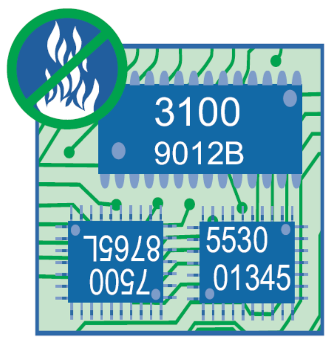
United States Environmental Protection Agency

Design for the Environment U.S. EPA

# FLAME RETARDANTS IN PRINTED CIRCUIT BOARDS

## Chapter 2




**FINAL REPORT**

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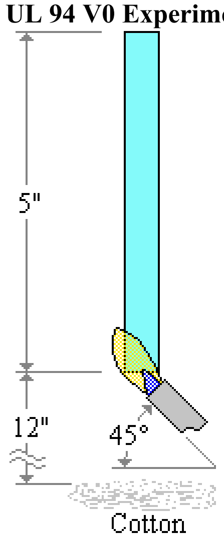
EPA Publication 744-R-15-001

# 2 FR-4 Laminates

Flame Resistant 4 (FR-4) laminates are flame-retardant systems of woven glass reinforced with epoxy-like resin, notable for their resistance to heat, mechanical shock, solvents, and chemicals. Unlike lower grade laminates, a finished FR-4 laminate can obtain a V0 rating in the UL (Underwriters Laboratories) 94 test, a vertical burning test for flammability. The UL 94 V0 test is typically conducted using a 5-inch by 0.5-inch test specimen (thickness may vary) (RTP Company, 2014). The specimen is fastened vertically with a holding clamp at the top so that the 5-inch side is perpendicular to the ground (Figure 2-1). A cotton indicator is located 12 inches below the bottom of the specimen to capture any flaming dripped particles from the specimen (Figure 2-1). A burner flame is applied at a 45° angle to the bottom of the specimen in two intervals. The burner is first applied for 10 seconds and is removed until all flaming stops (UL, 2014). The burner is then reapplied for an additional 10 seconds (UL, 2014). Two sets of five specimens are tested (UL, 2014). In order to meet the UL 94 V0 flammability standard: (1) the specimens must not burn with flaming combustion for more than 10 seconds after the burner is removed; (2) the total flaming combustion time for each set of five specimens must not be greater than 50 seconds; (3) any flaming or glowing combustion must not burn up to the holding clamp; (4) flaming dripped particles from the specimens must not ignite the cotton indicator; and (5) glowing combustion must not exceed 30 seconds after the second burner flame is removed from the specimen (UL, 2014).

**Figure 2-1. UL 94 V0 Experimental Setup**




Source: UL, 2014

FR-4 laminates can be categorized as (1) high glass transition temperature ($T_g$) FR-4 laminates,[4] (2) middle $T_g$ FR-4 laminates,[5] and (3) low $T_g$ FR-4 laminates.[6] Within each of those categories, individual FR-4 laminates are differentiated through reference to their physical properties (e.g., rate of water absorption, flexural strength, dielectric constant, and resistance to

[4] High glass transition temperature laminates have a $T_g$ above 170°C.
[5] Middle glass transition temperature laminates are usually considered to have a $T_g$ of approximately 150°C.
[6] Low glass transition temperature laminates are usually considered to have a $T_g$ of 130°C and below.

heat). With the introduction of halogen-free FR-4 materials,[7] a similar segmentation is emerging (e.g., high $T_g$ halogen-free, low $T_g$ halogen-free), leading to a multiplication of the number of FR-4 materials available (Beard et al., 2006; Bergum, 2007). As different formulations (different flame-retardant systems and different resin chemistries) result in different laminate properties, there can be different materials within one class (e.g., low $T_g$) having different performance (e.g., dielectrics, mechanics), thus addressing the different market needs. Such differences in performance are not specific to halogen-free materials and may also exist among brominated grades of the same $T_g$ class.

