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A New Non-Halogen Flame-Retardant System for Printed Wiring Boards

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Abstract

There is continued interest in utilizing alternatives to bromine-based flame retardants for printed wiring boards. As a result, a wide variety of phosphorus and non-phosphorus systems have been developed for various thermoset resin systems. The development of a new type of phosphorus flame-retardant material that performs in the curing reaction of epoxy resins is discussed in this paper. The new material is a solid that can be formulated in several common formulation solvents. The material contains phenolic functionality and provides a final resin system with very high thermal stability properties and Tg's in the 150 – 185 °C range, depending on the resins employed. As part of the curing agent system, the new flame retardant becomes incorporated into the cross-linked matrix as part of the polymer network. The curing reaction behaves like a typical novolac resin cure and no modifications in press cycle or B-stage conditions are required. This paper discusses the properties of the new flame retardant material along with use data depicting the handling characteristics from the formulation development stage to the final laminate. The laminates made using this flame retardant system meet UL-94 V-0 requirements and pass the Pressure Cooker and T-260 tests.

Introduction

A key requirement for epoxy laminate printed wiring board (PWB) materials in many applications is the requirement for flame retardancy. In many applications this requirement is given first priority. In electronic applications, it is absolutely necessary for the electrical laminate materials to be flame retarded, due to the substantial worth of the electronic components assembled thereon and for human safety.

Accordingly, it has been customary in the preparation of epoxy-containing laminates to incorporate into the epoxy resin compositions various additives and/or reactives to improve the flame retardancy of the resulting laminate. Many types of flame retardant substances have been used; however, the most common used commercially is the halogen containing compound tetrabromobisphenol A (TBBA). TBBA is typically reacted with an epoxy resin to make a chain-extended epoxy resin containing the TBBA in the backbone of the material. Typically, in order to reach the desired fire retardancy level (V-0 in the standard Underwriters Laboratory test method "UL-94"), the bromine level of such resin is on the order of 20 weight percent.

Generally, halogen-containing fire retardant epoxy resins such as those containing TBBA are considered to be safe and effective. However, there has been increasing interest by some to utilize flame-retarded epoxy systems that are not based on halogen chemistry. It is desirable for these new materials to be able to meet the requirements of fire retardancy and to display the same advantages of mechanical properties, toughness, and solvent and moisture resistance that are offered with the halogenated materials currently used.

This paper discusses the development of an alternative flame retardant (FR) system for PWB based on phosphine oxide chemistry with the goal of being able to utilize the current infrastructure and processing equipment for the laminate preparations and to provide a PWB that can be used in lead-free applications.

FR Approaches for PWB

Several approaches to flame retarding PWB materials have been disclosed in the literature.[1] The approaches discussed below cover both halogenated and non-halogenated (NH) classes and are only presented as brief background to a very large research area. The NH classes of FR materials can be used alone or, more often, in conjunction with each other, depending on the system. The halogenated material, TBBA, is effective for establishing FR properties on its own and will perform without other FR additives present.

TBBA has been used as a FR for PWB for several decades and is a well-known material whose properties and toxicity have been extensively studied.[2] It is typically incorporated into the PWB by a reaction with difunctional epoxy resins ("forwarding") to first form a chain-extended epoxy resin Figure 1. As a result, the TBBA molecule is covalently bonded into the polymer backbone as part of the resin system. The resulting brominated resin is formulated with hardeners and accelerators and cured under heat and pressure to form the final laminate product. After the resin is cured in the laminate, the covalently bonded TBBA property renders the TBBA moiety unavailable to diffuse out of the circuit board into the environment.

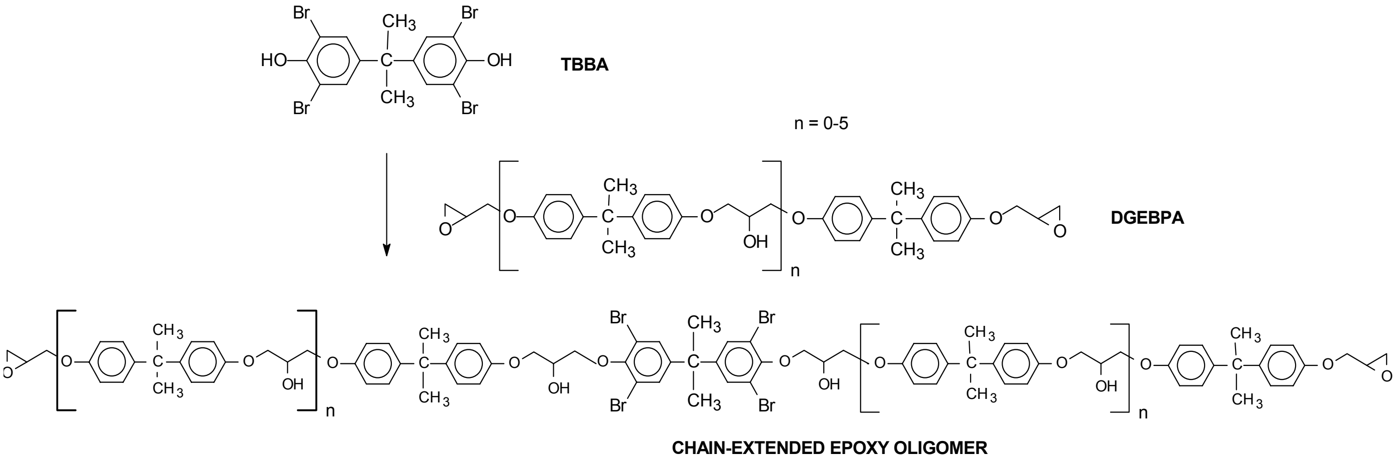


Figure 1 - Forwarding of DGEBPA Resin with Tetrabromobisphenol A

TBBA provides flame retardancy by the well-known free radical quenching of the fire chain reaction in the vapor phase.[3]

