New Phosphorus-Based Curing Agent for Copper Clad Laminates

S. Levchik
Supresta U.S. LLC
Ardsley, NY

Abstract
A new organophosphorus curing agent, Fyrol PMP, specially designed for electronic thermoset resins was recently introduced to the market. This paper describes the chemical structure and physical properties of this material. This curing agent has a unique mechanism of cross-linking epoxy resins. Because of high functionality it allows achieving high T_g and good thermal properties required for lead-free soldering. About 20 to 30 wt. % this material completely cures epoxy resin and provides a V-0 UL-94 flammability rating in the copper clad laminates. The loading of the material can be decreased to 10 wt. % when it is used in the combination with alumina trihydrate (ATH). In typical FR-4 laminate formulations, a glass transition temperature (T_g) of 150°C or higher can be achieved . Co-addition of benzoxazine resin raises the T_g to 190°C. The laminates pass the Delamination Test at the temperature of lead-free soldering (288°C) and securely pass the Pressure Cooker Test.

Introduction
Most of the modern printed wiring board (PWB) technology, where flame retardancy is required, is based on tetrabromobisphenol A (TBBA). Together with some limited use in thermoplastics TBBA is the largest (by commercial value) flame retardant sold in the marketplace. Industry has been using TBBA for over thirty years and the product performs well. However, recently TBBA together with brominated flame retardants in general is receiving some negative perception.

- TBBA is a major FR component of electronic and electrical equipment, and will require special recycling in Europe starting in 2006 which may necessitate separation of the waste streams containing brominated flame retardants.
- Under ongoing risk assessment in Europe, TBBA may be classified as dangerous for the environment and very toxic to aquatic organisms.[1] However, it should be remembered that where TBBA is reacted into the epoxy forming a polymeric structure, leaking of TBBA into the environment is likely to be very limited.

Concerns over brominated flame retardants have stimulated development of new halogen-free formulations with the main approaches being (1) inherently flame retardant resins and (2) phosphorus-based flame retardants. Both types of formulation may also contain inorganic fillers like alumina trihydrate (ATH) which helps further improve flame retardancy as well as electrical and physical properties of the laminates. For example, some ATH containing systems show low coefficients of thermal expansion and, as result, are more stable to delamination compared to brominated systems.[2]

Special resins containing either a high level of nitrogen or highly aromatic structures often fall into the category of inherently flame-retardant. Recently, these types of systems have received considerable attention in Japan and Southeast Asia. The formulations based on novolac derivatives including certain carbon-to-carbon bonded aromatic groups in the main chains[3] or naphthalene-based novolac epoxies.[4] display far higher flame retardancy than that of the epoxy resin compounds without those aromatic groups.

In order to provide better flame retardant performance and physical properties, epoxy resins can be copolymerized with other thermoset resins. For example, epoxy can be copolymerized with low molecular weight poly(phenylene ether)[5] which helps to achieve better electrical properties and lower flammability. Benzoxazines are shown in recent patents[6] for use in combination with an epoxy resin and phenolic novolac. These formulations give high glass-transition temperature and good flame retardancy. Combinations of poly(phenylene ether), benzoxazine and epoxy resin have been also patented.[7]

Usually inherently flame retardant resins do not provide the required level of V-0 UL 94 fire performance by themselves. Co-addition of convention flame retardans, brominated, phosphorus based or inorganics, is needed. In spite of excellent technical performance, the economic aspect limits the broad use of these resins, apart from specialty applications.

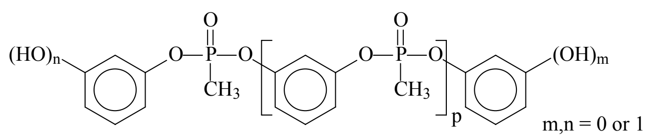
Phosphorus-containing products are particularly effective in epoxy resins because they actively involve the epoxies in charring. The char on the surface of the polymer serves as a good thermal insulation barrier, which is able to extinguish the flame by blocking heat and mass transfer. Furthermore, phosphorus-containing species, if delivered into the flame, become very potent scavengers of free radicals in the flame. For example, phosphorus at the same molar concentration in the flame,

