

## Development of Flame Retardant for Halogen-free Build-up Insulating Resin

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We prepared new phosphoric amide derivatives or phenol resin derivatives as flame retardant for halogen-free build-up insulating resin. Especially, phosphoric amide derivatives have some active hydrogen in this molecular structure. It became clear by gel permeation chromatography (GPC) analysis and nuclear magnetic resonance (NMR) analysis that the active hydrogen can react with epoxy resin. We applied the reactive flame retardant to halogen-free build-up insulating epoxy resin, instead of halogenated epoxy resin and halogenated flame retardant. In the cause of increased bridging points after cured, the network of the resin strengthened, and the hardened resin characterized to have effective flame-resistance and high glass transition temperature (T<sub>g</sub>). Furthermore, flame-resistance of the halogen-free resin is improved by using inorganic filler including crystal water. Especially, less than 1.0 micrometers of Al(OH)<sub>3</sub> filler resulted in a good fire-resistance. We found the reason in micro Al(OH)<sub>3</sub> which has low decomposition point and large endothermic volume by differential scanning calorimetry (DSC) analysis.

Key words: Flame retardant, Phosphoric amide, Epoxy resin, Halogen-free, Build-up insulation

### 1. INTRODUCTION

Halogenated flame retardant and antimonide are usually used for the epoxy resin that needs the fire retardancy, such as printed wire boards. However, these flame retardant will be replaced from an environmental problem in recent years. Although phosphoric ester derivatives such as Figure 1 are used as a flame retardant now, but those agents added to epoxy resin causes its glass transition point or mechanical properties to fall<sup>1)</sup>. Then, we decided to develop several reactive flame retardants incorporable into the matrix of epoxy resin so that the fall of physical properties might not be caused. Especially, we observed reactive phosphide, such as phosphate included phenol or amide, and then it found out that the active hydrogen in the phosphoric amide reacted with epoxy resin by heating at over 170°C in the presence of the imidazole catalyst. It succeeded in making flame retardants fix into the network of epoxy resin. Fire retardancy is improved by use of the inorganic filler including crystal water such as aluminum hydroxide, Al(OH)<sub>3</sub>, which is widely used as a fire-resistant filler<sup>2)</sup>. However, the effect cannot fully be demonstrated only by mixing or addition. We found out that the particle size less than 1.0 micrometers of Al(OH)<sub>3</sub> filler with beads-mill dispersion method, can improve fire retardancy. We applied the reactive flame retardant and the micro Al(OH)<sub>3</sub> filler to halogen-free build-up insulating epoxy resin. In the cause of high bridging point density in the insulation after baking, the glass transition temperature of the resin is increased as compared with the additional flame retardant. The micro Al(OH)<sub>3</sub> filler added to the resin caused excellent result in UL-94V test. We found the reason in fine Al(OH)<sub>3</sub> which has low decomposition point and large endothermic volume by DSC analysis.

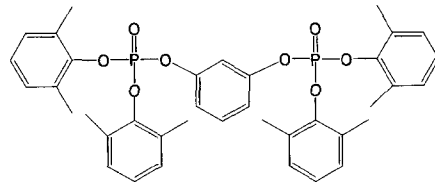


Fig. 1. Typical structure of flame retardant for halogen-free insulating resin (FP-500).

### 2. EXPERIMENTAL

#### 2.1 Materials

The solvent were purified in the usual way prior to use. Reagent grade diphenyl phosphoric chloride, aromatic diamine derivation, triethylamine, and 2,2-bis(4-glycidyloxyphenyl)propane were used in this study. 2-ethyl-4-methylimidazole (2E4MZ) as catalyst was obtained from Shikoku Corporation. PR-53194 as phenol resin were obtained from Sumitomo Bakelite Co., Ltd. FP-500 was obtained from Asahi Denka Kogyo Co., Ltd. Aluminum hydroxide were obtained from Sumitomo Chemical Co., Ltd. Silica gel were obtained from Japan Aerosil Co., Ltd. These materials were used without further purification.

