iNEMI BFR-FREE PCB MATERIALS EVALUATION PROJECT REPORT

Stephen Tisdale / Gary B. Long
Intel Corporation
Chandler, AZ / Hillsboro, OR
Stephen.Tisdale@Intel.com
Gary.B.Long@Intel.com

Roger Krabbenhoft
IBM Corporation
Rochester, MN
Rkrabben@us.ibm.com

Kostas Papathomas, Ph.D.
Endicott Interconnect
Endicott, NY
Kostas@eitny.com

Terry Fischer.
Hitachi Chemical
Beacon Falls, CT
Fischer@hitachi-chemical.com

Abstract

Brominated flame retardants, namely polybrominated diphenyl ethers (PBDEs), were one of the main materials used to reduce the flammability of consumer goods and electronics. Growing evidence shows that PBDE compounds are making their way into the environment. These chemicals may cause health effects, prompting many nations to ban or suspend their use in new consumer goods.

Bromine- and chlorine-containing flame retardants are still widely used in some products, including electronics, and the need for new alternatives is being driven by a combination of policy standards pressure from environmental groups. The European Union banned the use of two formulations, pentaBDE and octaBDE, in 2004, the same year they were withdrawn from the North American market. A third compound, decaBDE, was banned 1 April 2008 by the European Court of Justice. Asian countries and some U.S. states have similar legislation in the works.

The electronics industry is under pressure from environmental groups to remove potentially toxic compounds from their products, including the brominated flame retardants (BFRs) 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 task of this project was to investigate, through testing, claims by many early adopters that this new class of materials performed better than the status quo. The project avoided entering the emotional debate between Industry and the Environmental Groups.

Working together with the materials supplier base and volunteer printed wiring board manufacturers, we have used known designs from IBM and Intel to judge the electrical, mechanical, and reliability attributes of these “Halogen Reduced” materials. When this project was initiated, priority was given to those laminates which were most commonly used in the industry at that time, those that would provide minimal cost impact through their use, and those showing a propensity to be capable of surviving new lead free and/or lead reduced soldering processes. Since the start of this project, there have been many advances in not only brominated materials, but also their counterpart “halogen reduced” materials as well. The base materials industry is very dynamic, as is the industry of printed wiring boards. This committee would recommend the individual testing of any material for the specific application prior to its introduction into mass production.

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. Industry 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.

Goals of the Project:

- Identify commercially viable BFR-free materials capable of lead free processing
- Benchmark past work and key in on critical knowledge gaps and technical issues
- Design test vehicles and test methodologies
- Leveraging prior investigations, carry out the necessary testing to characterize viable materials
- Analyze results
- Publish recommendations

Materials and Methods

This section will be broken into 3 sub-sections, one for the **Materials Evaluation**, one for the **SMASPP / HOP31 Evaluation**, and one for the **MEB II Evaluation.**

Material Evaluations

The adoption of the halogen free alternatives require 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 materials. These materials have been deemed to be commercially available and were provided to Endicott Interconnect Technologies (EI) by the materials suppliers. This testing provides sufficient information to determine the relative robustness of each material with respect to basic properties both in the prepreg and laminate stages. The comparison between the halogen free materials and the brominated control was made by using only prepreg on 1080 glass cloth type having resin content in the range of 50-70%. Ultimately the goal was to identify the materials with the best performance based on these results and to predict their performance through the various processes, but this was not always achieved. In our normal protocol the materials that pass the basic material property requirements could then enter a second phase - building of a test vehicle to evaluate other material properties such as processability, drilling, hole cleaning, plating, dimensional stability, assembly and reliability performance. As mentioned earlier the prepreg type used for the evaluation was 1080 style with the corresponding characteristics listed in Table 1 as provided by the suppliers.

Product	Style	Resin Content (%)	Resin Flow (%)	Gel Time (Sec)	Volatile Content (%)
Material A	1080	70.3	--	87	--
Material B	1080	66.6	32.1	123	0.57
Material C	1080	70.1	42.7	111	--
Material D	1080	70.1	47.7	103	--
Material E	1080	70.1	47.6	139	--
Material F	1080	70.0	38	140	< 0.8
Material G	1080	64.6	36	160	0.52
Material H	1080	65.2	39.3	159	0.19
Material I	1080	68	40.17	142	0.32
Material J	1080	68.14	50.14	158	0.31
Material K	1080	70.5	NA	92	--

Table 1 - Halogen free Prepreg properties as reported by suppliers

Prepreg and Laminate Characterization:

Prior to lamination, the chemo-rheological properties of each resin extracted from the prepregs were investigated.

The magnitude of the minimum viscosity points out the relative liquidity of the resin as a function of temperature at a specific heating rate and can be used as a guide to adjust the lamination conditions of each resin under evaluation. The resin was flaked from the glass cloth and sieved to remove any remaining broken glass fibers. Measuring the glass transition temperature, heat of reaction and minimum viscosity of the resin gives a good indication about how the resin will behave during the lamination process. The resin content for the prepregs tested ranged from 64-70% and the flow as reported from the suppliers was in the range of 25-50%. The gel-time was 82-160 sec.