is about five times more efficient in decreasing the flame propagation then bromine and ten times more efficient then chlorine[8] and 1 wt. % phosphorus in epoxy resin may provide the same flame retardant effect as 13 wt. % bromine.[9]
The technical literature extensively reports the use of 9,10-dihydro-9-oxa-10-phosphaphenanthrene 10-oxide (DOPO), manufactured in Japan, Europe and China, and imported in the USA. Normally DOPO is pre-reacted with a multifunctional epoxy resin[10-12] which decreases the functionality of the resin. In order to preserve the functionality, DOPO is firstly reacted with benzoquinone which leads to a phosphorus-containing hydroquinone (DOPO-HQ), and this diol is used as a reactive flame retardant in the same way as TBBA[12,13].This diol product is probably available only in Japan.

Some phosphazenes due to their symmetrical structure show very good dielectric properties not typical for pentavalent phosphorus of tetrahedral configuration. This attracts attention to phosphazenes for new high frequency applications like cell phones, cell phone tower transmitters or computer motherboards. An example of the phosphazenes under consideration is a bridged phenoxyphosphazene.[14,15]

In this paper we will present chemical structure, physical properties and combustion performance for a newly developed phosphorus-containing flame retardant Fyrol PMP.[16-18] This product overcomes many problems typical of halogen-free substitutions for TBBA.

Experimental
The new flame retardant, available under a trademark, is a polymeric organophosphorus product.



It is compatible with epoxy resins, curing agents and other ingredients of PWB varnishes. It has very high phosphorus content of 17.5 % and is soluble in MEK and acetone, which are most commonly used solvents by the PWB industry.

Commercially available bisphenol A, phenolic novolac and cresol-novolac epoxy resins were used in this study to formulate varnishes. In some experiments benzoxazine resin was blended with epoxy. In most experiments our material was used as the sole curing agent, however sometimes phenol-formaldehyde novolac or other specialty novolacs were applied as co-curing agents. The curing process was catalysed by methylimidazole (AMI-2).

Copper clad laminates containing eight layers of glass fiber cloth were made using a laboratory press with the following curing cycle: 30 min at 130ºC and 60-90 min at 170-185ºC. The prepregs were prepared by brushing the glass fiber cloth with the epoxy varnish.

Flammability of the laminates was measured according to the UL-94 vertical test protocol.[19] The thermal stability was measured by thermogravimetry in an inert atmosphere. The glass transition temperature of the cured laminates was measured by TMA. Delamination was evaluated in a TMA apparatus at 260 and 288ºC. Hydrolytic stability was measured in the Pressure Cooker Test according to the IPC-TM-650 protocol.

Results and Discussion
Our material is a colorless or slightly amber glassy low-melting solid. Typical physical properties are shown in Table 1. The material is very thermally stable. It does not show any signs of degradation up to 330ºC and then slowly decomposes at 330-570°C. High thermal stability is an indication of the good potential of this phosphorus-based material in lead-free soldering formulations.

Although the material contains some terminal OH functional groups, its main curing process does not need to proceed through these groups, but goes via opening of epoxy groups and insertion into phosphonate ester bonds. Schematically, the curing mechanism is shown in Figure 1. The detailed mechanism has been published elsewhere.[20] It should be noted that every reaction of the phosphonate with epoxy, produces a branch in the polymer chain, which eventually becomes a cross-link. This is usually not the case with other phosphorus based products and even conventional curing agents.

Table 1 - Physical Properties

Physical property	Value
Softening temperature, °C	45-55
Pour point, °C	70-80
Average molecular weight	1000-1400
Phosphorus content, wt. %	17.5
Water content, wt. %	<0.3
Color, Gardner	6 max.
Solubility in water	Insoluble
Solubility in acetone, MEK	Soluble
Viscosity @ 120°C, cps	800-1200
Viscosity 70% in acetone @ 25°C, cps	90