#### 2.2 Apparatus

The <sup>1</sup>H-NMR spectra were performed on the JEOL models JNM-LA400 spectrometer. Molecular weight measurements were made with the aid of Hitachi D7000 Gel Permeation Chromatograph with Shodex column KF-803 and KF-805 and are based on polystyrene standards. The differential scanning calorimetry (DSC) analysis and glass transition temperature (T<sub>g</sub>) analysis were measured on the Seiko Instruments DSC-6200 and DMS-6100.

2.3 Synthesis of reactive flame retardant group included phosphorus.

2.3.1 Synthesis of branched multifunctional phosphoate-phenol resin

A mixture of 8.06g (0.03mol) diphenyl phosphoric chloride, 9.45g(105g/OH) PR-53194 as phenol resin and 50mL acetone were added to a 300 mL three-necked round bottom flask equipped with a magnetic stirrer, a reflux condenser, a nitrogen inlet and thermometer. The reaction mixture was stirred at room temperature until the resin completely dissolves. After that, the mixture kept to 0°C and 3.36g (0.033mol) triethylamine was added dropwise to the mixture in the flask for 1h at 0°C. The reaction mixture was warmed to 30°C for 0.5 h and heated to reflux for 2h. After an additional heating, there was no adsorption due to the diphenyl phosphoric chloride that could be detected by gel permeation chromatograph. The reaction mixture was cooled, and the acetone and excess triethylamine was removed under vacuum. The reaction crude was dissolved into 150 mL ethyl acetate, and washed by 100mL 5% ammonium chloride solution and 100mL distilled water twice. After washing, the ethyl acetate was removed under vacuum at 170°C. 15.2g (92.5% yield) of the branched diphenyl phosphoate-phenol resin (I) was obtained.

2.3.2 Synthesis of linear difunctional phosphate-phenol resin

A mixture of 29.25g(0.15mol) phenyl phosphoric dichloride, 22.0g(0.20mol) hydroquinone and 0.143g(0.0015mol) magnesium chloride as catalyst was added to a 300 mL three-necked round bottom flask equipped with a magnetic stirrer, a reflux condenser, a nitrogen inlet, thermometer and sodium hydroxide absorber to collect the hydrogen chloride gas which evolve from the reaction mixture. The reaction mixture was slowly heated under nitrogen atmosphere using oil bath heater at 105 °C for about 2 h. After an additional heating, there was no hydrogen chloride due to the diphenyl phosphoric chloride which could be detected by absorber. After cooling the reaction mixture, the crude was dissolved into 150mL propylene glycol mono methyl ether acetate (PGMAC), and washed by 100mL 5% ammonium chloride solution and 100mL distilled water three times. After washing, PGMAC was removed under vacuum at 170°C. 13.3g (34.9% yield) of linear difunctional phosphate-phenol resin (II) was obtained.

2.3.3 Synthesis of bis (4,4'-diphenylphosphonoaminophenyl) methane

A mixture of 59.5g (0.30mol) 4,4'-Methylenedianiline, 91.07g(0.90mol) triethylamine, 500mL tetrahydrofuran were added into a 1000 mL three-necked round bottom flask equipped with a magnetic stirrer, a reflux condenser, a nitrogen inlet and thermometer. The reaction mixture was stirred at room temperature until the resin completely dissolves. After that, the mixture kept to 0°C and 177.30g(0.66mol) diphenyl phosphoric chloride was added dropwise to the mixture in the flask for 1h at 0°C. The reaction mixture was warmed

to 30°C for 0.5 h and heated to reflux for 2h. After an additional heating, there was a peak due to the Bis(4,4'-Diphenylphosphonoaminophenyl)methane and which could be detected by gel permeation chromatograph. After reaction, the triethylamine hydrogen chloride salt was removed by filtration, and the tetrahydrofuran was removed under vacuum at 70°C. The reaction crude was dissolved into 200 mL ethyl acetate, and washed by 150mL 5% ammonium chloride solution and 150mL distilled water twice. After washing, the ethyl acetate was removed under vacuum at 100°C. Upon recrystallization from 200mL ethanol, 101.5g (51.1% yield) of Bis(4,4'-diphenylphosphonoaminophenyl) methane (III) was obtained.