### 2.1 Overview of FR-4 Laminates Market (Prismark, 2006)

In 2006, global printed circuit board (PCB) production exceeded $45 billion. PCBs are fabricated using a variety of laminate materials, including laminate, pre-impregnated material, and resin-coated copper. In 2006, $7.66 billion of laminate materials were consumed globally. Laminate materials can be sub-segmented according to their composition, and include paper, composite, FR-4, high $T_g$ FR-4, and specialty products (polytetrafluoroethylene (PTFE) and high-performance materials).

- Paper and composite laminates represent 17.1 percent of the global laminate market in value (Figure 2-2). These materials are used as the basic interconnecting material for consumer applications. The materials are low in cost, and their material characteristics are adequate for use in mainly low-end consumer products.

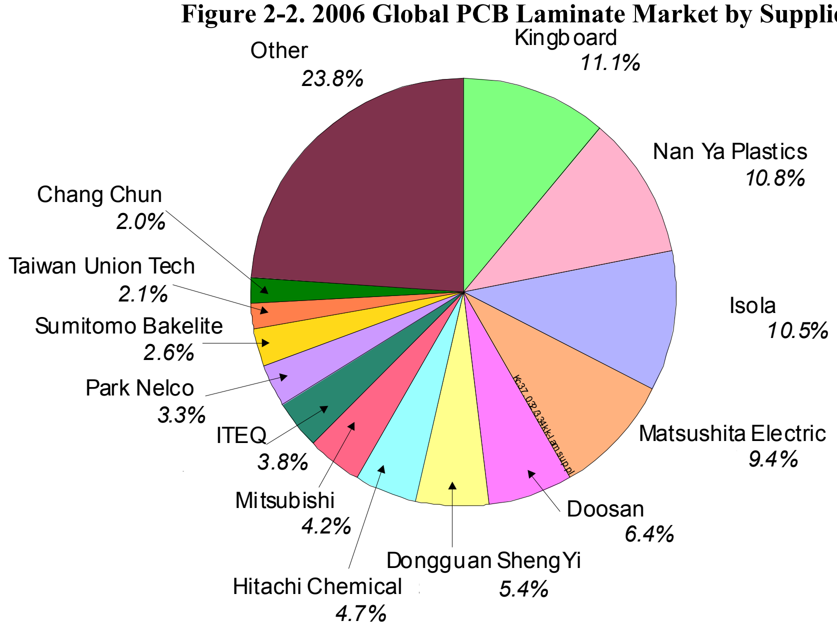
- The workhorse laminate for the PCB industry is FR-4. In terms of value, approximately 70.4 percent of the material used in the industry is FR-4 glass-based laminate (including high $T_g$ and halogen-free) (Figure 2-2). This material provides a reliable and cost-effective solution for the vast majority of designs.

- Many laminators offer halogen-free FR-4 laminate materials. These materials are typically designed to be drop-in replacements for current halogenated materials, but they carry a price premium. Halogen-free materials have been slowly gaining acceptance on a regional basis.

- There are special applications that call for laminate materials with characteristics beyond the capability of FR-4. These materials consist of special integrated circuit packaging substrates and materials for use in wireless or high-speed digital applications, including laminate containing bismaleimide-triazine resins, poly(p-phenylene oxide), high-performance PTFE, and polyimide.

[7] In accordance with IEC-61249-2-21, this report defines “halogen-free materials” [illegible] materials that are ≤900ppm by weight chlorine; ≤900ppm by weight bromine; and ≤1,500ppm maximum total halogens.