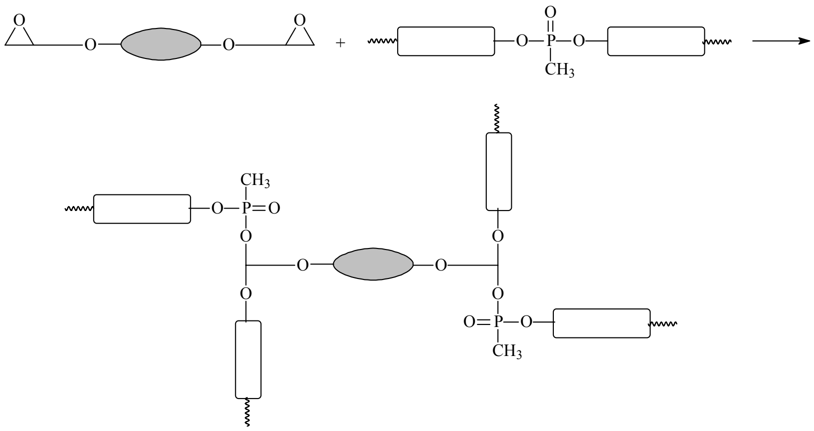


Figure 1 - Schematic Curing Mechanism of Bisphenol A Type Epoxy with our Material

Figure 2 shows schematic reactions of two phosphorus-based products, which are often used in halogen-free formulations. One of them is DOPO, a monofunctional molecule, and another is a product of reaction of DOPO with quinone, DOPO-HQ, a difunctional molecule (see also Introduction). It is clear that DOPO is a terminator of epoxy functionalities, because after it has reacted with the epoxy resin, the polymer chain has been terminated. Because of this, DOPO can be used only with multifunctional epoxies. On the other hand DOPO-HQ, participates in the chain extension reactions which results in linear oligomers (Figure 2). Further cross-linking should be performed with conventional curing agents.

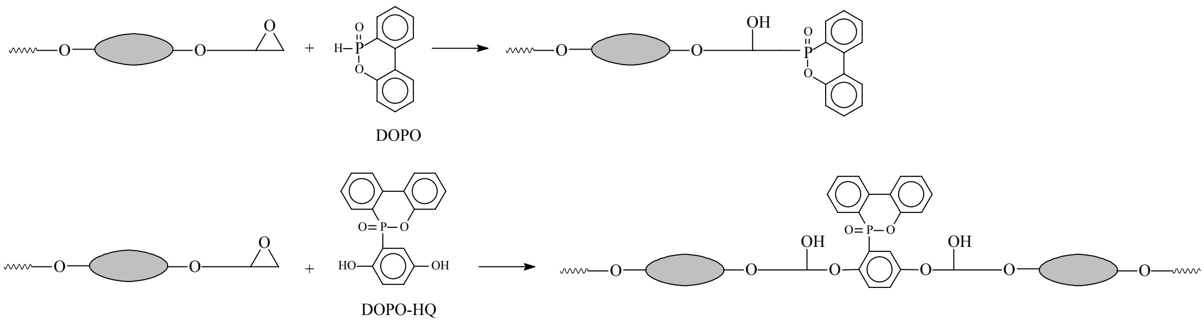


Figure 2 - Schematic reactions of DOPO and DOPO-HQ with Epoxy

The thermal stability of a cured epoxy resin depends on the presence and concentration of OH groups in the structure. Upon heating to above 300°C, the cured epoxy resin starts losing water because of dehydration of secondary alcohols (Figure 3). This water can cause mechanical failure of the laminates at extreme temperatures. Furthermore, double bonds created after dehydration weaken epoxy network and polymer chains start breaking relatively easily. As is seen in Figure 1, our material does not generate OH groups upon curing, which means that an intrinsically more thermally stable polymer network is formed.

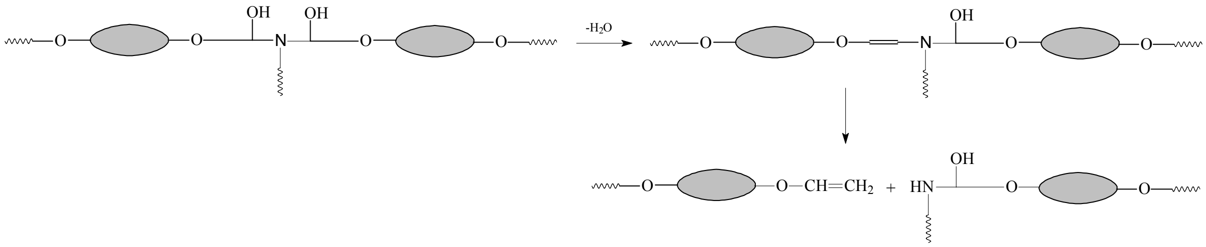


Figure 3 - Schematic of Decomposition of an Epoxy Resin Cured with an Amine

Our material was tested in different epoxy resins, where it was applied as a sole curing agent and a sole flame retardant. Eight ply copper clad laminates made with phenolic novolac type epoxy passed V-0 UL-94 rating at 20 wt. %. About 25 wt. % was required for cresol novolac epoxies and 30 wt. % for bisphenol A based epoxy resins.

