

Specification

TITLE OF THE INVENTION

Flame-retarded Thermosetting Resin Composition

BACKGROUND OF THE INVENTION

5 1. Field of the Invention

The present invention relates to a flame-retarded thermosetting resin composition. The flame-retarded thermosetting resin composition contains an aromatic phosphate.

2. Description of Related Art

10 Thermosetting resins typified by polyurethane and phenolic resin are widely used for electrical parts, electronic parts, automobile parts and the like since they can be obtained at relatively low costs and have remarkable characteristics such as good moldability. The resins, however,
15 are combustible and tend to cause uncontrollable combustion once they catch fire, and a lot of efforts have been made by the industry for their flame-retardation. Today in some fields using the resins, the flame-retardancy is legally required.

20 In order to give flame-retardancy to the thermosetting resin, a flame retardant is added at preparation of an article made of the resin. Examples of the flame retardants are inorganic compounds, organic phosphorus compounds, organic halides and organic halogen-containing phosphorus
25 compounds.

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Organic halides and organic halogen-containing phosphorus compounds exhibit excellent flame-retardancy, but generate hydrogen halide gas with heat decomposition.

5 The flame retardants which do not contain halogen(s) include inorganic compounds and organic phosphorus compounds.

10 The inorganic compounds typified by magnesium hydroxide and aluminum hydroxide have only a little flame-retardant effect and must be used in large quantity, which does damage to the intrinsic properties of the resin (e.g., workability and mechanical properties).

15 The organic phosphorus compounds typified by triphenyl phosphate (TPP), tricresyl phosphate (TCP) and cresyl diphenyl phosphate (CDP) have relatively good flame-retardant effect and are generally used. However, since they are volatile, the use thereof may impair the heat resistance and mechanical properties of the resin. Japanese Unexamined Patent Publication Nos. Hei1(1989)-242633 and Hei2(1990)-67310 disclose phenolic resins containing aromatic phosphates.

20 They are excellent in punchability at low temperatures, but the products made of them are found to be low in the electrical and mechanical qualities.

25 The thermosetting resin is widely used as an insulating substrate for electronic circuit in the form of a laminated sheet, and particularly is required to have good insulation quality and heat resistance. For example, when a laminated

sheet is made of phenolic resin, it exhibits a heat resistance for 15 to 40 seconds at soldering and an insulation resistance of 1×10^{10} to 1×10^{13} . However, when a sub-material is added for improving a property of the resin such as flame retardancy, the target property may be positively improved, while, at the same time, the principle qualities of the resin are often lowered, for example due to volatilization of the added sub-material.

Under these circumstances, there has been demand for a flame retardant for thermosetting resin which is low-volatile and does not impair the intrinsic properties of the resin.

SUMMARY OF THE INVENTION

Therefore, it is an object of the present invention to provide a flame-retarded thermosetting resin composition containing a flame retardant which is low-volatile and does not impair the intrinsic properties of the resin in order to eliminate the above-described drawbacks of the prior arts.

Specifically, the invention provides a flame-retarded thermosetting resin composition containing an aromatic phosphate with excellent flame-retardant effect which is so low-volatile that it does not lower the heat distortion temperature of the resin or does not impair the electrical resistance or mechanical properties of the resin.

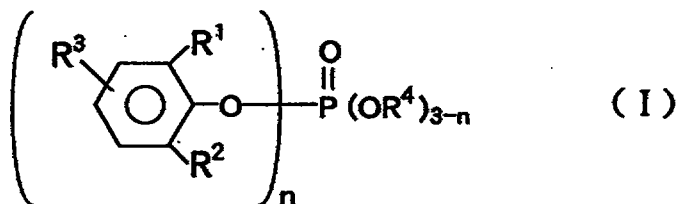
The inventors, having keen study in view of the above

problems, have found the following:

In addition to the excellent flame retardant effect, an aromatic phosphate represented by the formula (I) shows a significant improvement in preservation of the heat resistance, electrical resistance and mechanical properties of thermosetting resins when added as a flame retardant.