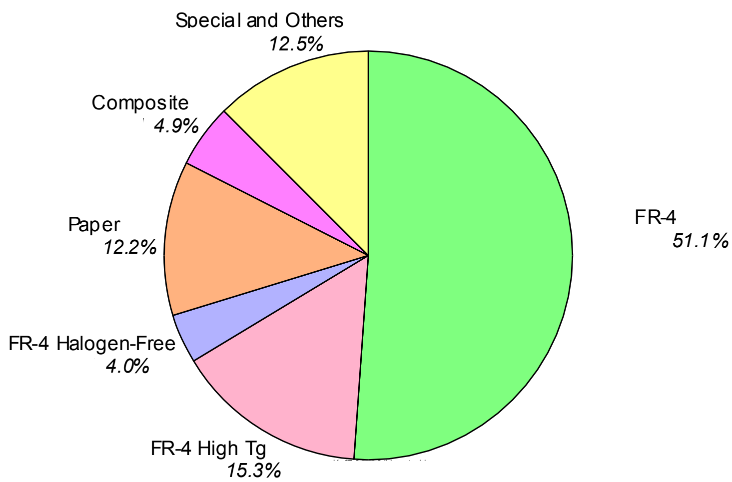
**Figure 2-2. 2006 Global PCB Laminate Market by Supplier**




**TOTAL: $7.66Bn**

*Note: This market includes prepreg and RCC values.*

**Figure 2-3. 2006 Global PCB Laminate Market by Material Type**




**TOTAL: $7.66Bn**

*Note: Includes prepreg*

Global sales of laminate materials in 2006 were estimated at $7.66 billion. In terms of area production, it is estimated that more than 420.2 million square meters of laminate was manufactured to support the PCB industry in 2006. The distribution of laminate sales geographically and the leading suppliers to each region are shown in Figure 2-4 and Figure 2-5.

**Figure 2-4. 2006 Regional Laminate Sales**

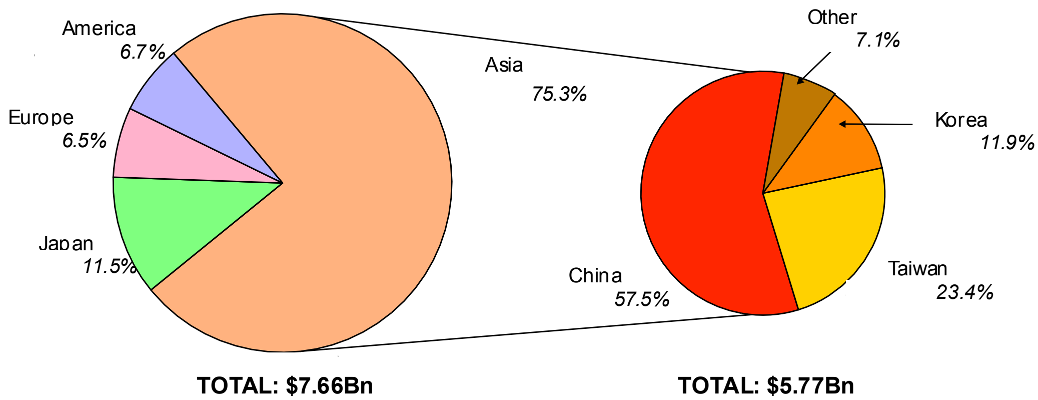
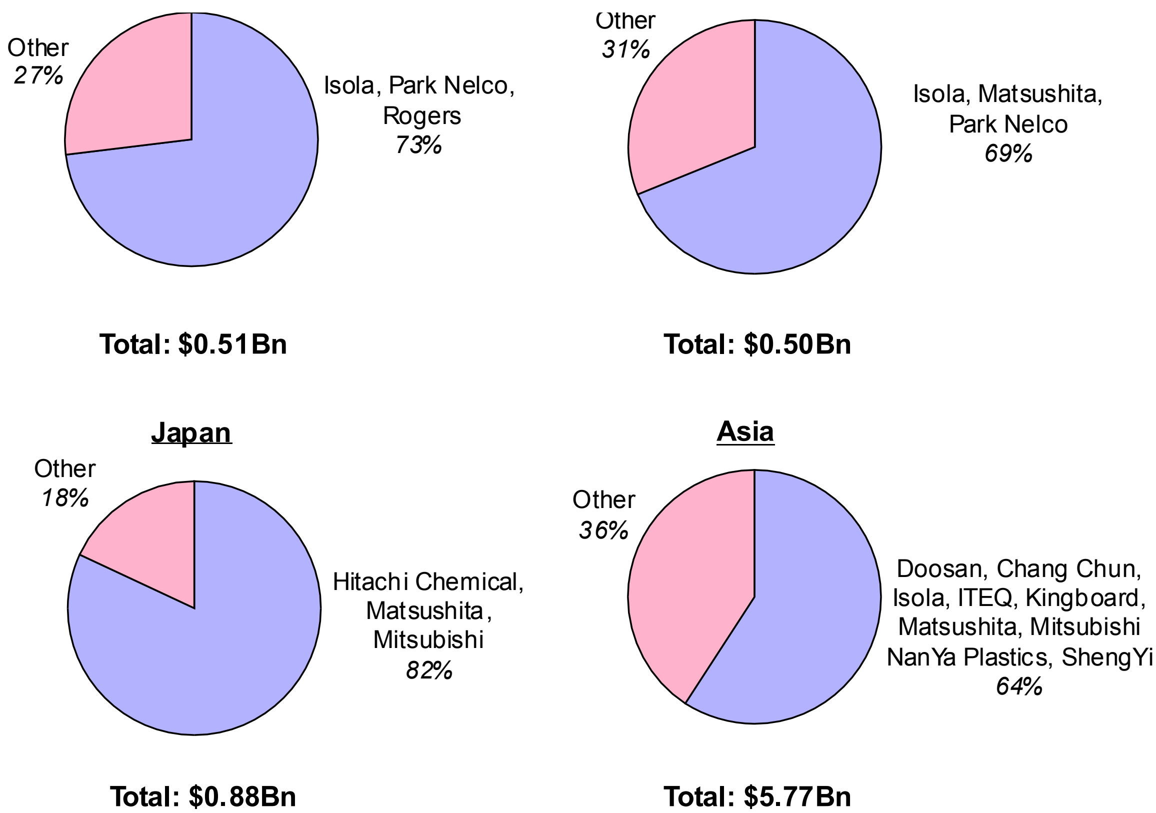