Various alternatives to TBBA technology have been sought to provide flame retardancy to PWB substrates. One approach has been to use inorganic metal hydrates as additives. The most popular of these has been the use of aluminumtrihydrate (ATH). This material releases water during heating to remove heat and to dilute the concentration of decomposition gases. The product is usually used in conjunction with other FR materials because extremely high loadings of ATH are required to meet V-0 requirements alone. This severely impacts the PWB physical properties. Without other FR materials, a loading of 250 phr was reported to meet V-0 requirements.[4]

Another approach has been to use specialty resins that are developed to contain inherent FR properties. These are typically highly aromatic in nature and contain a high degree of functionality to allow for some char formation. For example, the use of a dihydrobenzoxazine system with a triazine-modified novolac resin and 60 phr ATH has been reported to give V-0 performance.[5] Alternatively, a highly cross-linked specialty resin formulation has been reported that uses reduced quantities of additive type flame retardants to achieve V-0.[6] The basic strategy with these resins that typically meet V-1 requirements on their own is to use lower loadings of an FR adjuvant to push the specialty resin system to V-0 performance. Although a variety of approaches exists using this strategy, the specialty resins would be at a relatively higher cost than existing commercial resins and the availability is uncertain.

Perhaps the most widely researched method for NH PWB substrates is the use of phosphorus compounds. Many different types of phosphorus compounds have been studied as FR materials for PWB. One of the most discussed in the literature is 9,10-dihydro-9-oxa-10-phosphaphenanthren-10-oxide (“DOPO”). This material was originally used for polyesters, but has seen resurgence in the epoxy resin area in the last several years. Because of its monofunctional nature (which can lead to a reduction in Tg), DOPO is usually derivatized or reacted with novolac resins to make a P-containing resin.[7]

The phosphorus FR (PFR) approach is attractive because of the high degree of compatibility (solubility) of most materials in epoxy resin systems and the ease in which the materials can be modified to enhance performance properties. Potential drawbacks are the greater tendency of PFR materials to absorb moisture and the fact that many are known plasticizers and can lead to a reduction in the thermal performance of the systems.

The PFR performance can be attributed to either a vapor or condensed phase mechanism.[8] This FR action is highly dependent on the structure of the cured system as a whole and no single PFR solution exists for all epoxy resin systems.

FR Incorporation into PWB

The methods in which a PWB substrate can be flame retarded can be classified as being either additive or reactive, depending on the type of flame retardant used. The additive approach employs flame retardants that do not have functional groups capable of reacting with epoxy resin formulation components. These would be materials such as ATH or phosphate esters like triphenyl phosphate or resorcinol bis(di-2,6-xylyl phosphate), for example (Figure 2).

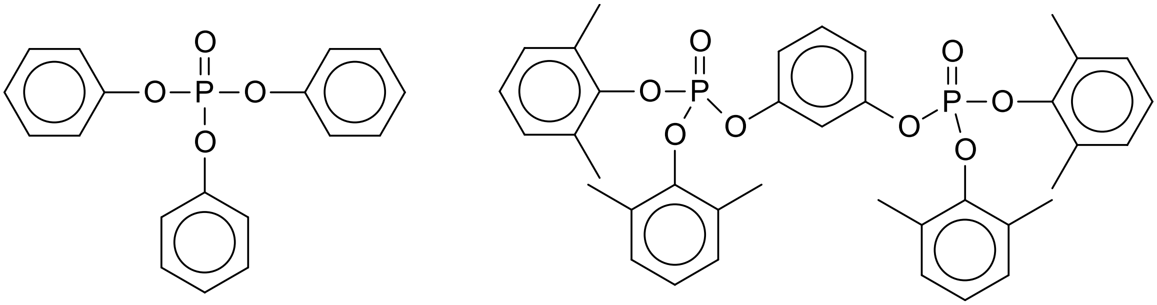


Figure 2 - Aryl Phosphate Examples

These materials would simply be added to the formulation and not take part in the curing chemistry per se.

A potential issue with the additive approach is the extraction of the FR materials out of the PWB and into the environment or processing baths. This would presumably become more of an issue for the organophosphorus materials than for the inorganic (ATH) materials, due to solubility profiles. Additionally, the matter of FR dispersion is present for an additive type approach, especially if the FR is not soluble in the system.

One approach in using these types of PFR additives that has been reported in the literature is to use a specialty resin that is inherently FR to allow the use of phosphates at lower loadings to achieve V-0, as discussed above. Our approach was to work at the FR side of the formulation to allow employment of standard commercial epoxy resins in this study.

The reactive approach can be utilized in one of two different modes: Epoxy resin mode (from a forwarding reaction, for example) or curing agent mode, depending on if the FR component is part of the epoxy resin or part of the curing agent (Figure 3). Both of these reactive modes incorporate the flame retardant directly into the cross-linked polymer matrix during the curing reaction. In the case of TBBA advanced resin as described above, the FR is incorporated into the PWB via epoxy resin mode.