A Wabash enclosed-vacuum, two-opening, electric press was used to laminate all the selected bromine free materials for the various tests. Lamination conditions suggested by the laminate suppliers were followed when available. Otherwise, a material was laminated at a dwell temperature slightly above its reported ultimate glass transition temperature (Tg). The lamination pressure was dependent upon the rheological properties of the prepreg. For unclad sample preparation, the copper was removed by etching in the cupric chloride bath set at 55°C. The samples were then dried in an oven at 110°C for 1 hour. The specific test methods followed for the evaluation of the bromine free laminate materials properties are internal Endicott Interconnect (EI) specifications, standard IPC, and ASTM methods. The IPC methods can be easily accessed at www.ipc.org under the section IPC-TM-650, while ASTM methods can be obtained at www.astm.org.
Our findings are discussed in the results section.

Laminate Electrical Characteristic and Reflow Compatibility Evaluation

This portion of the evaluation focused on the assessment of the frequency dependant dielectric constant and effective loss tangent as well as the propensity for the laminates to survive elevated temperature reflow environments. The ten halogen free and control laminate material were fabricated into two specific test vehicle designs. These designs are designated SMASPP2z and HOP31B.

SMASPP2z 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.

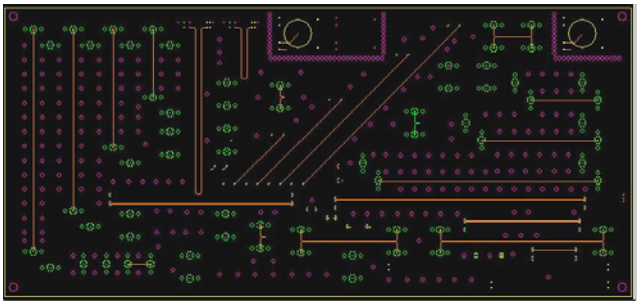


Figure 1 - SMASPP2z Test Vehicle Layout, Showing One Layer of Internal Wiring

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.

The core and prepreg within each stripline structure are matched for resin content to reduce any error introduced by averaging the electrical properties between the two pieces of laminate.. Each fabricator defines the specific glass cloth and resin content to be used w/in each stripline structure in order to meet the resin matching criteria as well as result in approximately 50 ohm single ended and 100 ohm differential impedance.

In an attempt to minimize the variability, it was requested that common reverse treat Cu foil (RTF) be used in the build of all the stripline structures.

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.

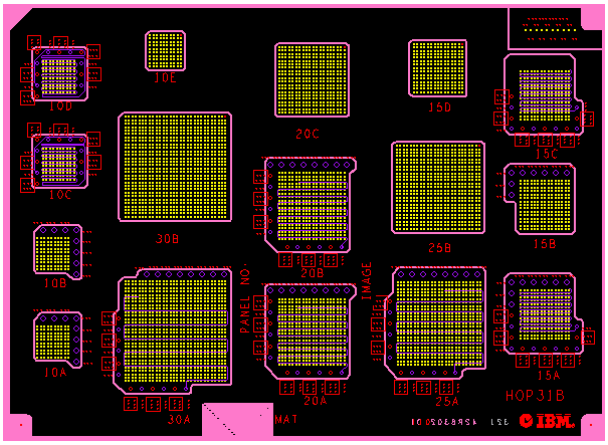


Figure 2 - HOP31B Test Vehicle Layout

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 report. 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.

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

Analysis Techniques:

The SMASPP2z test vehicles were assessed using the SPP technique before and after the assembly reflow simulations. This technique basically compares a time domain impulse which is propagated down a longer trace to one which is propagated down a shorter trace. The traces are first determined to be nearly electrically and physically identical through TDR and DC analysis. A TEK DSA8200 with 80E04 sampling head and PPL 5208 Impulse Forming Network are used to generate the impulse. Low frequency information is gathered on an LCR meter. The resulting data is then iteratively compared to model data output using a causal field solver, allowing the extraction of frequency dependant dielectric constant and effective loss tangent of the laminate material. This allows for a direct comparison of the relative performance of the laminate materials.

The technique outputs an 'effective loss tangent', which includes both the laminate loss tangent, as well as the effects attributed to Cu foil roughness. Skin effects are separated out, but the degree to which the Cu foil roughness exacerbates skin effects is generally not separated from the laminate losses. In attempt to minimize these impacts, RTF Cu foil was requested to be used on these test vehicles.

Many field solvers do not account for roughness in their output, and as such, the inclusion of these effects w/in the effective loss tangents allows the user of this information to ensure they are not overly optimistic in their modeled design performance.

The HOP31B test vehicles were assessed using cross section analysis after the assembly reflow simulations. For each laminate material, sixteen cross sections were taken across PTH arrays in four of the six test vehicles in each matrix cell. Visual inspection for any evidence of delamination and/or laminate cracking was performed.

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, 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. The 2 stack-ups built for each material set are represented in Tables 2 & 3.