**Figure 2-5. 2006 Laminate Sales by Region**

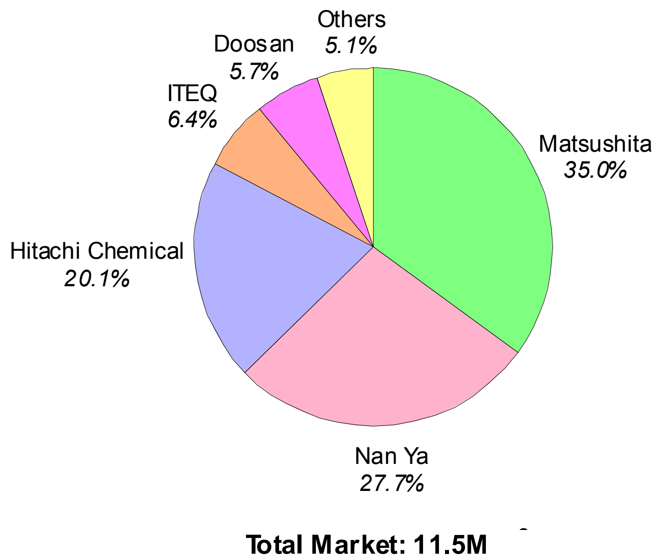



## 2.2 Halogen-Free Laminate Market

There has been a continuous increase in the demand for halogen-free material over the past few years. In 2003, the global halogen-free laminate market was approximately $60 million. In 2004 this market grew to $161 million, in 2005 it reached $239 million, and it is estimated at $307 million for 2006.

Most laminate suppliers now include halogen-free materials in their portfolio. Pricing for halogen-free laminate is still higher than conventional material by at least 10 percent, and often by much more. Tallying the production volumes of such leading laminate manufacturers as Hitachi Chemical, NanYa, Matsushita, ITEQ, Isola, Park Nelco, and others, Prismark has constructed a market segmentation, shown in Figure 2-6.

