 mm). The construction was a 1-8-1+ double lamination with microvias 1 to 2, 2 to 3, 9 to 8, and 10 to 9; buried vias from 2 to 9; and through hole via structures 1 to 10.

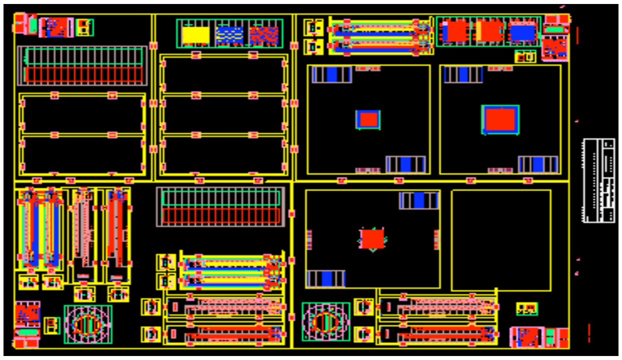
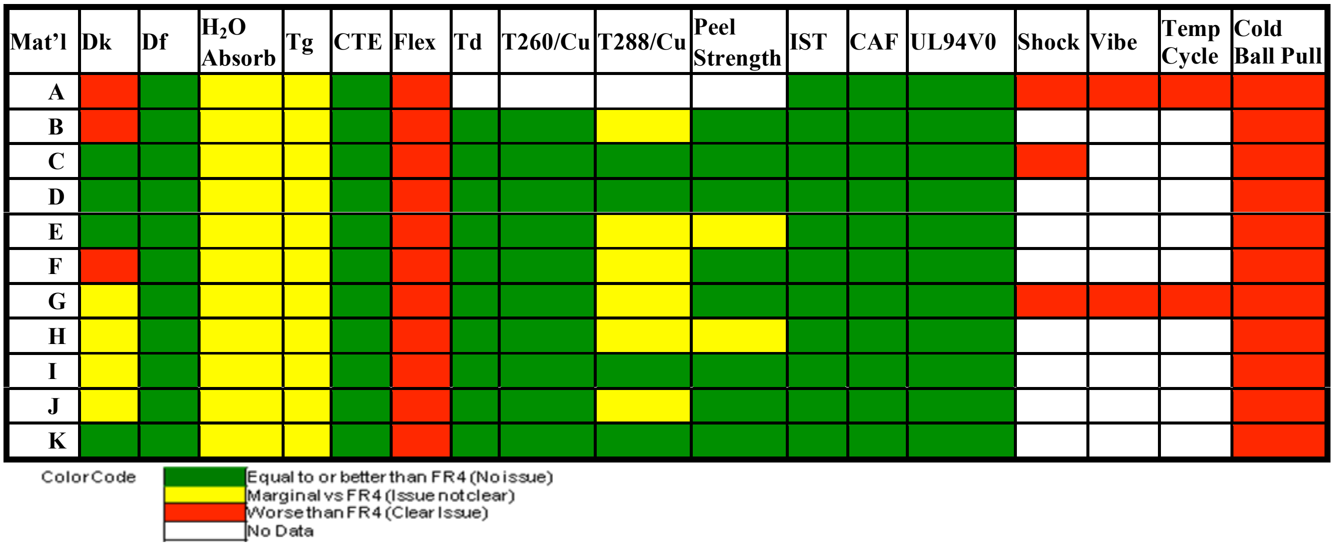


Figure 2 – MEB II Test Vehicle Layout

Overall, the team's investigation showed that not all halogen-free materials are equivalent, and none is equivalent to the FR4 baseline used (See table 1). Findings included:

- The halogen-free materials generally had higher dielectric constant (Dk) values and lower loss tangent (Df)
- Most of the halogen-free laminate materials did not exhibit resin cracking/delamination (issues normally associated with an incompatibility with higher reflow temperatures)
- In time-to-delamination tests at 260°C, 288°C and 300°C, the bromine-free materials in general did not show problematic results and were in line with brominated materials used by the electronics industry
- Moisture absorption at room temperature at 24 hours showed relatively low values, with a number of materials being below 0.20%
- Exposure to hydrothermal conditions pointed out interlayer weakness in some materials