MEB II

	Description		Thickness
Layer 1	Plated 1/2 oz Cu		1.6 mils
	Prepreg		2.4 mils - 1 ply 1080
Layer 2	Plated 1/2 oz Cu		1.2 mils
	Prepreg		2.4 mils - 1 ply 1080
Layer 3	Unplated 1/2 oz Cu		0.6 mils
	Core		4 mils - 1 ply 2116
Layer 4	Unplated 1/2 oz Cu		0.6 mils
	Prepreg		3.6 mils - 2 ply 106
Layer 5	Unplated 1 oz Cu		1.2 mils
	Core		6 mils - 2 ply 2112 Adjust to achieve overall thickness of 0.040"
Layer 6	Unplated 1 oz Cu		1.2 mils
	Prepreg		3.6 mils - 2 ply 106
Layer 7	Unplated 1/2 oz Cu		0.6 mils
	Core		4 mils - 1 ply 2116
Layer 8	Unplated 1/2 oz Cu		0.6 mils
	Prepreg		2.4 mils - 1 ply 1080
Layer 9	Plated 1/2 oz Cu		1.2 mils
	Prepreg		2.4 mils - 1 ply 1080
Layer 10	Plated 1/2 oz Cu		1.6 mils
			40 mils

Table 2 – MEB II 40 Mil Thick Board Stack-up

MEB II

	Description		Thickness
Layer 1	Plated 1/2 oz Cu		1.6 mils
	Prepreg		2.4 mils - 1 ply 1080
Layer 2	Plated 1/2 oz Cu		1.2 mils
	Prepreg		2.4 mils - 1 ply 1080
Layer 3	Unplated 1/2 oz Cu		0.6 mils
	Core		4 mils - 1 ply 2116
Layer 4	Unplated 1/2 oz Cu		0.6 mils
	Prepreg		3.6 mils - 2 ply 106
Layer 5	Unplated 1 oz Cu		1.2 mils
	Core		47 mils - 6 plies 7628 Adjust to achieve overall thickness of 0.080"
Layer 6	Unplated 1 oz Cu		1.2 mils
	Prepreg		3.6 mils - 2 ply 106
Layer 7	Unplated 1/2 oz Cu		0.6 mils
	Core		4 mils - 1 ply 2116
Layer 8	Unplated 1/2 oz Cu		0.6 mils
	Prepreg		2.4 mils - 1 ply 1080
Layer 9	Plated 1/2 oz Cu		1.2 mils
	Prepreg		2.4 mils - 1 ply 1080
Layer 10	Plated 1/2 oz Cu		1.6 mils
			80 mils

Table 3 - MEB II 80 Mil Thick Board Stack-up

All the suppliers participating in the MEB II builds were asked to provide the build material details for their boards. Table 4 below lists the material components of each supplier's build. Ten different halogen-free laminates were built at 6 different PCB fabricators (Materials B through K in Table 4). Additionally, a brominated FR4 laminate was built as a control for the testing (Material A in Table 4).

Laminate Material	PWB Supplier	Soldermask	Copper Foil	Via Plug Material
A	2	T - Green	Std HTE	X
B	5	T - Green	Std HTE	X
C	1	S - Green	Std HTE	Y
D	1	S - Green	Std HTE	Y
E	1	S - Green	Std HTE	Y
F	3	S - Green	Std HTE	None
G	6	S - Blue	VLP	X
H	6	S - Blue	VLP	X
I	4	T - Blue	Std HTE	X
J	4	T - Blue	Std HTE	X
K	7	T - Green	Std THE	None

Table 4 – Listing of all materials used by suppliers in the MEB II builds

Test Structures and Methods

Not all test capabilities of the MEB II board were utilized or completed at the time of this writing. The following are the structures and methods performed for the results included in this paper. Additional testing will be reported in later publications.

Registration testing is done electrically with an open circuit reading indicating a passing result and short indicating a failing result. The drill to innerlayer copper test structure uses a gridded hole pattern which has different clearances between the copper plane on a particular layer and the through hole via. The clearances can be sorted by magnitude and direction to determine registration and layer movement. The test probe is an Intel designed unit (Figure 3) which translates the opens and shorts output to a registration magnitude and direction for the board.

Figure 3. Intel registration probe

The IST testing utilized 2 coupon designs on the MEB II board. The first IST coupon was a through-hole design with 10 mil drill in a 20 mil pad on a 32 mil grid. The second coupon was a microvia coupon with a 5 mil drill in a 12 mil pad on a 20 mil grid. The microvia coupon had 2 circuits, one with microvias from layer 1 to 2 (S1), and the second with microvias from layer 2 to 3 (S2). The coupons were subjected to 5 different assembly conditions prior to IST testing. The conditions were: 1) As is, 2) 3 reflows at 245C peak temp, 3) 5 reflows at 245C peak temp, 4) 3 reflows at 260C peak temp and, 5) 5 reflows at 260C peak temp. Initial resistance measurements were taken to sort out any failed coupons prior to IST testing (coupons with shorts or opens). Additionally capacitance measurements were taken prior to testing to examine the impact of assembly on the coupon (delamination). The IST testing was conducted in accordance with IPC TM-650 2.6.26 test method. The coupons were tested until a resistance change of 10% was observed or a maximum of 1000 cycles completed. The through-hole coupons were cycled from room temp (72F or 22C) to 150C. The microvia coupons were cycled from room temp to 190C.