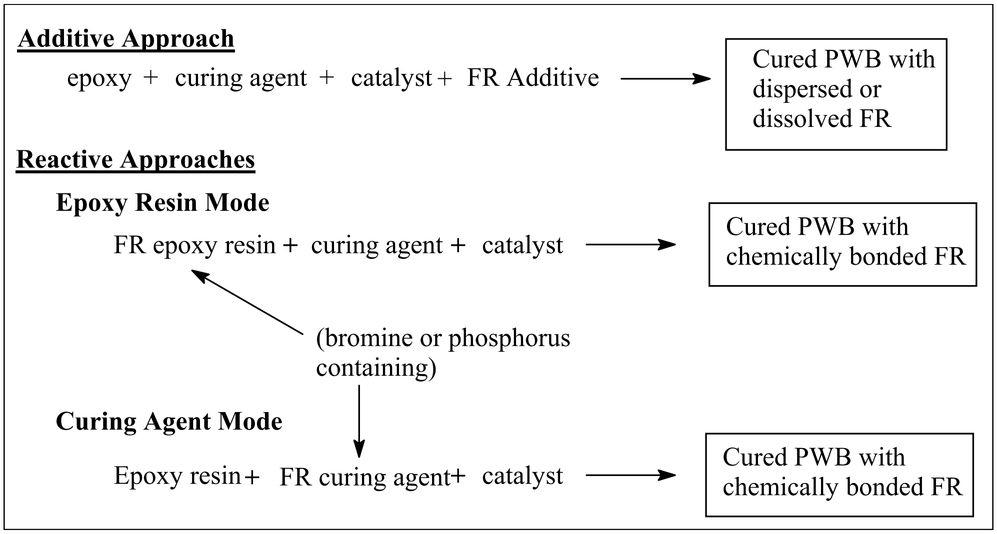


Figure 3 - Various Flame Retardant Approaches for PWB

Experimental

All reagents for synthesis and formulations were used as received. Synthesis chemicals were dried to <200 ppm water if necessary by the use of 4Å mol sieves. Materials were made and characterized by standard laboratory procedures.

The typical lamination procedure was to make an 8-ply laminate by using a paint brush to coat the 7628 glass fabric. A jar containing Micral 9400 ATH was charged with epoxy resin solution in Dowanol^{TM} PM, curing agent solution and 2-methylimidazole catalyst. The mixture was stirred at room temperature for 30 minutes using a paddle mixer. Several plies of glass cloth (12 × 12 in) were individually coated with the above varnish and hung on a rack for a few minutes. The impregnated sheets were then placed into a laboratory oven at a temperature of 170 °C for 1-3 minutes to form the prepregs. The time in the oven depended on the stroke-cure and DSC scan of the formulation. Then eight of the prepreg plies were stacked together (with or without copper foil) and sandwiched between steel plates with a Tedlar release sheet and pressed together in a hydraulic press for 2 hr at 180 °C to produce a consolidated laminate.

The laminate was trimmed and cut for testing. All laminate testing was done according to IPC recommended procedures unless otherwise stated. The moisture absorption test was conducted by weighing a 4 × 4 in. test specimen after exposure in the pressure cooker for 30 min at 15 psi. The burn tests were conducted according to UL-94 test protocol. All thermal equipment was from TA instruments: DSC scanning was at 10 °C/min using a DSC model 2910; TMA model 2940 was used for the T-260 tests; the TGA was a model Q500 and the heating rate was at 10 °C/min under nitrogen atmosphere.

Results and Discussion

For the development of an alternative flame retardant material for PWB that does not contain halogens (bromine), our initial goals were threefold:

1. Uses same processing conditions and equipment currently employed in the industry
2. Provides a product with high thermal stability, suitable for lead-free conditions
3. Uses a phosphorus material that is non-plasticizing and maintains a high Tg.

We looked at different types of phosphorus materials under different FR incorporation modes. The results of each of these studies are discussed below.

Phosphates as Flame Retardants for PWB

The use of simple phosphates with standard epoxy resins would most likely be the least expensive NH method of imparting flame retardancy, since a wide variety of phosphate flame retardants are available and they could conceivably be simply added to the formulation mix and B-staged as usual. However, besides the inherent problems associated with using an organic FR in additive mode discussed above, phosphate additives are well-known as plasticizers.[9] This was found to be true in epoxy resin chemistry also at load levels typically required to approach V-0 (2-4% P).[10] In our hands, a variety of aryl phosphate esters added to a DGEBPA-dicy type resin system (DGEBPA = diglycidylether of bisphenol A) gave cured products that were either liquids at room temperature, or, if a laminate was possible, the Tg was <100 °C at these phosphorus load levels.

A hydroxy aryl phosphate oligomeric ester (Figure 4) was examined to see what effect having a reactive type of material would have on the physical properties of the laminate. The oligomer was forwarded with DGEBPA resin to give a resin with phosphorus content of 2.4%. A dicy-cured laminate with this resin and DEN 438 as co-reactive gave a Tg of 75 °C. During the stroke-cure, the sample gave off an irritating "barnyard" type odor, which is indicative of dimethylphenol being liberated.

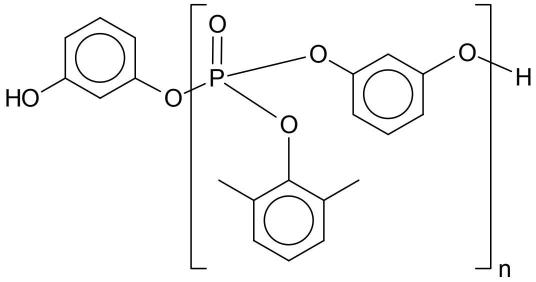


Figure 4 - Aryl Phosphate Oligomer

The plasticizing effect of some phosphate esters is an issue when used in the simple additive mode and can be an issue in reactive mode. This data also pointed to an issue with hydrolysis or transesterification of the phosphate esters. This would most likely occur during the B-stage where higher temperatures are encountered (Figure 5). This transesterification or hydrolysis issue would be a point of concern. If hydrolysis occurred, the resulting phosphorus moiety would contain a free acid group. This may lead to copper corrosion issues upon long-term storage.