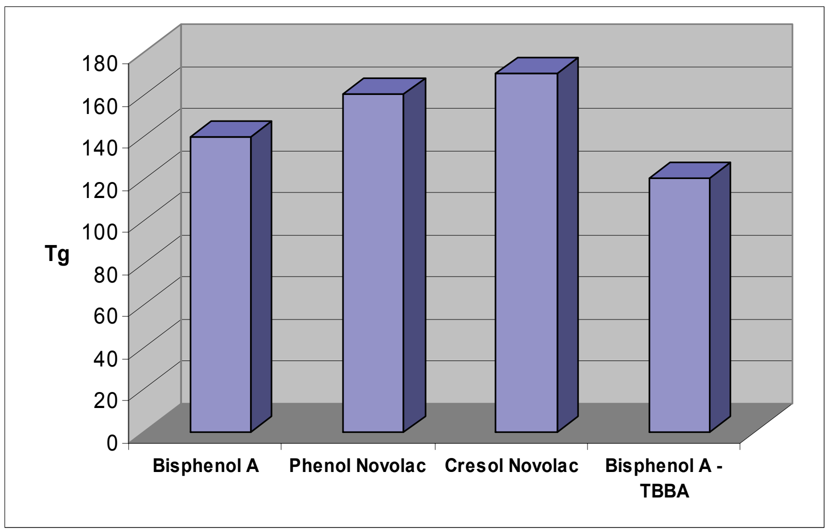


Figure 4 - Glass Transition Temperature for the Laminates Made with Different Epoxy Resins as Determined in TMA, at 10°C/min.

The glass transition temperatures of the laminates made with different epoxy resins are shown in Figure 4. As a comparison, a conventional FR-4 laminate containing tetrabromobisphenol A epoxy and cured with DICY is also shown in this Figure. All halogen-free formulations show relatively high glass transition temperatures indicating that the material does not cause plasticization, which is usually a matter of concern with phosphorus-containing additives. In contrast, our material behaves as a effective curing agent. All laminates in this series show a coefficient of thermal expansion, CTE = 50-60x10^{-6} mm/°C which is lower that CTE of brominated epoxy resin 70x10^{-6} mm/° (Figure 5).

The delamination performance of halogen-free formulations was evaluated in a TMA apparatus at 260 and 288ºC according to the IPC-TM-650 protocol. All the laminates withstood 60 min at the temperature required for lead-tin soldering (260°C) and 10-25 min at the temperature for lead-free solder (288°C). Although the bromine-containing FR-4 laminate survived 20 min at 260°C, it immediately cracked at 288°C. This data confirm once more the exceptional thermal stability of epoxy resins cured with our material.

With new developments of halogen-free laminates, hydrolytic stability is of special concern with phosphorus-containing flame retardants.[21] In our study the hydrolytic stability was measured in the Pressure Cooker Test according to the IPC-TM-650 protocol which calls for exposure of the laminate for 30 min to a steam in the autoclave and then immediate immersion into the molten tin-lead solder. As was found, cresol novolac based laminates with the material passed the Pressure Cooker Test at 30 min exposure to the steam, whereas the laminates based on bisphenol A or phenolic novolac epoxies even exceeded the requirements of the test (60 min).