Dk and total loss were extracted from S-parameter measurements taken using an Agilent E8364B Performance Network Analyzer (PNA). The test structures (Figure 4) were 5 mil traces, 3 inches long in 3 configurations: 1) outerlayer microstrip referenced to a plane on layer 2 with soldermask covering the trace, 2) outerlayer microstrip referenced to a plane on layer 2 without soldermask covering the trace and, 3) innerlayer stripline referenced to planes of both layers 1 and 3. The microprobe structure was a G-S-G configuration on 10 mil centers. The S-parameter measurements were taken across the full frequency range of the PNA (10MHz to 50 GHz).

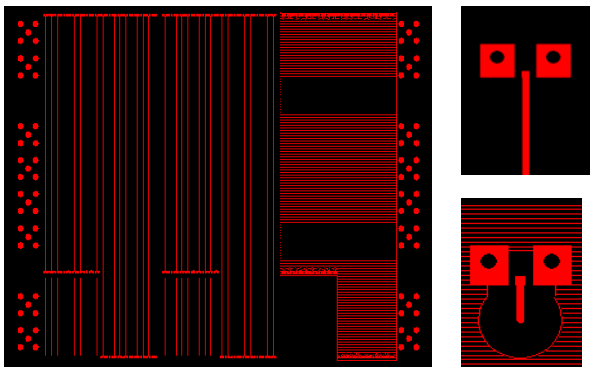


Figure 4 – Dk and total loss test structures.

Moisture testing was conducted by placing the coupons in an Espec ECL 2CA Temperature Humidity chamber and measuring the S-parameters using a HP 8510C VNA as the coupons are cycled through a controlled temperature humidity program[2]. The coupons (Figure 5) were connected to a 2-port VNA using coax cabled SMA connectors on each end of the test trace. The S-parameter measurements were taken across the full frequency range of the VNA (10MHz to 20 GHz) and recorded by time at 1 hour intervals. The program consists of: 1) initial readings, 2) dry bake at 105C/0%RH until readings reach asymptotic state and, 3) soak at 85C/85%RH until readings reach asymptotic state. The moisture diffusivity rate is determined by obtaining a Fickian fit with the data.

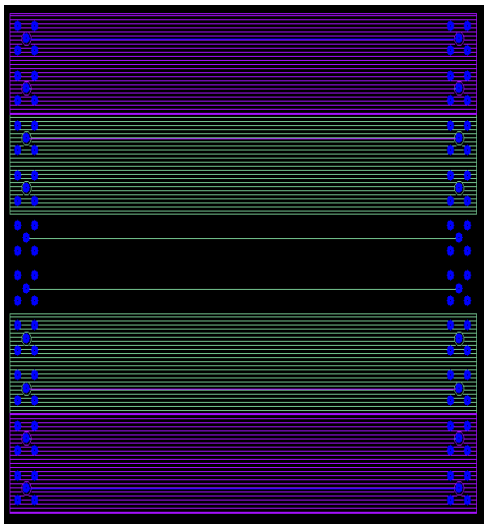


Figure 5 – Moisture testing coupon

RESULTS

Material Evaluations

In electronic applications, the laminates are generally required to possess a wide range of favorable properties including high mechanical strength, good thermal stability, good chemical resistance, low heat distortion, a high resistance to aging, good electric insulation properties, consistent dimensional stability over a wide temperature range, good adhesion to glass and copper, a high surface resistivity, a low dielectric constant and loss factor, ease of drillability, low water absorption and a high corrosion resistance.

Prepregs

All prepregs tested consisted of 1080 style cloth, were tack free and of good quality. The resin content ranges were from 64% - 70%, the flow was 32% - 50%, and the gel times were 82–160 seconds. The prepreg glass transition temperatures ranged from 47-68ºC and the minimum viscosity was 50-146 Pas. The viscosity minimums are relatively low compared to the brominated counterparts. The temperature of the minimum viscosity was in the range of 132-160ºC. The filler content of these prepregs was measured by removing the resin from the glass cloth and then ashing the samples at 700ºC in the presence of air. An assessment of the chemistry type and the shape or size of the filler particles was performed by Optical microscopy and electron dispersive methods such as EDSRepresentative photographs for some of the materials are shown in Figures 6 - 9. In general the fillers that are used as the source of flame retardancy are composed of Al and Mg inorganic

compounds. In the case of P based flame retardants the source could be either reactive phosphorous organic components or particulates. The inorganic filler content ranges were found to be 1 - 32% by weight.

Material A

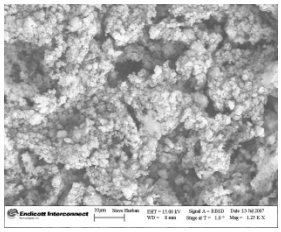


Figure 6

Material C

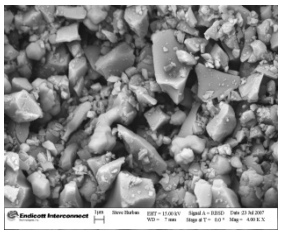


Figure 7

Material B

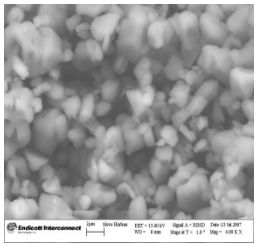


Figure 8

Material I

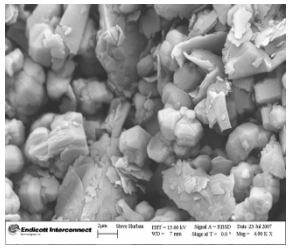


Figure 9

Laminates

Dielectric measurements were conducted using both two and four ply copper clad samples according to IPC-TM-650 Methods 2.5.5.6 and 2.5.5.1B. The majority of the tested materials showed a dielectric constant *(Dk)* in the range of 3.9 – 4.6 and dissipation factors (*Df)* in the range of 0.01-0.02, with Material B slightly lower at < 0.01 both at 1GHz frequency range.