**Figure 2-6. 2006 Global Halogen-Free Laminate Market**




## 2.3 Past Research Efforts

While demand for halogen-free laminates is increasing, there was a lack of information regarding their performance and environmental impact when this partnership was convened. The International Electronics Manufacturing Initiative (iNEMI) and the High Density Packaging User Group (HDPUG) have taken on separate but complementary roles in helping to fill information gaps.

iNEMI has carried out a series of projects to determine the key performance properties and the reliability of halogen-free flame-retardant PCB materials. Each project has observed different outcomes, with the latest findings indicating that the halogen-free flame-retardant laminates tested have properties that meet or exceed those of traditional brominated laminates. Technology improvements, especially those that optimize the polymer/fire retardant combinations used in PCBs, have helped shift the baseline in regards to the performance of halogen-free flame-retardant laminates.

In 2009, iNEMI completed a project focused on performance testing of commercially available halogen-free materials to determine their electrical and mechanical properties. In 2008 when this alternative assessment was first published, the list of laminate materials identified by iNEMI for further study include nine laminate materials from seven different suppliers:

- NanYa NPG-TL and NPG-170TL
- Hitachi BE-67G(R)

- TUC TU-742
- Panasonic R1566W
- ITEQ IT140G and IT155G
- Shengyi S1155
- Supresta FR Laminate

While not in the final list for further study, the following laminates were also identified as promising candidates by iNEMI:

- Isola DE156 and IS500
- TUC TU-862
- ITEQ IT170G
- Nelco 4000-7EF

The results of the testing and evaluation of these laminate materials were made public in 2009.[8] The overall conclusions from the investigation were (1) that the electrical, mechanical, and reliability attributes of the halogen-free laminate materials tested were not equivalent to FR-4 laminates and (2) that the attributes of the halogen-free laminates tested were not equivalent among each other (Fu et al., 2009). Due to the differences in performance and material properties among laminates, iNEMI suggested that decision-makers conduct testing of materials in their intended applications prior to mass product production (Fu et al., 2009).

iNEMI also conducted two follow-on projects to its HFR-free Program Report: (1) the HFR-Free High-Reliability PCB Project and (2) the HFR-Free Leadership Program. The focus of the HFR-Free High-Reliability PCB Project was to identify technology readiness, supply capability, and reliability characteristics for halogen-free alternatives to traditional flame-retardant PCB materials based on the requirements of the high-reliability market segment (e.g., servers, telecommunications, military) (iNEMI, 2014). In general, the eight halogen-free flame-retardant laminates tested outperformed the traditional FR-4 laminate control (Tisdale, 2013). The other project, the HFR-Free Leadership Program, assessed the feasibility of a broad conversion to HFR-free PCB materials by desktop and laptop computer manufacturers (Davignon, 2012). Key electrical and thermo-mechanical properties were tested for six halogen-free flamed-retardant laminates and three traditional FR-4 laminates. The results of the testing demonstrated that the computer industry is ready for a transition to halogen-free flame-retardant laminates. It was concluded that the halogen-free flame-retardant laminates tested have properties that meet or exceed those of brominated laminates and that laminate suppliers can meet the demand for halogen-free flame-retardant PCB materials (Davignon, 2012). A "Test Suite Methodology" was also developed under this project that can inform flame retardant substitution by enabling manufacturers to compare the electrical and thermo-mechanical properties of different laminates based on testing (Davignon, 2012).

In contrast to the iNEMI project, HDPUG collected existing data on halogen-free flame-retardant materials; no performance testing was conducted. HDPUG created a database of information on the physical and mechanical properties of halogen-free flame-retardant materials, as well as the environmental properties of those materials. The HDPUG project, completed in 2011, broadly

[8] http://thor.inemi.org/webdownload/newsroom/Presentations/SMTA_South_China_Aug09/HFR-Free_Report_Aug09.pdf

examined flame-retardant materials, both ones that are commercially viable and in research and development (R&D). For more information about the database and other HDPUG halogen-free projects, visit: http://hdpug.org/content/completed-projects#HalogenFree.