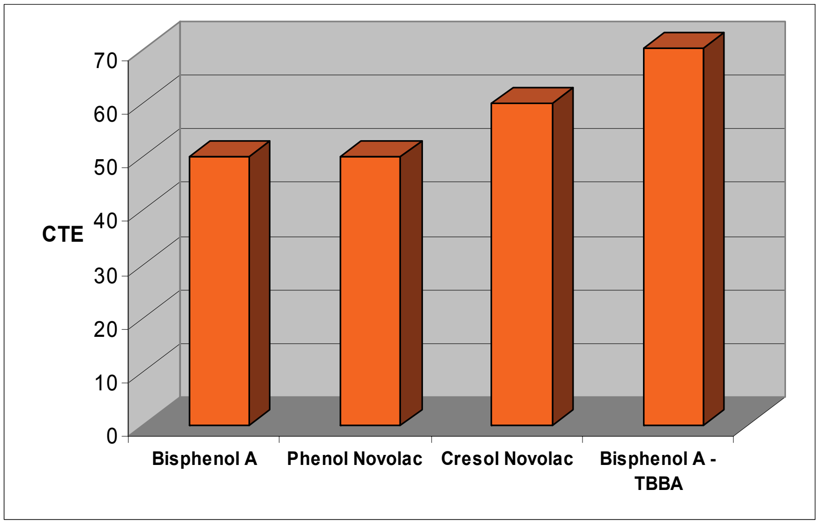
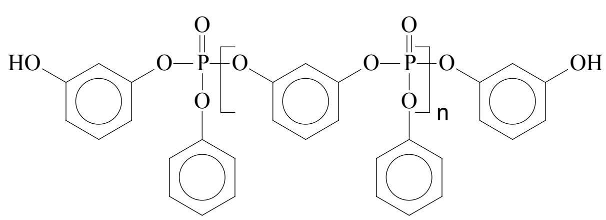


Figure 5 - Coefficient of Thermal Expansion, CTE, mm/°C*10^6 for the Laminates made with Different Epoxy Resins

As was discussed in the Introduction, there is a trend of using ATH along with phosphorus-containing flame retardants in halogen-free formulations. Apart from cost saving, this also leads to improvement of some physical properties like CTE and resistance to delamination. It is also reported[22] that ATH helps to achieve temperature stable dielectric constants and low dissipation factors. Therefore we made attempts to formulate with ATH. Table 2 shows the formulations, their fire performance and some physical properties of copper clad laminates made with bisphenol A epoxy and cured with our material. As is seen, a V-0 rating can be achieved with only 10 wt. % in the formulation # 1 containing 50 wt. % ATH. This laminate has very low CTE and it passes the Delamination Test at 288°C as well as the Pressure Cooking Test (PCT).

In order to improve the glass transition temperature (T_g) a polybenzoxazine resin was added to the formulations. Very high T_g = 190°C was achieved in formulation # 2 containing 15 wt. % polybenzoxazine resin, 50 wt. % ATH and only 10 wt. % . This formulation has also very good delamination performance, low CTEs and improved hydrolytic stability (PCT = 60 min). In some formulations reported in the patent literature[23,24] melamine-phenol novolac was used instead of regular phenol novolac in order to improve hydrolytic stability. As is seen in formulation #3, the use of this novolac helps to boost hydrolytic stability even further (PCT = 90 min), however flame retardant performance suffers because only a V-1 rating has been achieved.

The next step in this study was comparison of performance of our material and an aromatic phosphate oligomer which is structurally similar, but which reacts with epoxy only via terminal OH groups.



As it is seen in Table 2 this phosphate does not provide required flammability (formulation #4). The laminate also shows relatively low T_g, high CTE and it fails the Delamination and Pressure Cooker Tests.

Table 2 - Combustion Performance and Physical Properties of Laminates Containing ATH

	1	2	3	4
Formulation, wt. %				
Epoxy	40	20	20	35
Benzoxazine		15	15	
Phenolic Novolac		5		
Melamine-Phenol Novolac			10	10
ATH	50	50	35	35
Our material	10	10	20	
Aromatic phosphate oligomer				20
Physical property				
T_g, °C	120	190	160	120
UL-94, rating	V-0	V-0	V-1	Fail
PCT, time (min)	30	60	90	Fail
Delamination at 288°C, min	>60	>60	>60	Fail
CTE, < T_g, 10^6 mm	30	30	40	60
> T_g, 10^6 mm	160	160	165	200

Conclusions

A new halogen-free flame retardant curing agent, our material, is a phosphorus-containing polymeric product reactive with epoxy resins. The material cures resin by insertion of epoxy group into the phosphonate linkage, which effectively cross-links the resin and ensures its high thermal stability. It is soluble in solvents commonly used in the industry and it is compatible with various epoxy resins. Copper clad laminates pass UL-94 test at 20 – 30 wt. % content of the material. Combinations of 10 wt. % of our material and 50 wt. % ATH provide laminates with low CTE and exceptional hydrolytic and thermal stability. Further co-addition of polybenzoxazine resin boosts T_g to 190°C and use of melamine-phenol novolac helps to extend the Pressure Cooker Test exposure to 90 min. The laminates containing our material pass the Delamination Test at the temperature of lead-free soldering.