In addition to satisfying the bromine free or "green" requirements, halogen free laminates must comply with the flammability requirements as governed by the UL-94, as well as fulfill the expected mechanical and electrical requirements. The results show that all laminates tested appear to be meeting the V0 rating. It was noticed that materials I & J showed prolonged side burning and violating the T1 flame time requirements of no greater than ten seconds.

To determine if each material is capable of providing good inter- and intra- layer reliability in an actual product application, several adhesion tests are normally performed. Generally, the greater the adhesion, the better the material will perform through assembly and thermo-cycling or during use of the product. Using Gould JTCS 1.0 oz., test data shows that the copper-to-laminate adhesion is in the range of 5-9 lbs/in with materials B, F and K exceeding 8 lbs/in. The interlaminate adhesion is shown to be in the range of 3 lbs/in with materials F & K being the highest at 4-5lbs/in. Employing bond film as the oxide alternative, the adhesion is shown to range between 2-3 lbs/in with material F to have values greater than 4 lbs/in.

The x, y, and out of plane thermal expansion values for the various halogen 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. The above Tg out of plane expansion ranges between 250-350 ppm/ºC.

The glass transition temperatures were determined to be at 140 – 200ºC as measured by the DSC middle point method, with the majority being in the range of 150ºC.

The thermal degradation temperature (5% weight loss) for all laminates was above 330ºC. T260 values with Cu on the outside ranged from 18 to >120 minutes, with materials B & J being in the low end of this range. T-300 values with Cu on the outside ranged from 0 to >120 minutes, with the majority in the 0 – 26 minute range.

Along with thermal stability, moisture also plays a key role in determining whether a material is capable of withstanding lead-free processing conditions or simply assembly conditions. At elevated temperatures, the vapor pressure of trapped moisture absorbed in the resin can lead to rapid delamination. Obviously, the lower the moisture level present in the material, the better. A major concern regarding bromine free materials is that alternative flame retardants used (organo-phosphorus, nitrogen containing polymers, and inorganics) can be hygroscopic and may increase moisture levels in the resins. Moisture up-take at the 24hr RT exposure and 1 hour PCT show saturation levels between 0.1 and 0.35 percent. The moisture absorption levels are relatively low. The 1 hr PCT exposure does point out some weakness in some of the samples having levels as high as 1.4%. Others, such as materials B, E & J show rather comparable moisture absorption levels as the phenolic brominated material. The extent of hydrothermal stability of the halogen free laminates was evaluated by exposing the one-sided copper clad laminate samples in a pressure cooker vessel (ten 4"x 4" x 0.035") for 30 min, 60 min, 4 hr, and 8 hr time periods. The samples were then dipped in 500 ^{o}F (260 ^{o}C) molten Sn/Pb solder contained in a Waage melting pot. An individual sample fails if blistering larger than 0.25" occurs. The results show that at the 8 hr exposure the laminates made from materials B, E, G, H, F & J prepregs were passing where materials C, D, E & I performed less favorably by showing excessive blistering.

Dielectric Constant and Loss Tangent Assessment Using Short Pulse Propagation

The ranges of dielectric constant (Dk or Er) and effective loss tangent (Df) are shown below in Tables 5 - 8. Both resin rich and resin poor structures were assessed. The

laminate resin contents varied from 51 – 73%. Differences between this test data and other data in this report may be explained by the specific resin content of the structures tested, as well as differences driven by measurement technique. The structures tested here are representative of those used in actual product.

		Effective Dk*			
HF Laminate	Resin Content Rich/Poor	1GHz Dk	5GHz Dk	10GHz Dk	20GHz Dk
Material A (control)	Rich, 66%	4.026	3.931	3.886	3.836
	Poor, 55%	4.396	4.3	4.256	4.206
Material B	Rich, 70%	4.242	4.16	4.125	4.09
	Poor, 53%	4.502	4.413	4.398	4.364
Material C	Rich, 73%	3.985	3.917	3.886	3.854
	Poor, 53%	4.499	4.421	4.389	4.356
Material D	Rich, 73%	4.019	3.959	3.933	3.902
	Poor, 53%	4.481	4.419	4.39	4.357
Material E	Rich, 73%	3.999	3.931	3.901	3.869
	Poor, 53%	4.45	4.368	4.333	4.299
Material F	Rich, 73%	4.285	4.198	4.161	4.124
	Poor, 53%	4.708	4.632	4.6	4.566
Material G	Rich, 73%	4.064	3.978	3.942	3.906
	Poor, 53%	4.596	4.518	4.486	4.451
Material H	Rich, 73%	4.19	4.1	4.062	4.025
	Poor, 53%	4.687	4.612	4.579	4.541
Material I	Rich, 70%	4.109	4.016	3.98	3.943
	Poor, 51%	4.688	4.585	4.541	4.499
Material J	Rich, 70%	4.154	4.055	4.01	3.963
	Poor, 51%	4.751	4.646	4.599	4.551
Material K	Rich, 67%	4.056	3.964	3.928	3.895
	Poor, 53%	4.347	4.274	4.243	4.212