The above improvement of the properties is considered to be due to steric hindrance of the aromatic phosphate. That is, the aromatic phosphate of the formula (I) characteristically has substituents at 2- and 6-positions of the benzene ring. It is considered that the steric hindrance also results in improved resistance to hydrolysis over a long time.

The invention, therefore, provides a flame-retarded thermosetting resin composition containing (a) a thermosetting resin and (b) an aromatic phosphate represented by the formula (I):



, wherein R^1 and R^2 are, the same or different, a lower alkyl group, R^3 is a hydrogen atom or a lower alkyl group, R^4 is a C_{6-20} aromatic hydrocarbon residue and n is an integer 2 or 3.

In the flame-retarded thermosetting resin composition of the present invention, the thermosetting resin (a) is mixed with the aromatic phosphate (b).

Examples of the thermosetting resins (a) of the invention include an acrylic resin, polyurethane resin, phenolic resin, epoxy resin, melamine resin, urea resin, unsaturated polyester resin and diallyl phthalate resin. The above resins may be used as a mixture of two or more thereof.

The aromatic phosphate used as the component (b) is represented by the formula (I).

The lower alkyl group represented by R^1 , R^2 and R^3 in the formula (I) includes a C_{1-4} straight-chain or branched chain alkyl group such as methyl, ethyl, propyl, isopropyl, butyl and isobutyl groups. Examples of the C_{6-20} aromatic hydrocarbon residues represented by R^4 include a phenyl or naphthyl group optionally substituted by a C_{1-4} lower alkyl group (e.g., methyl or ethyl group), specifically phenyl, tolyl, xylyl, mesityl, cumenyl, naphthyl, methylnaphthyl, dimethylnaphthyl and ethylnaphthyl groups.

Preferred examples of the aromatic phosphates of the formula (I) include tris(2,6-dimethylphenyl)phosphate, tris(2,4,6-trimethylphenyl)phosphate, bis(2,6-dimethylphenyl)phenyl phosphate, bis(2,4,6-trimethylphenyl)phenyl phosphate, bis(2,6-dimethylphenyl)cresyl phosphate, bis(2,4,6-trimethylphenyl)cresyl phosphate, bis(2,6-dimethylphenyl)xylyl phosphate, bis(2,4,6-trimethylphenyl)xylyl

phosphate, bis(2,6-dimethylphenyl)naphtyl phosphate and bis(2,4,6-trimethylphenyl)naphtyl phosphate, among which tris(2,6-dimethylphenyl)phosphate, tris(2,4,6-dimethylphenyl)phosphate and bis(2,6-dimethylphenyl)cresyl phosphate are particularly preferred.

The aromatic phosphate as the component (b) can be produced by a per se known method. For example, it is produced by reacting an aromatic monohydroxy compound with phosphorus oxychloride, or by reacting an aromatic monohydroxy compound with phosphorus trichloride followed and then oxidizing the resultant.

In such a production, a compound represented by the formula (I) wherein $n=1$, e.g., diphenyl(2,6-dimethylphenyl)phosphate, may be produced as a by-product. Such a by-product does not have to be separated out when the amount thereof is small enough not to affect significantly the properties of the resin composition, and the produced aromatic phosphate can be directly used as the component (b). When the aromatic phosphate contains about 10% or more such a by-product, it adversely affects the resistance to hydrolysis and heat resistance of the resin composition.

The aromatic phosphate (b) is either crystalline solid or liquid, and both the crystalline solid and liquid aromatic phosphates can be used in the composition of the present invention. Additionally, the component (b), being an apt

flame retardant itself, substantially preserves the heat distortion temperature and properties of the component (a).

The resin composition of the present invention may contain, if necessary, various additives such as other flame retardants, fillers, lubricants and coloring agents.

In addition, the flame retardant as the component (b) can be used with a thermoplastic resin as well as the thermosetting resin (a).