<sup>1</sup>H-NMR (DMSO-d<sub>6</sub>): d =3.8 (C-CH<sub>2</sub>-C), 7.0 (P-NH-C), and 6.9-7.3 ppm (aromatic protons).

2.3.4 Synthesis of bis (4,4'-Diphenylphosphonoaminophenyl)ether

The method of synthesis was similar to that described in 2.3.3. 60.0g (0.30mol) 4,4'-diaminodiphenylether, 91.07g(0.90mol)triethylamine, 500mL tetrahydrofuran, 177.30g (0.66mol) diphenylphosphoric chloride were used. Upon recrystallization from 200mL ethanol, 143.5g (72.0%yield) of Bis(4,4'-diphenylphosphonoaminophenyl) methane(IV) was obtained. <sup>1</sup>H-NMR(DMSO-d<sub>6</sub>):d=6.8-7.4(aromatic protons) and 8.7ppm(P-NH-C).

2.3.5 Synthesis of diphenylphosphonoaminobenzene

The method of synthesis was similar to that described in 2.3.3. 27.92g(0.30mol) aniline, 91.07g(0.45mol) triethylamine, 500mL tetrahydrofuran, 88.65g (0.33mol) diphenyl phosphoric chloride were used. After recrystallization from 200mL ethanol, 58.5g (60.1%yield) of diphenylphosphonoaminobenzene(V) was obtained. <sup>1</sup>H-NMR(DMSO-d<sub>6</sub>):d= 6.8-7.4(aromatic protons) and 8.8ppm (P-NH-C).

Table I  
Structure of Reactive Flame Retardant

Compound	notation
	(I)
	(II)
	(III)
	(IV)
	(V)

### 3. RESULTS AND DISCUSSION

#### 3.1 Reactivity of phosphoric amide derivatives with epoxy resin

Having prepared some phosphoric amide derivatives, it was desirable to obtain some information about their relative reactivity. Usually, the active hydrogen in the phosphoric amide derivatives cannot react with epoxy resin in the presence of catalyst such as phenols, Lewis acids and phosphine. But, it was found that the active hydrogen could react with epoxy resin when the mixture of epoxy resin and phosphoric amide derivatives were heated over 170°C in the presence of imidazole derivatives such as 2-ethyl-4-methylimidazole (2E4MZ). If the reaction temperature is under 170°C, it was not able to react with each other<sup>3)</sup>.

As typical reaction, compound (III) were allowed to react with 2,2-bis(4-glycidyoxyphenyl)propane for 1h at 170°C in the presence of 2E4MZ. Figure 2 shows GPC chart about reaction with (III) and epoxy resin. As the reaction proceeds, the peak due to (III) was gradually decreased, whereas this molecular weight was increased. The NMR spectrum of this reaction is shown in Figure 3. At the end of this reaction, the NMR shows the absence of the peak at 6.3ppm due to N-H proton. Those results reveal that the active hydrogen in the phosphoric amide can react with epoxy resin by use of imidazole catalyst such as 2E4MZ.

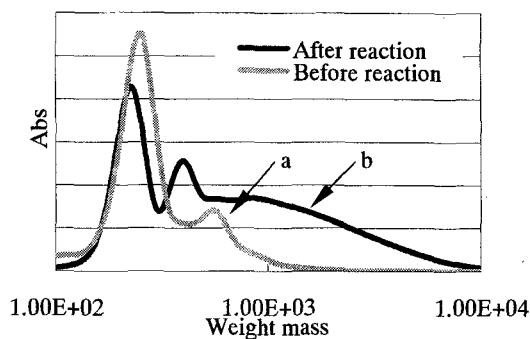


Fig. 2. GPC chart of the polymer mixture before and after reaction with epoxy resin and compound (III); a) compound (III), b) resulting high polymer.

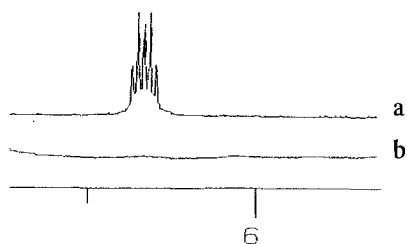


Fig. 3. NMR spectra of N-H proton derived from phosphoric amide; (a) before reaction, (b) after reaction.