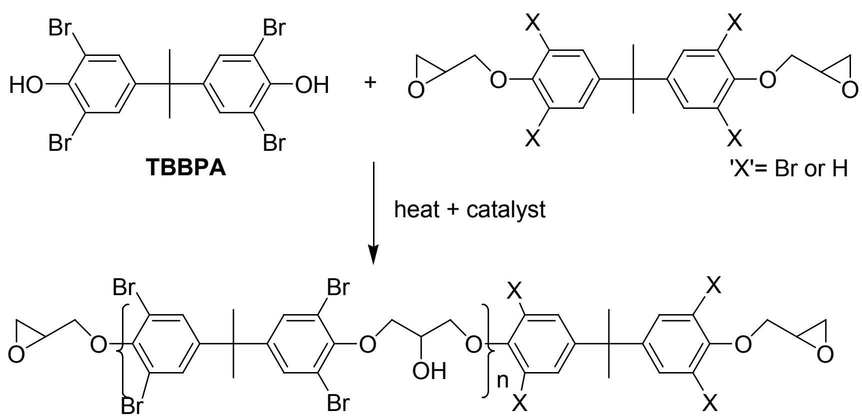
Even though they are taking on different roles, HDPUG and iNEMI have been in contact with each other, as well as this DfE partnership project, to ensure minimal duplication in scope. The results of their efforts help inform companies that want to select halogen-free laminate materials.

## 2.4 Process for Manufacturing FR-4 Laminates

This section describes general processes for manufacturing epoxy resins and laminates. Specific chemicals and process steps can differ between manufacturers and intended use of the product.

### 2.4.1 Epoxy Resin Manufacturing

The process for making brominated epoxy resins that are used to make FR-4 laminates is shown below. Two different classes of oligomers (low molecular weight (MW) linear polymers) are in common use. The simplest are prepared by reacting TBBPA with a "liquid epoxy resin" ("X" is hydrogen in this case). The products (for example D.E.R. 500 Series) have an $M_n$ (number average MW) of 800-1,000 g/mole and contain about 20 percent bromine by weight  After the oligomers are prepared, they are dissolved in a variety of solvents such as acetone or methyl ethyl ketone (2-butanone) to reduce the viscosity. The $M_w$ (average MW) is typically about 2,000 g/mole. An excess of the epoxy resin is used, and therefore essentially all of the TBBPA is converted.

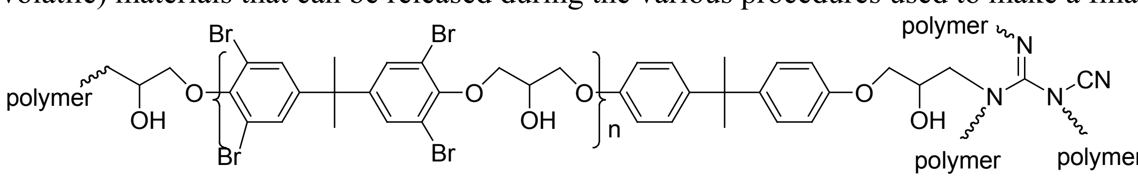



In cases where it is desired to have an oligomer with a higher concentration of bromine, the liquid epoxy resin (LER) is replaced with a brominated epoxy resin ("X" = Br in the above structure). The products (D.E.R.™ 560 is a typical example) have similar MWs, but the content of bromine is higher (about 50 percent bromine by weight). These "high-brominated" resins are typically used when other non-brominated materials must be added to the formulation (or "varnish").

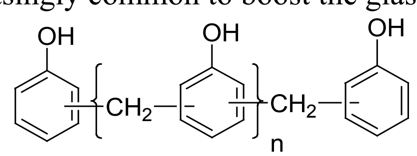
In the past a large majority of laminate varnishes would be prepared by simply combining the 20 weight percent brominated resin with 3 percent weight "dicy" (dicyandiamide) as a curing agent, along with additional solvent. After the solvent was removed and the laminate pressed, the thermoset matrix would contain about 20 percent bromine by weight. This is sufficient bromine to allow the thermoset matrix to pass the V0 performance requirements in the standard UL 94 test. The cure chemistry of dicy is very complex and poorly understood. However, it is known to be capable of reacting with 4, 5, or even 6 epoxy groups.