Table 5 - Effective Dielectric Constant Prior To Bake/Reflow

		Effective Df**			
HF Laminate	Resin Content Rich/Poor	1GHz Df	5GHz Df	10GHz Df	20GHz Df
Material A (control)	Rich, 66%	0.0231	0.0252	0.0269	0.0284
	Poor, 55%	0.0209	0.0231	0.0245	0.0259
Material B	Rich, 70%	0.0176	0.019	0.019	0.019
	Poor, 53%	0.0147	0.0163	0.017	0.0175
Material C	Rich, 73%	0.0167	0.0175	0.0183	0.019
	Poor, 53%	0.0161	0.017	0.017	0.0175
Material D	Rich, 73%	0.0141	0.0156	0.0165	0.0179
	Poor, 53%	0.0131	0.0147	0.0158	0.0167
Material E	Rich, 73%	0.0161	0.0174	0.018	0.0192
	Poor, 53%	0.0168	0.018	0.0181	0.0181
Material F	Rich, 73%	0.0193	0.0201	0.0202	0.0207
	Poor, 53%	0.0154	0.0162	0.0164	0.0174
Material G	Rich, 73%	0.0196	0.0207	0.0207	0.0207
	Poor, 53%	0.0158	0.017	0.017	0.0182
Material H	Rich, 73%	0.02	0.021	0.021	0.021
	Poor, 53%	0.0153	0.0166	0.0175	0.019
Material I	Rich, 70%	0.0203	0.0216	0.0211	0.0217
	Poor, 51%	0.0198	0.0215	0.0215	0.0215
Material J	Rich, 70%	0.0227	0.0247	0.0256	0.0264
	Poor, 51%	0.0206	0.0225	0.0231	0.0237
Material K	Rich, 67%	0.0209	0.0213	0.0203	0.02
	Poor, 53%	0.0155	0.0165	0.0165	0.0165

Table 6 - Effective Loss Tangent Prior To Bake/Reflow

		Effective Dk			
HF Laminate	Resin Content Rich/Poor	1GHz Dk	5GHz Dk	10GHz Dk	20GHz Dk
Material A (control)	Rich, 66%	N/A	N/A	N/A	N/A
	Poor, 55%	N/A	N/A	N/A	N/A
Material B	Rich, 70%	4.253	4.167	4.129	4.092
	Poor, 53%	4.497	4.416	4.379	4.341
Material C	Rich, 73%	4.029	3.951	3.917	3.884
	Poor, 53%	4.495	4.427	4.399	4.366
Material D	Rich, 73%	3.974	3.9	3.87	3.838
	Poor, 53%	4.461	4.397	4.367	4.334
Material E	Rich, 73%	3.977	3.897	3.863	3.828
	Poor, 53%	4.45	4.369	4.333	4.297
Material F	Rich, 73%	4.318	4.231	4.192	4.154
	Poor, 53%	4.721	4.64	4.604	4.568
Material G	Rich, 73%	4.04	3.955	3.919	3.883
	Poor, 53%	4.563	4.481	4.447	4.411
Material H	Rich, 73%	4.153	4.064	4.029	3.994
	Poor, 53%	4.654	4.572	4.538	4.5
Material I	Rich, 70%	4.085	3.989	3.951	3.914
	Poor, 51%	4.681	4.583	4.543	4.502
Material J	Rich, 70%	4.132	4.028	3.982	3.937
	Poor, 51%	4.735	4.63	4.583	4.535
Material K	Rich, 67%	4.034	3.943	3.906	3.871
	Poor, 53%	4.373	4.301	4.271	4.241

Table 7 - Effective Dielectric Constant After Bake/Reflow

		Effective Df**			
HF Laminate	Resin Content Rich/Poor	1GHz Df	5GHz Df	10GHz Df	20GHz Df
Material A (control)	Rich, 66%	N/A	N/A	N/A	N/A
	Poor, 55%	N/A	N/A	N/A	N/A
Material B	Rich, 70%	0.0189	0.0201	0.0203	0.0204
	Poor, 53%	0.017	0.0184	0.019	0.019
Material C	Rich, 73%	0.0182	0.0191	0.0192	0.0192
	Poor, 53%	0.0144	0.0153	0.0159	0.0172
Material D	Rich, 73%	0.0171	0.0182	0.0183	0.0187
	Poor, 53%	0.0136	0.0151	0.016	0.0168
Material E	Rich, 73%	0.0188	0.0201	0.0203	0.0209
	Poor, 53%	0.0169	0.0183	0.0188	0.0195
Material F	Rich, 73%	0.0196	0.0203	0.0206	0.021
	Poor, 53%	0.0166	0.0173	0.0176	0.018
Material G	Rich, 73%	0.0197	0.0207	0.0207	0.0207
	Poor, 53%	0.0169	0.018	0.018	0.0189
Material H	Rich, 73%	0.0202	0.0206	0.02	0.0209
	Poor, 53%	0.0166	0.0177	0.018	0.0192
Material I	Rich, 70%	0.0213	0.0224	0.0217	0.0222
	Poor, 51%	0.019	0.0205	0.0205	0.0214
Material J	Rich, 70%	0.0236	0.0253	0.0256	0.026
	Poor, 51%	0.0207	0.0225	0.0231	0.0237
Material K	Rich, 67%	0.0209	0.0216	0.021	0.0207
	Poor, 53%	0.0151	0.016	0.016	0.016