The mixing ratio for the components in the flame-retarded thermosetting resin composition of the present invention may be suitably determined depending on the kind of the resin used and a desired flame retardancy. In general, 0.1 to 100 parts by weight, preferably 5 to 50 parts by weight, of the component (b) are used with 100 parts by weight of the component (a).

The resin composition of the present invention is prepared in a known method, i.e., by blending the thermosetting resin (a) with the aromatic phosphate (b) with a blender and mixing them with heating with a heated roller or Kneader, and is further formed into a flame-retarded form.

Also the resin composition of the present invention may be made into a varnish form with a solvent, and be applied to or impregnated into a base material to give flame retardancy thereto. Examples of the solvents are toluene, alcohol, methylethylketone, acetone, dimethylformamide and styrene. Examples of the base materials are paper, glass

cloth, glass nonwoven and synthetic cloth. The flame-retarded base material, in one layer or in two or more layers, can be heated and pressured to provide a laminated sheet.

5 The aromatic phosphate used as the component (b) of the invention is low-volatile, does not lower the heat distortion temperature of the flame-retarded thermosetting resin composition, shows a great improvement in preservation of the electrical resistance and mechanical properties of the resin and exhibits such an excellent flame retardant effect
10 that the conventional flame retardant of organic phosphorus base does not provide.

The present invention will be further described with reference to the following examples; however, these examples are intended to illustrate the invention and are not to be
15 construed to limit the scope thereof. In the examples, a part/parts means a part/parts by weight unless otherwise indicated.

Synthetic Example 1

2,6-Xylenol (366g, 3.0 moles) and anhydrous aluminum
20 chloride (6.1g) as a catalyst were fed in a four-neck flask provided with a stirrer, a dropping funnel, a thermometer and a condenser connected with a water scrubber, and were mixed with heating. When the temperature of the reaction solution was raised to 100°C, phosphorus oxychloride (153g,
25 1.0 mole) was added in about 2 hours, while generated hydro-

chloric acid gas was sent into the water scrubber. After the addition of phosphorus oxychloride, the reaction temperature was gradually raised to 230°C in four hours, then the reaction mixture was matured at the same temperature for 2 hours, and further matured under a reduced pressure of 300 torr for 8 hours, thereby the reaction being completed. The reaction mixture was washed with an acid and with hot water. Then an aromatic phosphate was precipitated. The precipitated crystals were separated by filtration, washed with methanol and dried under reduced pressure. White crystalline powder of tris(2,6-dimethylphenyl)phosphate was obtained in an amount of 308g (a 75% yield). The purity of the crystals was measured on gas chromatography and found to be 99.8% or more. The melting point was 137 to 138°C. This will be referred to as Compound 1.

Synthetic Example 2

The same reaction as described in Synthetic Example 1 was conducted except that 2,4,6-trimethylphenol (409g, 3.0 moles) was used instead of 2,6-xylenol (3.0 moles). Tris(2,4,6-trimethylphenyl)phosphate was obtained in an amount of 353g (a 78% yield). The purity of the crystals measured on gas chromatography was 99.8% or more. The melting point was 108 to 109°C. This will be referred to as Compound 2.

Synthetic Example 3

2,6-Xylenol (244g, 2.0 moles) and anhydrous magnesium

chloride (1.5g) as a catalyst were fed in a four-neck flask provided with a stirrer, a dropping funnel, a thermometer and a condenser connected with a water scrubber, and were mixed with heating. When the temperature of the reaction solution was raised to 120°C, phosphorus oxychloride (153g, 1.0 mole) was added in about 2 hours, while generated hydrochloric acid gas was sent into the water scrubber.

After the addition of phosphorus oxychloride, the reaction temperature was gradually raised to 180°C in 2 hours, thereby the reaction being completed.