“Catalysts” such as 2-methylimidazole are used to increase the cure rate. Imidazoles are not true catalysts: they initiate polymer chains, and become covalently bound to the matrix.

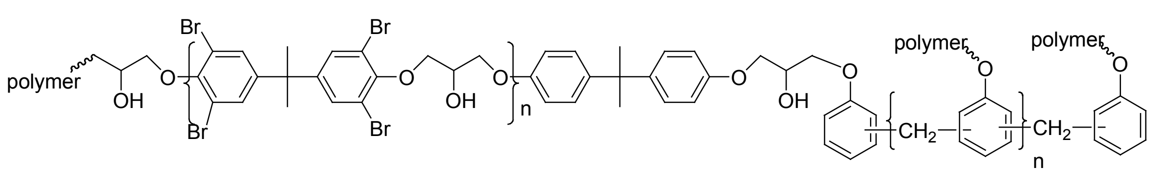
A simplified representation of the final thermoset is shown below. In a properly cured laminate all of the resin has become one molecule, meaning every atom is covalently linked into one three-dimensional structure. This is desirable because it means that there are no leachable (or volatile) materials that can be released during the various procedures used to make a final PCB.



With the advent of lead-free solders that melt at higher temperatures, phenolic hardeners (in place of dicy) are becoming more common. Such formulations typically have higher decomposition temperatures. A common phenolic hardener is an oligomer prepared from phenol and formaldehyde that has the structure shown below. These “novolaks” typically have 2.5 to 5.5 phenolic groups per molecule, which translates to $M_n$s of 450 to 780 g/mole. Bisphenol A novolak is also becoming increasingly common to boost the glass $T_g$.



The cross-linked matrix formed in this case is represented below. The use of phenolic hardeners in the formulation has the effect of reducing the bromine concentration in the final cured resin. In some cases additional flame retardant is needed to meet the UL 94 V0 classification. This is typically a solid additive such as alumina trihydrate or other fillers. Other methods are to mix in a fraction of the fully brominated resin that contains 50 percent bromine by weight. Finally, additional TBBPA and LER can be mixed into the crosslinked matrix to increase the bromine concentration of the final cured resin, although it is unclear how common this practice is among epoxy resin manufacturers (Mullins, 2008).



This description does not cover all of the formulations used by laminate producers to meet their product specifications. Various epoxy novolaks can be added.

The process of making epoxy resins containing alternative flame retardants is similar to the process used for making brominated epoxy resins. In the case of phosphorus-based flame retardants, the epoxy resin is produced by reacting diglycidyl ether of bisphenol A or an epoxy novolak with a stoichiometric deficiency of phosphorus flame retardant. This produces a new resin containing both an epoxy group and covalently bound phosphorus. Alternatively, a phosphorus-containing hardener can be prepared by condensing a phenolic compound with a phosphorus-containing flame retardant. For example, hydroquinone can condense with phosphorus-containing flame retardants in the presence of an oxidizing agent to give a hydroquinone-phosphorus compound. The laminator uses this hardener in conjunction with an epoxy resin (such as an epoxy novolak) and catalysts. A laminate can also be made halogen-free by using solid inorganic flame retardants (or fillers) to achieve the V0 requirement of the UL 94 fire safety standard. A phosphorus content of about 4 to 5 percent by weight in the laminate is generally sufficient to achieve the V0 requirement of the UL 94 fire safety standard.

### 2.4.2 Laminate Manufacturing

Most PCBs are composed of 1 to 16 conductive layers separated and supported by layers (substrates) of insulating material. In a typical four-layer board design, internal layers are used to provide power and ground connections with all other circuit and component connections made on the top and bottom layers of the board. The more complex board designs have a large number of layers necessary for different voltage levels, ground connections, and circuit package formats.