#### 3.2 Thermal decomposition characteristic of aluminum hydroxide.

To examine the effect of the difference of particle diameters, the insulating resin including aluminum

hydroxide of average particle diameter of  $D_{50}=1.0, 7.0$  and  $14.0\mu\text{m}$  were produced under different condition at the time of beads-mill dispersion. Figure 4 and Table II indicate the result of measurement with the differential scanning calorimeter (DSC).

As shown in Table II, with the cured resin using aluminum hydroxide of  $14.0\mu\text{m}$  that underwent the secondary coagulation, the peak of crystal water thermolysis was 307°C. As the particle diameter of aluminum hydroxide became smaller, the temperature gradually decreased, and with the particle of diameter of  $1.0\mu\text{m}$ , the temperature decreased to 266.6°C. Furthermore, heat absorption also increased, and that of  $1.0\mu\text{m}$  item was 1.2 times higher than that of  $14.0\mu\text{m}$  item. We consider that because of the particle diameter, the higher the thermal conduction efficiency. Another reason is that the smaller the particle is, the easier the crystal water inside aluminum hydroxide can be discharged. It is suggested those phenomena will result in an excellent fire retardancy of build-up insulating resin.

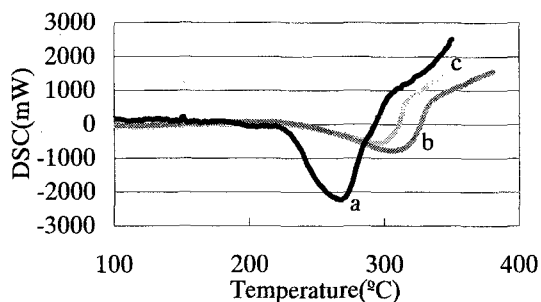


Fig. 4. Measurement results of thermolysis curve with the differential scanning calorimeter; The particle diameter of aluminum hydroxide are a)  $1.0\mu\text{m}$ , b)  $7.0\mu\text{m}$ , and c)  $14.0\mu\text{m}$ .

Table II

Results of thermal decomposition peak and endotherm.

Particle diameter ( $\mu\text{m}$ )	Decomposition peak ( $^{\circ}\text{C}$ )	Endotherm volume (mJ/mg)	Start point of decomposition ( $^{\circ}\text{C}$ )
1.0	266.6	201	222
7.0	300.5	168	229
14.0	307.9	176	226

#### 3.3 Preparation of build-up insulating resin film

Table III shows actual mixing or compounding weight to prepare build-up insulating resin. Typical examples of preparation of insulation resin are as follows.

2,2-bis(4-glycidyoxyphenyl)propane (DGEBA) was dissolved in PGMAC as solvent. After that aluminum hydroxide and silica gel were added to the epoxy resin solution. The mixture was stirred and dispersed by beads-mill machine until the average particle size became less than  $1.0\mu\text{m}$ . On the other hand, phenol resin, reactive flame retardants and catalyst were dissolved in methyl ethyl ketone (MEK) so that amide value and phenol value equal epoxy value. Then the mixture of epoxy resin was added to the phenol hardener solution with stirring. This prepared solution as varnish

was coated about 50 $\mu$ m in thickness, and it was heated in a clean oven for 1h at 180°C. After curing, it was obtained the build-up insulating resin film for several examinations. In case of carrying out flame retardancy test (UL94V test), the varnish was coated onto both sides of FR-4 (0.8mm in thickness) substrate without copper, and it was cured.

Table III  
Mixing or compounding weight of the materials for build up insulating resin.