After cooling, the reaction mixture was admixed with p-cresol (108g, 1.0 mole) and anhydrous magnesium chloride (1.5g), and heated. The temperature of the reaction mixture was gradually raised to 180°C in 2 hours for dehydrochlorination. Then the reaction mixture was matured at the same temperature for 2 hours and further matured under a reduced pressure of 200 torr for 2 hours, thereby the reaction being completed. Then the reaction mixture was washed with an acid and with hot water. With distillation, white solid of bis(2,6-dimethylphenyl)p-cresyl phosphate was obtained in an amount of 376g (a 95% yield). The purity of the solid measured on gas chromatography was 98.5% or more. The melting point was 70 to 71°C. This will hereafter be referred to as Compound 3.

Synthetic Example 4

The same reaction as described in Synthetic Example 3 was conducted except that xylenol (122g, 1.0 mole) was used instead of cresol (1.0 mole). Yellow liquid of bis (2,6-
5 dimethylphenyl)xylyl phosphate was obtained in an amount of 390g (a 95% yield). The purity of the liquid measured on gas chromatography was 98.0% or more. This will be referred to as Compound 4.

Examples 1 to 4

10 Each of the compounds from 1 to 4 of Synthetic Examples from 1 to 4 (250g) was subjected to a Pressure Cooker Test under a saturated vapor pressure of 2 atm at 120°C/100%RH for 96 hours, then the acid value and resistance to hydroly-
sis thereof were determined.

15 The results are shown in Table 1.

Table 1

	Examples				Comparative Examples		
	1	2	3	4	1	2	3
	Compound 1	Compound 2	Compound 3	Compound 4	Compound 5 (TFP)	Compound 6 (TCP)	Compound 7 (TXP)
Initial Acid Value	0.03	0.03	0.03	0.03	0.03	0.03	0.03
Acid Value after Pressure Cooker Test	5.30	6.50	16.1	7.80	180.2	125.0	69.6

Comparative Examples 1 to 3

The same determination as described in Examples 1 was conducted on the following compounds from 5 to 7 instead of the compounds of Synthetic Examples from 1 to 4:

5 Compound 5 : Triphenyl phosphate (manufactured by Daihachi Chemical Industry Co., Ltd., Japan; trade name TPP)

 Compound 6 : Tricresyl phosphate (manufactured by Daihachi Chemical Industry Co., Ltd.; trade name TCP)

10 Compound 7 : Trixylyl phosphate (manufactured by Daihachi Chemical Industry Co., Ltd.; trade name TXP)

The results are shown in Table 1.

Table 1 clearly shows that the aromatic phosphates of the present invention are better in resistance to hydrolysis.

15 Examples 5 to 8

 To component (a): 100 parts of commercially available phenolic resin vanish with a solid content of 60%, component (b): 15 parts of one of the above synthetic compounds from 1 to 4 was added and mixed, which was then impregnated into a sheet of linter paper and dried to provide a resin-impregnated sheet with a resin content of 45%. The sheets were laminated in 9 layers, and were pressured at 150°C under 90g/cm² for 50 minutes to give a laminated sheet of 2mm in thickness. By repeating the above procedure on the other synthetic compounds, 4 laminated sheets were obtained.

 The obtained laminated sheets were tested according to

the following methods: The flame retardancy was tested on the UL (Underwriters Laboratories) -94 standard and classified into 4 categories, V-0, V-1, V-2 and HB; The heat resistance at soldering was tested on JIS (Japanese Industrial Standards) C-6481 and shown as a time period (seconds) till the beginning of bulging or peeling at 260°C; The punchability was tested at 18.6kg/cm² on ASTM (American Society for Testing Materials) standard D-617; The insulating properties were tested on JIS C-6481; and the tracking resistance was tested on the electrolyte dropping method.

The results were shown in Table 2.