Table 8 - Effective Loss Tangent After Bake/Reflow

Even though RTF Cu foil was requested to be used on all parts, which typically results in IPC VLP-like Cu foil roughness parameters, instead, there was a wide variety of Cu foil profiles observed within the parts.

- 1oz Cu foil: Peak to valley distance: 0.15 – 0.306 mils. Control material: 0.122 mils.
- 1/2oz Cu foil: Peak to valley distance: 0.125 – 0.34 mils. Control material: 0.059 mils.

In general, the larger the effective surface area of the signal trace, the more impact there is on signal performance. The effective loss tangent which is reported in this analysis is a lumping of the laminate losses and the effects due to Cu foil roughness as received by the laminate vendor or imparted by the adhesion promotion treatment at the fabricator.

One can separate out the effects of Cu foil roughness if an additional set of test vehicles is built with smooth Cu foil which allows one to effectively designate those losses attributed specifically to material losses vs. those which are attributed specifically to Cu foil roughness. This extra step was not completed in this exercise.

The Cu resistivity was determined through resistance measurement of the long and short traces, calculating the effective resistance per unit length. That information was used with the knowledge of the trace cross section obtained during multiple physical sections along each trace to calculate the effective Cu resistivity.

- 1oz: 1.81 – 1.99 uohm-cm
- 1/2oz: 1.83 – 2.07 uohm-cm

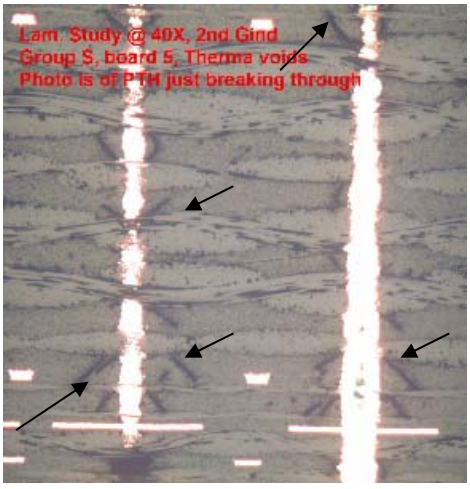
With this information, the overall losses can then be accurately modeled and compared in a consistent fashion, so the performance of the materials can be compared without manufacturing tolerances or differing design points affecting the data. This analysis was not completed at the time this paper was published.

Laminate Material Compatibility With Higher Reflow Temperature Using The HOP31B Test Vehicle:

The cross section analysis of the HOP31B test vehicles showed that only one of the halogen free laminate materials exhibited characteristics consistent with thermal degradation issues. This manifested itself as characteristic cracks radiating out from the PTHs in the resin rich PTH antipad regions.

- These cracks were present in both the 40 mil and 80 mil thick test vehicles using material D. See Figure 10.

No inner plane separation was noted in any of the laminate material samples.



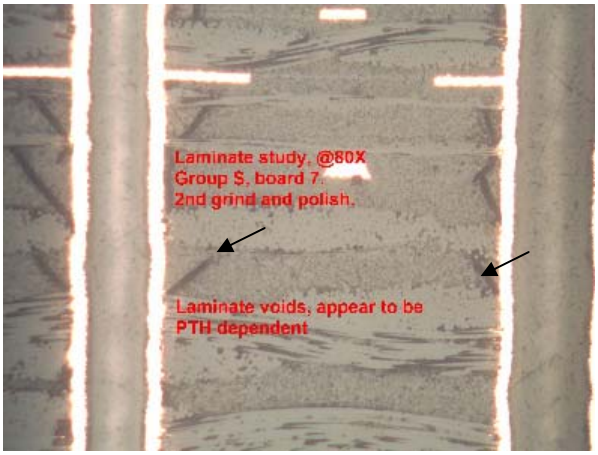


Figure 10 - Laminate Material Cracks After 245°C Reflow

MEB II Results

Complete results for the MEB II testing were not available at the time of this publication. Two of the halogen free materials and the FR4 control material were not received in time to include their results. In addition, several of the test results did not conclude in time on the received materials to be included in this report. A full report will be issued in the future which will include all the results agreed to be tested by the iNEMI project team.

The via registration results ranged from +/- 4 mils to +/- 8 mils for all the boards measured. Fabricators 3 and 7 which built with materials F and K respectively had the worst registration tolerance. Most of the boards were built with via registration tolerances of +/- 5-6 mils.