Mat'l	Dk	Df	H_2O Absorb	Tg	CTE	Flex	Td	T260/Cu	T288/Cu	Peel Strength	IST	CAF	UL94V0	Shock	Vibe	Temp Cycle	Cold Ball Pull
A	🟥	🟩	🟨	🟨	🟩	🟥	⬜	⬜	⬜	⬜	🟩	🟩	🟩	🟥	🟥	🟥	🟥
B	🟥	🟩	🟨	🟨	🟩	🟥	🟩	🟩	🟨	🟩	🟩	🟩	🟩	⬜	⬜	⬜	🟥
C	🟩	🟩	🟨	🟨	🟩	🟥	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟥	⬜	⬜	🟥
D	🟩	🟩	🟨	🟨	🟩	🟥	🟩	🟩	🟩	🟩	🟩	🟩	🟩	⬜	⬜	⬜	🟥
E	🟩	🟩	🟨	🟨	🟩	🟥	🟩	🟩	🟨	🟨	🟩	🟩	🟩	⬜	⬜	⬜	🟥
F	🟥	🟩	🟨	🟨	🟩	🟥	🟩	🟩	🟨	🟩	🟩	🟩	🟩	⬜	⬜	⬜	🟥
G	🟨	🟩	🟨	🟨	🟩	🟥	🟩	🟩	🟨	🟩	🟩	🟩	🟩	🟥	🟥	🟥	🟥
H	🟨	🟩	🟨	🟨	🟩	🟥	🟩	🟩	🟨	🟨	🟩	🟩	🟩	⬜	⬜	⬜	🟥
I	🟨	🟩	🟨	🟨	🟩	🟥	🟩	🟩	🟩	🟩	🟩	🟩	🟩	⬜	⬜	⬜	🟥
J	🟨	🟩	🟨	🟨	🟩	🟥	🟩	🟩	🟨	🟩	🟩	🟩	🟩	⬜	⬜	⬜	🟥
K	🟩	🟩	🟨	🟨	🟩	🟥	🟩	🟩	🟩	🟩	🟩	🟩	🟩	⬜	⬜	⬜	🟥

Color Code
🟩 Equal to or better than FR4 (No issue)
🟨 Marginal vs FR4 (Issue not clear)
🟥 Worse than FR4 (Clear Issue)
⬜ No Data

Table 1: Material Evaluation Summary

- Most of the materials exhibited relatively good adhesion to copper
- In-plane expansion is similar to brominated materials, in the range of 17-22 ppm/°C
- Out-of-plane data indicate relatively lower values with an average of around 45 ppm/°C below Tg
- The significance of the differences in the halogen-free material properties and performance will be dependent on the design and demands of the products in which they are incorporated. The iNEMI project team recommends individual testing of any material for its intended application prior to mass production.

HFR-Free High Reliability PCB

This project is a follow-on to the HFR-Free PCB Material Evaluation Project. Its focus is to identify technology readiness, supply capability and reliability characteristics for “HFR-free” alternatives to conventional printed wiring board materials and assemblies, based on the requirements of the high-reliability market segment. Project goals are to:

- Identify commercially viable materials
- Benchmark past work and key in on critical knowledge gaps and technical issues
- Build on industry knowledge and capability, including the iNEMI HFR-Free PCB Material Evaluation Project
- Design test vehicles and test methodologies and, leveraging prior investigations, carry out the necessary testing to characterize viable materials

The team has identified seven HFR-free materials to be evaluated, and a typical halogenated material as a control. Test vehicle lay-ups have been completed for the material evaluation testing as well as the board-level reliability testing and test vehicles are currently being built utilizing the materials being supplied by each of the seven material suppliers, with testing to begin as soon as all materials / TVs have been received.

HFR-Free Leadership Program

Several major OEMs are evaluating the elimination of HFRs from their PCB materials. While mobile phone manufacturers are well along in this effort, the next area of impact will likely be driven by high volume client computer applications.

An industry-wide conversion to HFR-free materials faces numerous challenges:

- Reliability of materials with alternative flame retardants has not been fully qualified
- Complete “technology envelopes,” or technical specifications, have not been established for various product applications
- Incomplete design knowledge in segments of the supply chain increases risk of conversion issues
- A rapid complete conversion of computer products will have a major impact on the supply chain and needs to be coordinated

iNEMI is working with a number of our OEM members to assess the feasibility of a broad conversion to HFR-free PCB materials. Although IPC and JEDEC are developing halogen-free standard specifications and numerous companies have compliant materials, significant questions remain regarding overall readiness to make a transition to these materials. For example:

- What electrical properties are needed to meet high speed signaling requirements?
- With many HFR-free materials showing higher stiffness, what mechanical properties are needed to ensure system reliability isn’t degraded?
- Can design modifications reduce sensitivity to electrical and material properties?

As a result, two projects have been established: HFR-Free Signal Integrity and HFR-Free PCB Materials.

HFR-Free Signal Integrity

The iNEMI HFR-Free PCB Signal Integrity Work Group has been in formation for the past 3 months and presently has 13 companies actively involved. The work groups' goal is to identify the critical electrical parameters of HFR-Free dielectric materials, set limits on those parameters so that signal integrity will not be jeopardized for high speed buses, and communicate those electrical limits to the material suppliers so they can focus resources on producing products the industry requires, which in turn should help ensure adequate volume for product launches and reduced costs.

A critical goal of the work group is to develop a common measurement methodology that will ensure consistent and accurate evaluation of the electrical parameters of the dielectric and allow apples-apples comparison of the industries HFR-Free materials. The measurement methodology will also be used by the material suppliers as the "standard evaluation method" for reporting the electrical values of the critical parameters on the material data sheets.