The basic layer of the PCB is a woven fiberglass mat embedded with a flame-resistant epoxy resin. A layer of copper is often placed over this fiberglass/epoxy layer, using methods such as silk screen printing, photoengraving, or PCB milling to remove excess copper. Various conductive copper and insulating dielectric layers are then bonded into a single board structure under heat and pressure. The layers are connected together through drilled holes called vias, typically made with laser ablation or with tiny drill bits made of solid tungsten carbide. The drilled holes can then be plated with copper to provide conductive circuits from one side of the board to the other (How Products Are Made, 2006).

Next, the outer surfaces of a PCB may be printed with line art and text using silk screening. The silk screen, or “red print,” can indicate component designators, switch setting requirements, test points, and other features helpful in assembling, testing, and servicing the circuit board. PCBs intended for extreme environments may also be given a conformal coat made up of dilute solutions of silicone rubber, polyurethane, acrylic, or epoxy, which is applied by dipping or spraying after the components have been soldered. This coat will prevent corrosion and leakage currents or shorting due to condensation.

Once printed, components can be added in one of two ways. In through-hole construction, component leads are electrically and mechanically fixed to the board with a molten metal solder, while in surface-mount construction, the components are soldered to pads or lands on the outer surfaces of the PCB. The parts of the circuit board to which components will be mounted are typically “masked” with solder in order to protect the board against environmental damage and solder shorts. The solder itself was traditionally a tin-lead alloy, but new solder compounds are now used to achieve compliance with the Restriction of Hazardous Substances directive in the European Union, which restricts the use of lead. These new solder compounds include organic surface protectant, immersion silver, and electroless nickel with immersion gold coating (Oresjo and Jacobsen, 2005). Tin-silver-copper alloys have also been developed, some containing small amounts of an additional fourth element (IPC, 2005; Lasky, 2005).

After construction, the PCB's circuit connections are verified by sending a small amount of current through test points throughout the board. The PCB is then ready to be packaged and shipped for use (Electronic Interconnect, 2007).

## 2.5 Next Generation Research and Development

Most R&D is oriented around improving the performance of FR-4 laminates. For example, manufacturers are seeking to improve the glass $T_g$ of FR-4 laminates in order to produce laminates better able to withstand heat. A higher $T_g$ is generally compatible with the use of lead-free solder, which often requires a higher soldering temperature (Thomas et al., 2005). Manufacturers often consider $T_g$ together with the decomposition temperature ($T_d$) when assembling lead-free assemblies. $T_d$ is the temperature at which material weight changes by 5 percent. Due to marketplace concerns over potential environmental impacts of TBBPA, such as the generation of halogenated dioxins and furans during combustion, as supported by this project's combustion testing (Chapter 6), the development of non-halogen flame retardants (discussed in Section 3.2) has also been a priority of manufacturers. However, concerns over the human health and environmental impact, as well as the expense and performance of laminates containing these non-halogen flame retardants, are still an issue.

There are many types of FR-4 laminates under development that have a resin design different from the epoxy-based construction described above. These typically include more thermally stable inflexible structures (such as biphenyl or naphthalene groups) and/or nitrogen heterocyclic structures (such as reacted-in triazine, oxazoline, or oxazine rings). Another alternative to epoxy resin, polyimide resin, can be produced through condensation reactions between aromatic dianhydrides and aromatic diamines (Morose, 2006). IF Technologies has manufactured an aliphatic LER system produced from epoxidized plant oils and anhydrides that reduces emissions, decreases toxicity, and replaces bisphenol A and epichlorohydrin. Other technologies in development use substances such as keratin, soybean oil, or lignin in the manufacturing process.

Improvements in the lamination process are also being developed. Technologies may soon enable the formation and multi-layering at room temperature of ceramic film on resin circuit boards, allowing for further multi-functionality, miniaturization, and cost reduction of electronic devices (PhysOrg, 2004). Laser drilling techniques will allow for the production of smaller microvias, which may allow for the creation of smaller circuit boards (Barclay, 2004). Lasers can also be used for direct copper ablation, as they can quickly vaporize copper without damaging the epoxy and glass substrate (Lange, 2005).

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