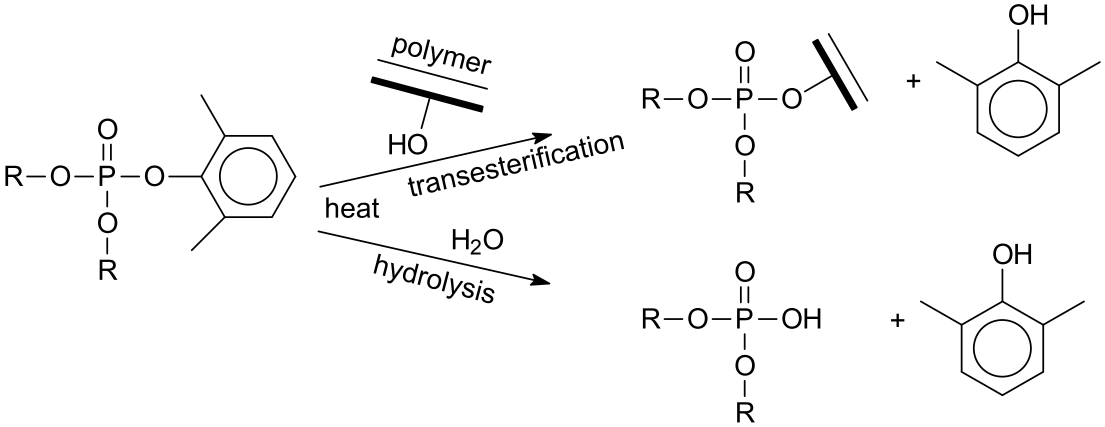


Figure 5 - Generic Transesterification or Hydrolysis of Phosphate Ester

This survey was not comprehensive, but did point to some inherent problems associated with the use of phosphate materials. The characteristics of using phosphate esters as non-halogen flame retardants for PWB materials are summarized in Table 1 below.

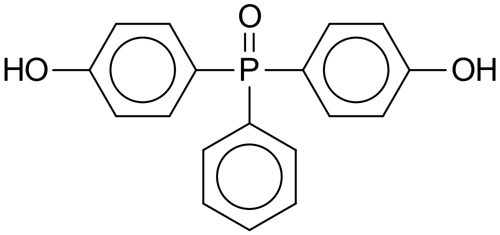
Table 1 - Characteristics of using Phosphate Esters as non-halogen Flame Retardants for PWB Materials

Advantages	Disadvantages
• Easy to use • Relatively low cost • Readily available	• Plasticizing; lowers Tg • Subject to hydrolysis or transesterification • Possible medium to low thermal stability • Odor release if hydrolyzed / transesterified • Possible extractability • Possible long-term corrosion issue

Phosphine Oxides as Flame Retardants for PWB

Phosphine oxides, which contain P-C bonds, are in general much more stable chemically and thermally compared to phosphorus materials that contain P-O-R bonds.[11] In fact, phosphine oxides that do not contain β-hydrogens have very high thermal stability, often exceeding 400 °C.[12] Additionally, the inherent affinity of phosphates to absorb moisture is believed to be due to the polarity of the P-O bonds, which should be less of an issue with P-C bonded structures.

Attention was focused on aryl phosphine oxide materials. The rigid aromatic structures would lead to reduced polymer chain flexibility and result in a higher Tg. In particular, when looking at the structure of TBBA, which is used in the forwarding reaction with epoxy resins as discussed above, an analogous phosphine oxide structure is bis(hydroxyphenyl)phenyl phosphine oxide, compound **1** (Figure 6). This material has been reported previously.[13]



1

Figure 6 - Bis(4-hydroxyphenyl)phenylphosphine Oxide (Compound 1)

Compound **1** should be usable in epoxy resin mode by the forwarding reaction with commercial epoxy resins, similar to TBBA (Figure 7). Indeed, the material was reacted with DGEBPA at different %P levels to make the chain-extended resin that contains phosphorus in the backbone. The relevant analytical data for those resins is depicted in Table 2.

Table 2 - Forwarding Reaction of DGEBPA with Compound 1

Run No.	%P	EEW
1	1.4	275
2	1.7	400
3	3.0	Solidified

EEW = Epoxide equivalent weight

This material can be advanced into a DGEBPA type resin safely at up to the 2% phosphorus level. The 3% level formed a solid, which points to a potential issue with this approach in being able to control the reaction safely. When using a 2% phosphorus-containing resin, the final P content in the fully formulated material with curing agents and other additives would be lower, making it more difficult to meet the V-0 FR requirement.