Acknowledgment

The author is thankful to Dr. John Yao, Dr. Andrew Piotrowski and Dr. Sophia Dashevsky from Supresta LLC for synthesis, study of curing mechanism, testing of combustion performance and physical properties. Contributions of Prof. Edward Weil from Polytechnic University of New York in the development effort and valuable discussion of this paper are also acknowledged.

References

1. V. Steukers, S. Kroon and D. Drohmann, in *Flame Retardants 2004*, Interscience Communications, London, 2004, p.1.
2. R. Demaree, in *Proc. IPC Conf. EXPO 2001*, Anaheim, CA, (2001).
3. M. Iji and Y. Kiuchi, *Polym. Adv. Technol.,* **12**(2001)393.
4. T. Shobara, S. Okuse, T. Aoki and H. Kato (to Shin-Etsu), *US Patent 6,143,423* (2000).
5. G. Yeager (to GE), *US Patent 6,774,160* (2004).
6. H. Nagase, T. Aizawa, Y. Y. Hirai and Y. Sato (Hitachi) *US Patent 5,945,222* (1999).
7. K.-Y. Hwang, A.-P. Tu, M. Liang, C.-Y. Ju, S.-Y. Wu, C.-H. Kao and F.-S. Su (to Chang Chung Plastics) *US Patent 6,900,269* (2005).
8. V. Babushok and W. Tsang, *Combust. Flame*, **124**(2000)488.
9. J.-Y. Shieh and C.-S. Wang, *J. Polym. Sci., Polym. Chem.*, **40**(2002), 369.
10. R. Ultz and S. Sprenger (to Schill and Sellacher) *European Patent Application 0,806,429* (1997).
11. C.-S. Wang and C.H. Lin, (to National Science Council of Taiwan) *US Patent 6,291,627*, (2001).
12. J. Gan and A. Goodson, (to Dow Chemicals) *US Patent 6,645,631* (2003).
13. T. Sagara, T. Takata, K. Ihara, H. Kakiuchi, K. Ishihara, C. Asano, M. Gunji and H. Sato (to Matsushita) *US Patent 6,933,050* (2005).
14. T. Sumiyoshi, A.Mizushima, K. Oota, Y. Fujeda, H. Nikaido and T. Aihara (to Sumitomo Bakelite) *European Patent Application EP 1,287,071,* (2003).
15. Y. Tada and S. Nakaho (to Otsuka) *European Patent Application 1,270,668,* (2003).
16. S.V. Levchik, S. Dashevsky, E.D. Weil and Q. Yao, (to Akzo Nobel) *PCT Patent Application* WO 03/029258 (2003)
17. S.V. Levchik and M. Buczek, (to Akzo Nobel), *PCT Patent Application WO 04/044054* (2004).
18. S.V. Levchik and A.M. Piotrowski, (to Akzo Nobel), *PCT Patent Application WO 04/113411* (2004).
19. *Plastics Flammability Handbook*, 3rd edition, Ed. J. Troitzsch, Haser, Minich, 2004.

20. T. Wu, A.M. Piotrowski, Q. Yao and S.V. Levchik, *J. Appl. Polym. Sci.* (accepted for publication)
21. N. Brown and M. Aggleton, *Reinforced Plastics*, (1999)(Oct.) 44.
22. T. Fischer, Y. Takeda, N. Desai and J. Zollo, in *Proceedings of IPC EXPO 2003*, Long Beach, CA, 2003, p. S08-3-1.
23. A. Tobisawa and T. Honjoya (to Sumitomo Bakelite) *US Patent 6,486,242* (2002).
24. T. Fukuzawa, T. Hirai, T. Imura and Y. Ohnuma (to Resolution) *European Patent 1,259,566* (2004).