The work group has identified 4 critical electrical parameters; 1) dielectric permittivity (Dk), 2) loss tangent (Df), 3) moisture absorption (specifically how it affects Dk and Df) and 4) breakdown voltage. Based on the high-speed signaling needs required by each company, the limits of each parameter will be identified. Samples of HFR-Free materials will then be evaluated (using the common measurement methodology) and the results will be mapped into the requirements providing a design data base that companies can use to select adequate materials for products.

HFR-Free PCB Materials

The iNEMI HFR-Free PCB Materials Work Group has been in formation for the past 3 months and presently has 17 companies actively involved in the PCB Materials Work Group. The work groups' goal is to identify material/technology limitations involved in transitioning to HFR-free PCB materials.

Areas of Concern			
1	UL Fire ratings (V0-V1)	13	Fracture Toughness of Resin / Resin Cohesive Strenght
2	Glass transition temperature (Tg)	14	Stiffness/Flexural Strength
3	Decomposition temperature (Td)	15	Copper Pad Adhesion (CBP/Hot Pin Pull/ Shear or Tensile)
4	Coefficient of thermal expansion (z-axis and x-, y-axes)	16	Co-Planarity Warpage characteristics
5	Moisture absorption	17	Long term life prediction, (IST or thermal shock test)
6	UL CTI rating	18	CAF resistance
7	MOT Maximum Operating Temperature	19	Delamination characteristics under mechanical or thermal stress
8	Punchability/Scoring/Breakoff Performance	20	Resin system dependency/hardening/curing agents
9	PCB fabrication process, drill wear, lamination & desmear cycle	21	Affect of Fillers
10	Rework (Pad Peeling)	22	Plastic and elastic deformation characteristics
11	Micro and macro hardness	23	Shock & Vibe and Drop test data
12	Electrical Properties (Dk & Df)	24	Transient Bend

Table 2: Areas of Concern by HFR-free PCB Materials Project

The work group (WG) has identified 24 "areas of concern" (See Table 2), including thermo-mechanical performance characteristics and is now determining if these are in the critical path for the halogen-free PCB material transition. The WG is beginning its' evaluation of metrologies and test methods which can quantify these characteristics. The WG will build test boards to verify the sensitivity of the test methods/metrology ability to quantify the areas of concern. It is expected that the test methods will include standard metrology already used in the industry with modified limits or ranges required in some cases. New test methods/metrologies will be developed if no standard method can be applied. The test methods will become part of a test suite used to evaluate HF laminate materials and provide feedback from the OEM/ODM to the laminate suppliers. This project will identify the technical risks of a broad transition to HF PCB platforms/systems, initially focusing on Desktop and Mobile notebook including the assessment of manufacturing and supply chain capacity for high volume HF transition.

PVC Alternative Initiative

This new initiative is one of the projects proposed at the iNEMI Sustainability Summit (September 2008). This effort will investigate "PVC-free" alternative materials, focusing on:

- Environmental lifecycle assessment (LCA) comparing PVC compounds with PVC-free compounds for US-based detachable desktop power cord applications (cable, connectors and wire)
- Cradle-to-grave LCA, including end-of-life aspects (recycling, incineration, landfill, etc.)
- Comparison of equivalent functional units that meet UL requirements
- Performance testing to gain a better understanding of the electrical, mechanical and safety aspects of PVC free alternatives

Conclusions

Our investigation has shown that not all halogen free materials are equivalent, and none are equivalent to our FR4 baseline. Compared to the baseline material, we see generally higher Dk values and lower Df values for halogen free materials. The significance of the halogen free material property and performance differences will be dependent on the design and demands of the products in which they are incorporated.

While the dielectric constant was relatively unaffected by the assembly reflow processes, the effects on the effective loss tangent were more noticeable, albeit not consistent. This may be due to the varying moisture content of the laminate materials as manufactured at the laminate vendor and PCB fabricator, and the relative sensitivity of the loss tangent vs. the dielectric constant.

The thermal expansion coefficient measurements for the various bromine free laminates, both below and above the glass transition temperature, indicate that the in-plane expansion is similar to the brominated materials, in the range of 17-22 ppm/ºC. The out of plane data indicate relatively lower values with an average of around 45 ppm/ºC below Tg. The lower out of plane expansion is due to the constraining properties of the fillers used to impart V0 rating.

This project teams recommend the individual testing of any material for the specific application by the designer prior to mass production

Acknowledgments

iNEMI HFR-Free PCB Materials Evaluation Project Team, Fabricators & Laminate Suppliers

- Albemarle, Cisco, Clariant, HP, IBM, ITEQ, Sun Microsystems, Vitronics-Soltec, Hitachi Chemical, Nan Ya, Shengyi, Isola, Panasonic, TUC, Multek, Chin Poon, GCE, Meadville, Nan Ya PCB, E&E, Sanmina, PWB Interconnects, IST

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iNEMI HFR-Free Leadership Teams - the Signal Integrity and PCB Materials Work Groups

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