Sample No.	1	2	3	4	5	6
DGEBA	100	100	100	100	100	100
PGMAC	100	50	50	50	50	50
Al(OH) <sub>3</sub>	51	25	25	25	25	25
Silica gel	10	5	5	5	5	5
PR-53194		50	50	50	50	58
Compound (I)	250					
Compound (II)		20				
Compound (III)			20			
Compound (IV)				20		
Compound (V)					22	
FP-500						20
2E4MZ	3	3	3	3	3	3
MEK	100	50	50	50	50	50
P content (wt%)	1.6	1.6	1.6	1.6	1.6	1.6

### 3.4 Characteristic of build-up insulating resin by use of the reactive flame retardant

#### 3.4.1 Flame resistance test (UL94V test)

Flame resistance specified in UL94 is required for build-up insulating resin. Table IV shows results of UL94V flammability classification. Sample 3, 4 and 5 had good flame resistance. It is assumed that because of dehydrating and carbonating catalytic action of phosphoric acid, polyphosphoric acid, or polymetaphosphoric acid generated by heat adsorption due to crystal water discharge of aluminum hydroxide or by thermal decomposition of phosphide, sufficient oxide film was formed. In such cases, it is suggested that decomposition of aluminum hydroxide and dehydration or carbonation of phosphide function more effectively than the other samples. On the other hand, sample 1, 2 and 6 were not good in flame resistance test. In the case of sample 2, it is presumed that the phosphorus atom of compound (II) is integrated into main chain of this polymer. Therefore, the flame retardant is difficult to be decomposed by heat of combustion. And the amount of flame retardant in sample 1, 6 were insufficient to achieve UL94-V0.

Table IV  
Results of UL94V test of the insulating resin with halogen-free copper-clad laminate.

Sample No.	UL94 Flammability classification
1	V1
2	V1
3	V0
4	V0
5	V0
6	V1

### 3.4.2 Glass transition temperature

Figure 5 shows glass transition temperature of typical examples vs. amount of additional flame retardant in build-up insulating resin by measurement of DMS. The additional flame retardant such as FP-500 result in a lowering of glass transition temperature of insulating resin, because of the flame retardant act as a plasticizer<sup>4)</sup>. By use of monofunctional reactive flame retardant, compound (V), glass transition temperature was maintained constant. On the other hand, Compound (III) was integrated into the network of resin after curing, and glass transition temperature gradually rose with increasing the amount of addition of flame retardant. It was found that reactive flame retardants such as bifunctional phosphoric amide could prevent a lowering of glass transition temperature.

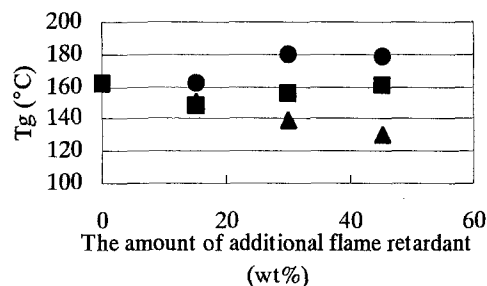


Fig. 5. Relationship between the amount of addition of flame retardant and glass transition temperature; (●) Compound (III), (■) Compound (V), (▲) FP-500.

## 4. CONCLUSION

It is revealed that the active hydrogen in the phosphoric amide can react with epoxy resin in use of imidazole catalyst at over 170°C by measuring GPC and NMR analysis. Heat absorption of 1.0 $\mu$ m of aluminum hydroxide is 1.2 times higher than that of 14.0 $\mu$ m, and by the combined use of the micro aluminum hydroxide and the reactive phosphoric amide flame retardant, fire retardancy obtained was in good result in UL94-V test. It was found that the bifunctional reactive flame retardants such as compound (III) could prevent a lowering of glass transition temperature compared to an additional flame retardant. From those evidences, it turned out that the reactive phosphoric amide flame retardants is very useful for halogen-free build-up insulating resin or the other substrate.

### Reference

- [1] I. Narusawa, Fracture toughness of plastics, H. Nishizawa, First edition, M. Takahashi, SIGUMASHUPPAN, 1993
- [2] H. Nishizawa, Flame resistance of polymers, third edition, H. Hideo, TAISEISHA, 1992
- [3] M. Shimbo, K. Ochi and T. Nakaya, *The Chemical Society of Japan*, 8, 1400-06 (1982)
- [4] M. Ochi, S. Ando, S. Inada, M. Shimbo, *Journal of Adhesion Society of Japan*. Vol.14, No.3, 86-94 (1978)