Table 2

	Examples					Comparative Examples				
	5	6	7	8		4	5	6		
(a) component	100	100	100	100		100	100	100		
Phenolic resin										
(b) component	15	-	-	-		-	-	-		
Compound 1	-	15	-	-		-	-	-		
Compound 2	-	-	15	-		-	-	-		
Compound 3	-	-	-	15		-	-	-		
Compound 4	-	-	-	-		-	-	-		
Compound 5	-	-	-	-		15	-	-		
Compound 6	-	-	-	-		-	15	-		
Compound 7	-	-	-	-		-	-	15		
Flame Retardancy	V-0	V-0	V-0	V-0		V-1	V-1	V-0		
Insulating	10 ¹² -10 ¹³	10 ¹² -10 ¹³	10 ¹² -10 ¹³	10 ¹² -10 ¹³		10 ⁹ -10 ¹⁰	10 ⁹ -10 ¹⁰	10 ⁹ -10 ¹⁰		
Properties (Ω)	>600	>600	>600	>600		500	500	500		
Tracking										
Resistance (V)	68	73	57	62		15	23	55		
Heat Resistance	Good	Good	Good	Good		Bulging	Bulging	Good		
at soldering										
(sec)	0	0	0	0		X	X	X		
Punchability										
Bleeding										
Resistance*										

* Determined on oil bleedings perceived with the naked eye after 48 hours' preservation at 120°C.

Comparative Examples 4 to 6

Laminated sheets were obtained in the same way as described in Example 5 except that the compounds from 5 to 7 were used as compounds (b) instead of the compounds of Synthetic Examples form 1 to 4. The obtained sheets were tested as in Example 5.

The results are shown in Table 2.

From Table 2, it is clearly recognized that the flame-retarded thermosetting resin compositions containing the aromatic phosphates according to the invention outperform the thermosetting resin compositions containing the conventional flame retardants not only in the flame retardancy and punchability at low temperatures, but also in the resistance to bleeding of the flame retardants from the laminated sheets, particularly in the tracking resistance and insulating properties due to the good resistance to hydrolysis.

Examples 9 to 12

To component (a): 100 parts of commercially available epoxy resin vanish with a solid content of 50% and 3 parts of dicyandiamide, component (b): 15 parts of one of the compounds from 1 to 4 of Synthetic Examples from 1 to 4 was added and mixed. Then four laminated sheets were obtained in the same way as in Example 5.

The obtained laminated sheets were tested as described in Example 5.

The results are shown in Table 3.

Table 3

	Examples				Comparative Examples			
	9	10	11	12	7	8	9	
(a) component Epoxy resin Dicyandiamide	100 3	100 3	100 3	100 3	100 3	100 3	100 3	
(b) component Compound 1	15	-	-	-	-	-	-	
Compound 2	-	15	-	-	-	-	-	
Compound 3	-	-	15	-	-	-	-	
Compound 4	-	-	-	15	-	-	-	
Compound 5	-	-	-	-	15	-	-	
Compound 6	-	-	-	-	-	15	-	
Compound 7	-	-	-	-	-	-	15	
Flame Retardancy Insulating Properties (Ω) Tracking	V-0 10 ¹³ -10 ¹⁴	V-0 10 ¹³ -10 ¹⁴	V-0 10 ¹³ -10 ¹⁴	V-0 10 ¹³ -10 ¹⁴	V-0 10 ¹⁰ -10 ¹¹	V-0 10 ¹⁰ -10 ¹¹	V-0 10 ¹⁰ -10 ¹²	
Resistance (V) Heat Resistance at soldering (sec)	>600 110	>600 121	>600 87	>600 96	500 35	500 Bulging	500 63	
Punchability Bleeding Resistance*	Good O	Good O	Good O	Good O	Bulging X	Bulging X	Good X	

* Determined on oil bleedings perceived with the naked eye after 48 hours' preservation at 120°C.

Comparative Examples 7 to 9

Laminated sheets were obtained in the same way as described in Example 5 except that the compounds 5 to 7 were used instead of Compounds 1 to 4 of Synthetic Examples 1 to 4.

The obtained laminated sheets were tested as described in Example 5.

The results are shown in Table 3.