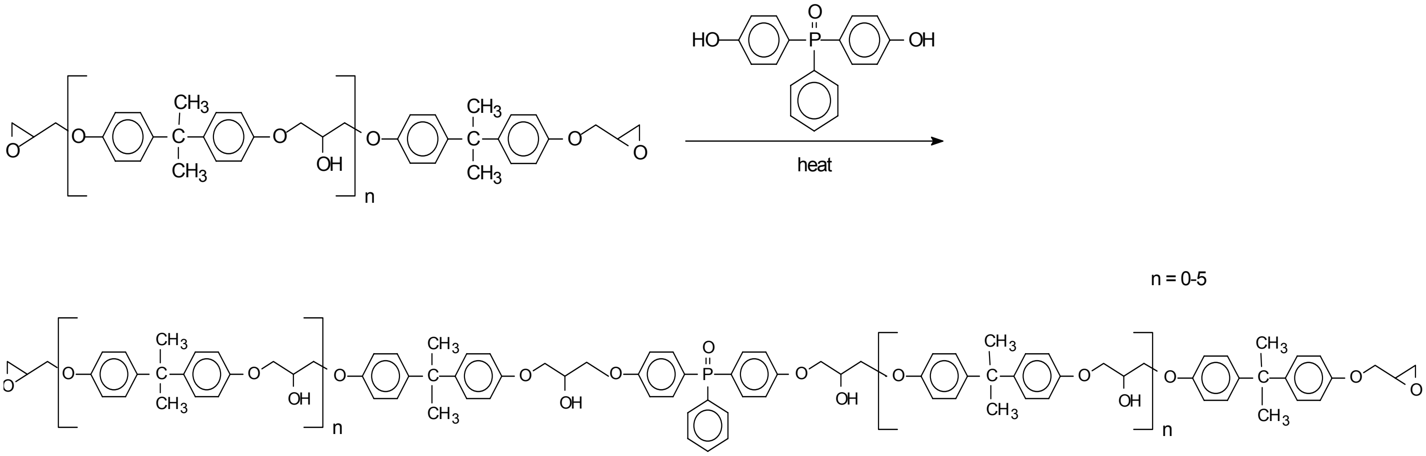


Figure 7 - Forwarding Reaction of DGEBPA Resin with 1

The synthesis of **1** required a fairly expensive intermediate raw material, dichlorophenylphosphine oxide. To overcome that problem, the preparation of a mixture of mono-, bis-, and tris-hydroxyphenyl phosphine oxides was prepared using a 1:2 stoichiometric ratio of reagents (Figure 8).[14] This gives the mixture compound **2**. This way, the dichlorophenylphosphine oxide intermediate is not required and the mixture can be prepared from standard phosphorus oxychloride.

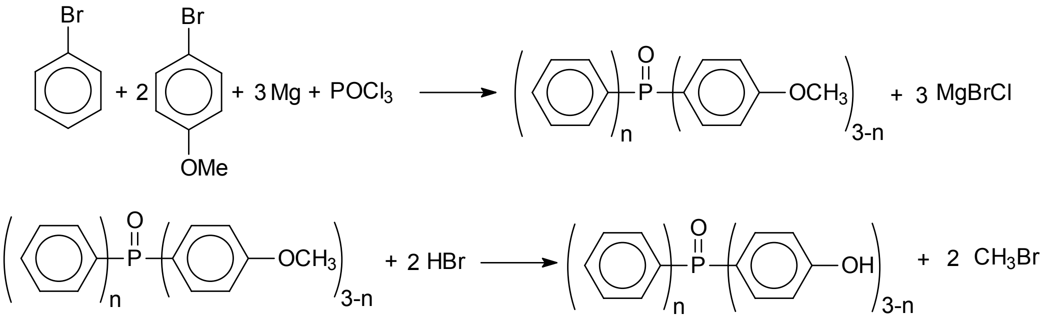


Figure 8 - Synthesis of Phosphine Oxide Mixture (Compound 2)

The ratio of mono-, bis-, and tris-hydroxyphenyl groups in the mixture can be easily adjusted in the reaction if needed by simple altering of the reaction stoichiometry (Table 3). The ratios were determined by ^{31}P NMR. Material represented by run no. 2 was used the experiments discussed in this paper.

Table 3 - Preparation of 2 at Different Reagent Ratios

				Product Ratios		
Run No.	PhBr Equiv.	MeOPhBr Equiv.	$POCl_3$ Equiv.	Mono	Bis	Tris
1	0.60	2.4	1	0.10	0.38	0.52
2	1.0	2.0	1	0.24	0.47	0.29
3	1.5	1.5	1	0.42	0.43	0.15

This mixture product **2** can also be advanced into DGEBPA resins with ease at 2% phosphorus (Table 4). At the 3% P level, the material could also be advanced with DEGBPA resin, but the reaction product was very thick and almost a gel. The amount of tris component present in the forwarding reaction of **2** (which would normally lead to a glass) is off-set by the mono material present. This allows forwarding reactions to occur under standard conditions, where the 3%P content would be the safe upper limit.

Table 4 - Forwarding Reaction of DGEBPA Resin with Compound 2 Mixture

Run No.	%P	EEW
1	1	206.3
2	2	396.4
3	3	748.4

This approach still has the above disadvantages of giving a relatively low formulated P content, and used DGEBPA resins, which are known to be more difficult to flame retard. Other difunctional epoxy resins of course could also be treated in this manner.

The forwarded material of **2** does, however, display FR properties (Table 5). When using a simple formulation based on the DGEBPA advanced resin of **2** (2% P) with a dicy cure, the laminates were self-extinguishing, gave a T-260 test without fail for 18-19 minutes (time at which the test was stopped), and a Tg in the range of 145 °C.

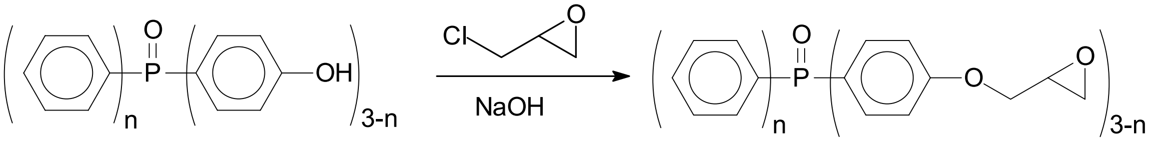
Table 5 - Laminate Properties of DGEBPA Adduct of Compounds 1 and 2(a)

FR Cmpd Resin	% P	Cure	Tg, °C (TMA)	TGA 5% loss, °C	PCS D	UL 94 Ave t_1, t_2 (sec)(b)	T-260 (min.)
DGEBPA	0	dicy	118	385	---	Total consumption	---
TBBA + DGEBPA	0	dicy	136	308	5	1,3 (V-0)	9
2 + DGEBPA	1.8	dicy	146	372	5	55, 0	>18(c)
1 + DGEBPA	1.9	dicy	143	374	5	75, 0	>19(c)
2 + DGEBPA	1.4	PFN[d]	151[e]	402	5	13, 31	---

a) Formulation contained Epon 828 advanced resin of **1** or **2** at 2% P and used dicy curing with 2MI catalyst adjusted to give 170 °C stroke cure of 300 s.
b) FR **2** gave self-extinguishing flames with only approximately one-third of the coupon being consumed at the edges only. FR **1** burned to the clamp at the edges only.
c) The test was stopped at the time indicated.
d) PFN = phenol-formaldehyde novolac resin.
e) By DSC analysis.