The dielectric constant of the halogen free laminate materials as measured by PNA showed similar overall ranges to those reported by other methods in this paper. The nominal Dk values were different for individual materials while the individual Dk ranges were similar when looking at specific test structures. Table 9 shows the nominal Dk values for stripline test structures between 1080 prepreg dielectric ground references (layer 9 referenced to layers 8 and 10 of each test board).

	Dk at Indicated Frequency					
Material Code	1GHz	5GHz	10GHz	20GHz	30GHz	40GHz
B	4.92	4.80	4.74	4.68	4.64	4.62
C	4.35	4.21	4.15	4.09	4.06	4.04
D	4.32	4.18	4.12	4.06	4.03	4.01
E	4.39	4.25	4.18	4.13	4.09	4.07
F	4.88	4.74	4.68	4.62	4.58	4.55
G	4.42	4.32	4.27	4.22	4.20	4.17
H	4.47	4.36	4.31	4.27	4.24	4.22
K	4.18	4.07	4.03	3.99	3.96	3.94

Table 9 - Dk vs. Frequency for 1080 Stripline Structures

Loss measurements were extracted as total loss in dB/in using the PNA. The total loss is a combination of the dielectric and copper losses for each test structure. Additional work is being done to extract the dielectric loss from the total loss measured. Table 10 shows the nominal

total loss values for the same test structures on which the Dk was reported in Table 9.

	Total Loss in dB/in at Indicated Frequency	
Material Code	1GHz	5GHz
B	-0.31	-1.11
C	-0.30	-1.01
D	-0.28	-0.94
E	-0.28	-0.97
F	-0.40	-1.13
G	-0.23	-0.94
H	-0.20	-0.95
K	-0.35	-0.89

Table 10 - Total Loss in dB/in for 1080 Stripline Structures

IST results for the halogen free materials tested to date showed variable responses. Materials B, C, D, E, and H all passed 1000 cycles for all assembly preconditions on the microvia IST coupons. Materials F, K and G all had at least one 1000 cycle pass at the most severe assembly precondition, but also had multiple failures on coupons with less severe preconditioning. This indicates potential fabrication issues which are confounding the IST results. Cross section FA analysis of selected failures are being examined to confirm the root cause of the early failures.

The through hole IST coupon performance indicated potential fabrication issues confounding the data as well. Only one material (E) passed 1000 cycles for all the assembly preconditions. Two additional materials (G and H) had only one or 2 random failures prior to 1000 cycles. In general, the cycles to failure dropped for the remaining materials as the assembly conditions became more severe. Cross section FA analysis of selected failures are being examined to confirm the root cause of the early failures on the through hole coupons as well.

Moisture diffusivity testing showed an increase in the Dk of the materials tested from the dry condition to the fully saturated condition. The percent change in the Dk of each material is shown in Table 11.

Material Code	Change in Dk from Dry to Saturated @ 5GHz and 85C
B	7.70%
F	8.56%
G	8.96%
H	9.69%
K	10.50%

Table 11 - Change in Dk with moisture saturation

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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.

As a class, with one exception, the halogen free laminate materials did not exhibit resin cracking/delamination issues normally associated with an incompatibility with higher reflow temperatures. The applicability of this data to the product environment must consider the use of the pre-bake in this analysis, i.e. if pre-bakes are not employed in the product environment, the infusion of moisture during the fabrication process may lead to different results. The IST coupons need x-section analysis to draw any conclusions on via performance, but there does appear to be differing performance levels among the HF materials tested.

The bromine free prepregs tested in general appeared to be tack free and of good quality. Although having significant inorganic content, their minimum viscosities indicated that there is sufficient flow during lamination. In general, the flame retardancy is achieved by the introduction of a combination of inorganic fillers based on Si, Al, Mg and P containing compounds.

With the advent of lead-free solder technology pushing the limits of laminate materials, thermal stability of these materials is increasingly important. Laminates may have to survive extended periods of time at elevated temperature during processing. The time to delamination tests at 260^{o}C, 288^{o}C, and 300^{o}C, as detected by rapid fluctuations in the TMA expansion probe position, are regarded as a good measure of the resistive thermal properties of the laminates to withstand high temperature assembly conditions. The bromine free materials in general do not show problematic results and are in line with the brominated materials used by the electronics industry at the present.

The majority of the candidates showed a glass transition temperature in the range of 150 C, as measured by the DSC middle point method.

Moisture absorption at room temperature / 24 hr showed relatively low values, with a number of materials being below 0.20%. Exposure to hydrothermal conditions pointed out some materials to have interlayer weakness. Most of the materials exhibited relatively good adhesion to copper (Gould JTCS-1oz), with the best adhesion being materials B, J & K all exhibiting >8lbs/in adhesion values. The Interlaminate Adhesion and oxide alternative (bond film in this case).

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 team recommends the individual testing of any material for the specific application by the designer prior to mass production.

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- Chin Poon
- GCE
- Nan Ya
- Meadville
- E&E
- Sanmina

Assembly Partner

- Vitronics Soltec

Test Partner

- PWB Interconnects (IST)

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