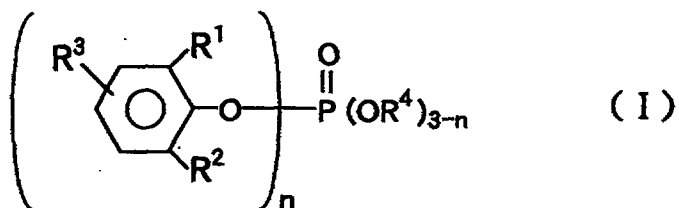
Table 3 shows that the flame-retarded thermosetting resin compositions containing the aromatic phosphates according to the present invention are more excellent than the thermosetting resin composition containing the conventional flame retardants not only in the punchability at low temperatures, but also in the resistance of bleeding of the flame retardants from the laminated sheets, particularly in the tracking resistance, heat resistance and insulating properties.

The flame-retarded thermosetting resin composition containing the aromatic phosphate of the present invention, compared with the thermosetting resin composition containing the conventional flame retardant, exhibits better punchability at low temperatures, better resistance to bleeding of the flame retardant from the laminated sheet, particularly showing remarkable improvement in the tracking resistance, heat resistance and insulating properties.



What is claimed is:

1. A flame-retarded thermosetting resin composition comprising (a) an thermosetting resin and (b) an aromatic phosphate represented by the formula (I):



5 , wherein R^1 and R^2 are, the same or different, a lower alkyl group, R^3 is a hydrogen atom or a lower alkyl group, R^4 is a $\text{C}_6\text{-20}$ aromatic hydrocarbon residue and n is an integer 2 or 3.

10 2. A composition according to claim 1 in which 0.1 to 100 parts by weight of the component (b) are mixed to 100 parts by weight of the component (a).

 3. A composition according to claim 1 in which 5 to 50 parts by weight of the component (b) are mixed to 100 parts by weight of the component (a).

15 4. A composition according to claim 1 in which R^1 and R^2 of the formula (I) are the same lower alkyl groups.

 5. A composition according to claim 1 in which the aromatic phosphate (I) is tris(2,6-dimethylphenyl)phosphate, tris(2,4,6-dimethylphenyl)phosphate or bis(2,6-dimethylphenyl)cresyl phosphate.

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6. A composition according to claim 1 in which the component (a) is any one selected from the group consisting of an acrylic resin, polyurethane resin, phenolic resin, epoxy resin, melamine resin, urea resin, unsaturated polyester resin and diallyl phthalate resin.

7. A composition according to claim 1 in which the component (a) is a phenolic resin.

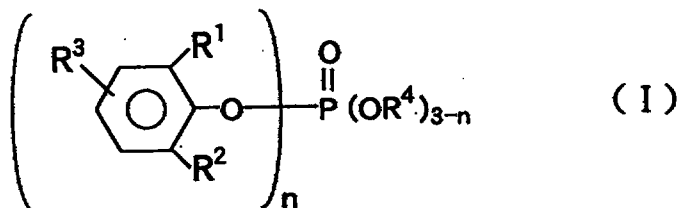
8. A composition according to claim 1 in which the component (a) is an epoxy resin.

9. A flame-retarded base material obtained by application or impregnation of a solution of any of the components of claims from 1 to 8 in an organic solvent.

ABSTRACT OF THE DISCLOSURE

Flame-retarded Thermosetting Resin Composition

A flame-retarded thermosetting resin composition comprising (a) a thermosetting resin and (b) an aromatic phosphate represented by the formula (I):



5 , wherein R¹ and R² are, the same or different, a lower alkyl group, R³ is a hydrogen atom or a lower alkyl group, R⁴ is a C₆₋₂₀ aromatic hydrocarbon residue and n is an integer 2 or 3. The composition, compared with resin compositions containing conventional flame retardants, has excellent punchability at low temperatures, resistance to bleed-
10 ing of the flame retardant from a laminated sheet, and particularly shows significant improvement in the tracking resistance, heat resistance and insulation properties.

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