From the data in Table 5, it is evident that these phosphine oxide materials display FR properties and do not negatively impact the Tg of the resin system. Compound **2** demonstrated improved inherent FR properties vs. **1**, as evidenced by the self-extinguishing nature in the UL-94 test and the relative burn times. A V-0 was not obtained in these simple formulations, which is an indication that some additional FR assistance is needed when using standard DGEPBA epoxy resins. The laminate Tg properties of all these materials were in the 140-150 °C range and no plasticizing effects were observed. High thermal stability is apparent as evidenced by the high values obtained in the TGA and T-260 analyses. In fact, the 5% TGA wt. loss temperature value for the material that was cured with the phenol-formaldehyde novolac (PFN) resin was above 400 °C. These materials met the goal of formulating and processing (B and C staging) in the same manner as TBBA systems and showed that the plasticizing problem present with phosphates was not present. The typical stroke-cure at 170 °C was ~300 seconds and the B-stage at 170 °C was ~3 minutes. The typical press cycle was 2 hr at 180 °C.

One way to overcome the forwarding reaction limitations of a relatively low P loading is to make the epoxy resin directly from **2** by reaction with epichlorohydrin (compound **3**, Figure 9). The idealized structure is shown, but oligomers could be present depending on the conditions of the reaction. This material would still introduce the phosphorus group into the cured PWB via epoxy resin mode (Figure 3), but with higher achievable phosphorus loadings.



2 **3**

Scheme 5 - Preparation of 3 by Reaction of 2 with Epichlorohydrin

Compound **3** was evaluated with different curing agents and with other epoxy resins as co-reactives. The results are shown in Table 6. These results show that good FR performance was obtained, but the thermal stability in the solder dip test was poor, possibly due to the use of a higher P load in this system or to unoptimized curing conditions.

Table 6 - Evaluations of 3 in Various PWB Systems

Run No.	Co-resin	Cure	Co-FR	%P	Tg	TGA	PCSD	UL-94
1	DEN 438	dicy	none	3.8	181	358	1	V-1
2	DGEBPF	dicy	none	3.8	147	351	1	V-1
3	None	dicy	2% ZB	6.4	177	304	1	V-0
4	DEN 438	BGN	30% ATH	3.0	167	359	2	V-0
5	DEN 438	PFN	30% ATH	4.0	177	389	1	V-0 borderline

BGN: benzoguanamine-co-phenol formaldehyde novolac resin
PFN: phenol formaldehyde novolac resin
ZB: zinc borate

In spite of the obvious poor PCSD results, the Tg values were quite high. This strategy was not investigated further because the approach suffers from having an extra synthetic step in the sequence, which would render the product more costly.

We next turned to using **2** as a co-curing agent in conjunction with standard PFN resins. Novolac resins are known to display some inherent FR properties through the formation of char residue.[15] The TGA data in Table 4 using novolac curing also showed better thermal stability compared with dicy systems.

The cure behavior of using **2** as a co-curing agent was studied by DSC (Table 7). The DSC scans show that the amount of reactivity left after reaching the gel point in the straight novolac cure is quite high (181 J/g) compared with the cases where **2** is used, indicating that the extent of conversion of the compound **2** reactions is much further at the gel point. However, the typical B-stage conditions for the co-curing system were a reasonable 170 °C for two minutes. The cured resin has a lower Tg when curing with **2** only, a characteristic that is improved when using the co-curing agent approach.

Table 7 - Comparison of Gel and Thermal Properties of Different Curing Approaches

	Formulation No. (phr)		
Varnish Components	**1**	**2**	**3**
DEN 438 Epoxy	100	100	100
Compound **2**	79	0	51.2
PFN	0	62	18.8
2-MI	0.05	0.05	0.05
Reactivity / Properties			
Gel Time @ 170°C (sec)	210	265	215
ΔH (DSC, J/g)[(a)]	96	181	117
Exo Peak (DSC, °C)[(a)]	183	191	178
Tg (DSC, °C)[(b)]	151	181	161
%P	4.4	0	3.0
OH/Epoxy Eq ratio	0.9	0.9	0.9

a) DSC of gelled material
b) DSC of gelled material after overnight post cure at 200 °C

Base laminates were prepared using DEN 438 epoxy resin with **2** and PFN resin as co-curing agents and 2MI catalyst with no other additives. The intrinsic flame-retardant ability of **2** in this co-cure mode is shown for each laminate by comparing the UL-94 burn times (Table 8). When using the hydroxyaryl phosphine oxide / PFN co-curing agent system, the same level of flame retardancy was achieve as when using compound **2** as the sole curing agent, but at a reduced phosphorus level and with an improved glass transition temperature.

Table 8 - Laminates Made Using DEN 438 Epoxy Resin Cured with 2 and PFN Resin

				UL-94 Ave[a]		
Run	**Curing Agent**	**%P**	**Tg, °C (DSC)**	**t1**	**t2**	**Total**
1	**2**	4.1	129	3	19	112
2	PFN	0.0	168	---	---	---
3	**2** / PFN	3.0	164	6	15	83

a) 8-ply laminate using 7628 glass, 5 test coupons each

The above laminates showed good FR properties, but were not V-0. To bring the material into the V-0 range, the use of ATH as co-FR was employed (Table 9). These laminates were made and tested for flame retardancy according to the UL-94 test. Alternative epoxy resins and novolac resins were also examined for comparison.

Table 9 - Co-curing Agent Formulations of 2 Using ~30% ATH on Organics

Formulation (phr)	1	2	3	4
DEN 438 Epoxy	100	100	0	100
Epon 164 Epoxy	0	0	100	0
Compound **2**	0	55	48.5	52.2
PFN	62	25	10.4	0
BGN	0	0	0	21.8
2MI	0.10	0.06	0.07	0.001
ATH	44	54	48	52.2
Physical Properties				
Formulation Organics %P	0	3.0	3.0	3.0
Cured Resin Tg, °C (DSC)	171	166	184	165
TGA 5%, °C	390	378	380	324
Laminate UL-94 Burn Results	Fail	V-0	V-0	V-0
Total Burn Time (5 coupons), sec.	298	10	26	5

The formulation using straight novolac curing (formulation 1) failed the UL-94 burn test with 30% ATH. Using **2** as a co-curing agent with the PFN resin or BGN resin (BGN = benzoguanamine-co-phenol formaldehyde novolac) allowed the laminates to pass the UL-94 test with a V-0 rating. The Tg was improved further when a cresol epoxy novolac (Epon 164) was used in place of DEN 438. Typical moisture absorption results ranged from 0.30 to 0.42 % moisture using the pressure cooker method. These systems were not optimized.

Properties of Compound 2

The properties of **2** are listed in Table 10. The material has been used in our laboratories most conveniently as a 50% solution in Dowanol^{TM} PM solvent.

Table 10 - Physical Properties of Mixture Compound 2

Physical Property	**Value**
melt range, °C	200-230
Hydroxyl Equivalent Weight (g/eq)	160-165
% Phosphorus	9.6 – 9.8
Solubility in water, acetone, chloroform	Insoluble
Solubility in Dowanol^{TM} PM, THF, methanol	Soluble
Viscosity at 51% in Dowanol^{TM} PM @ 25°C, cps	381
5%TGA, °C	337

A representative TGA scan of the neat compound **2** is shown in Figure 10. This shows good thermal stability of **2** with the 2% wt loss at 300 °C and 5% loss at 337 °C. In the cured laminate, the 2% and 5% TGA wt. losses were 330 and 407 °C, respectively (Figure 11). The T-260 test showed no delamination after 1 hr (Figure 12).

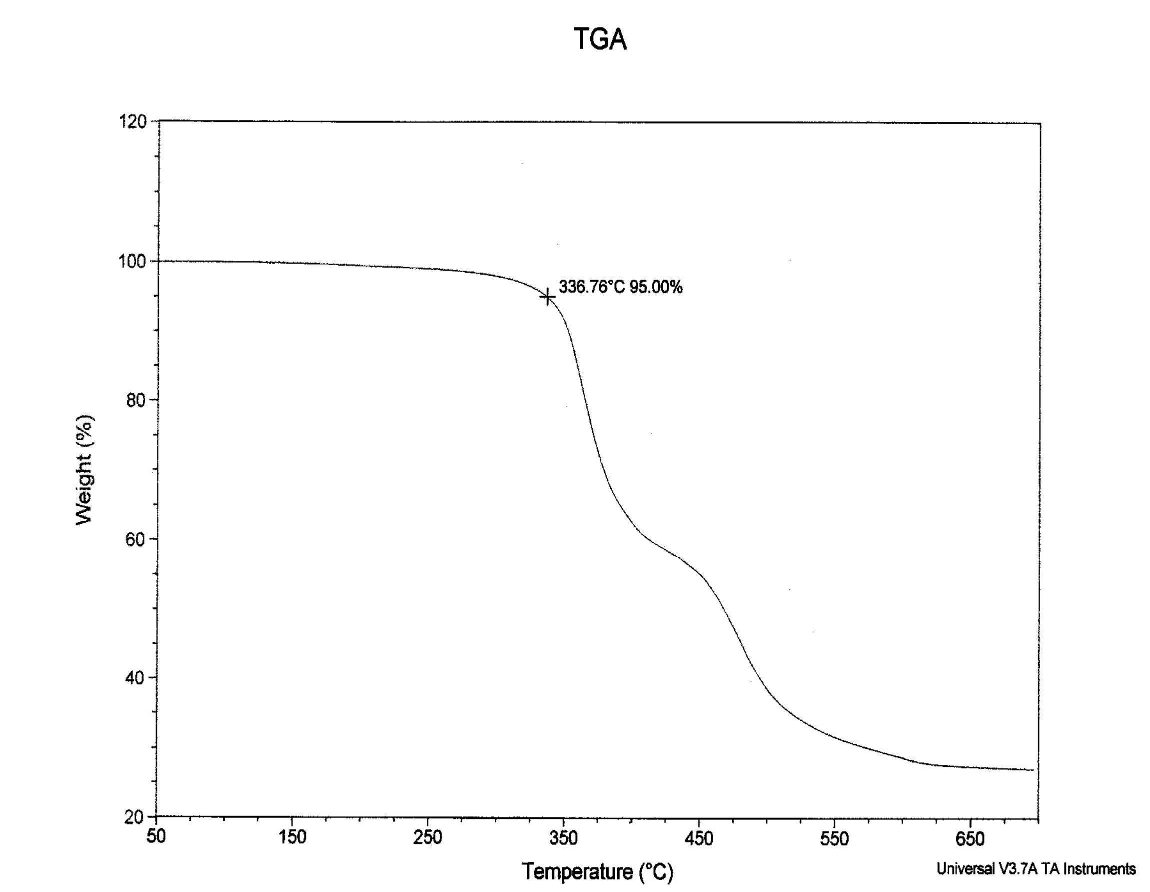


Figure 10 - TGA Scan of 2

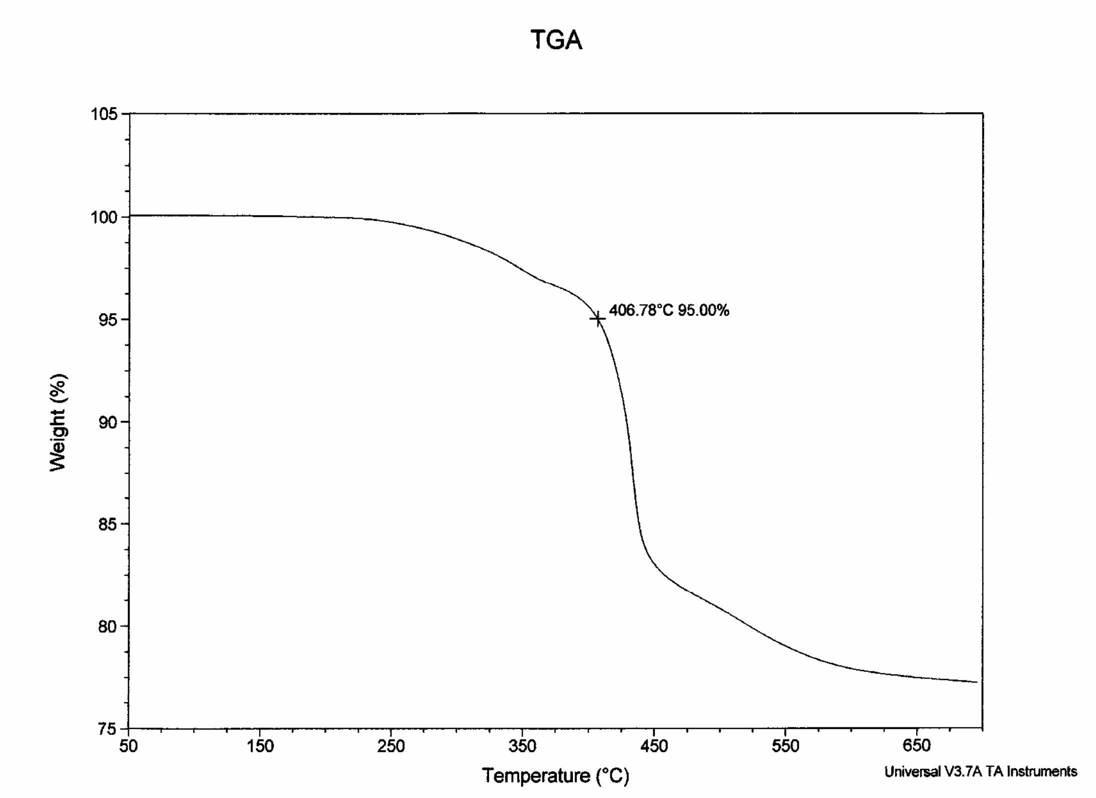


Figure 11 - TGA Scan of Laminate #2 from Table 9

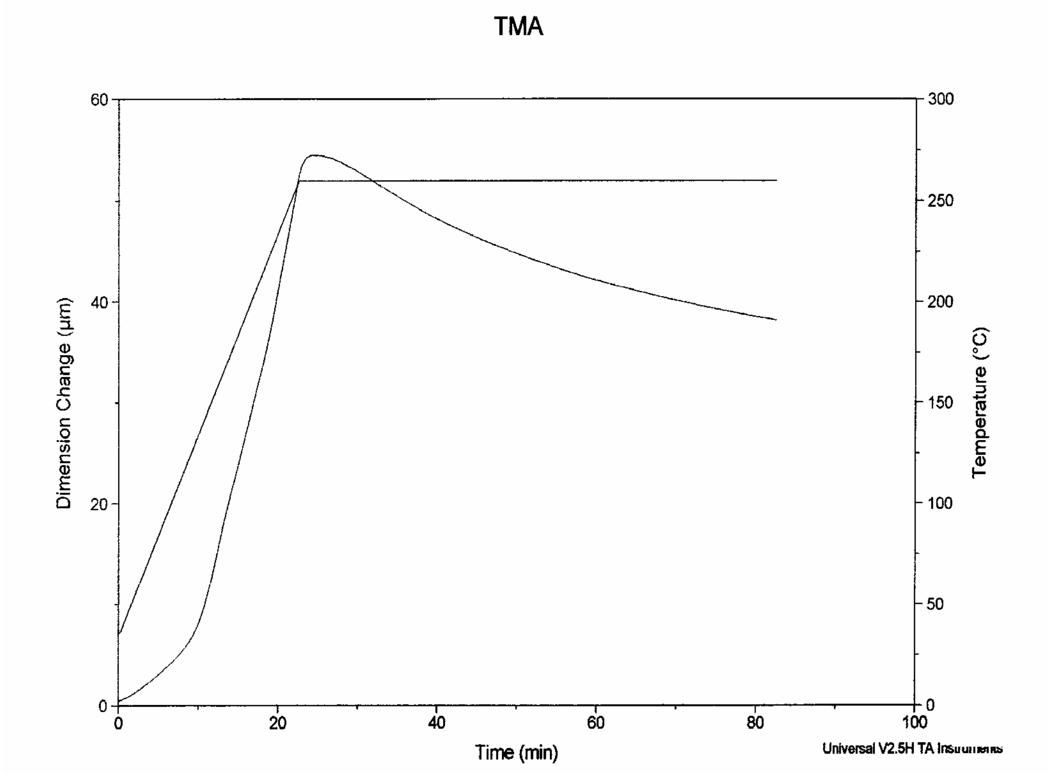


Figure 12 - T-260 Test of Laminate #2 from Table 9

Conclusions

The use of a mixed hydroxyphenylphosphine oxide (**2**) has been demonstrated to give laminates with good thermal stability and high Tg. The material was used as part of a curing agent system. This FR material does not have issues associated with the phosphate type FR products, such as hydrolysis or transesterification. The laminates displayed inherent FR properties and met V-0 specifications at 30% ATH loading. The moisture absorption levels were reasonable at around 0.3-0.4%. This curing agent system approach causes the phosphorus materials to become reacted into the cross-linked structure and, like TBBA, would not be available to leach out of the PWB.

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