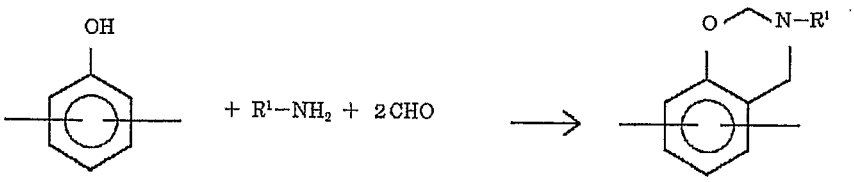
EPOXY RESIN COMPOSITION CONTAINING REACTIVE FLAME RETARDANT PHOSPHONATE OLIGOMER AND FILLER

The present invention relates to an epoxy resin composition that can be used, for example, in printed wiring boards for electronic applications and that represents a novel improvement, for example, over the type of compositions described in Japanese Patent Publication No. 2001/302,879 to Shin Kobe Electric Manufacturing Co. Ltd./Hitachi Chemical Co. Ltd.

The composition of the present invention contains, as one essential component, an epoxy resin. This component is present at from about 20% to about 50%, by weight of the total weight of the composition. Preferably, this component is a non-halogen containing epoxy resin, such as a bisphenol A-type of epoxy resin, or other resins of this general type that have utility for the manufacture of printed wiring boards or other electronic substrate materials of that type (bisphenol F epoxy, phenolic novolak epoxy, cresol novolak epoxy, and/or bisphenol A novolak epoxy resins). Compatible mixtures of any of these resins may be employed.

An additional optional, but preferred, component for the compositions of the present invention is a polybenzoxazine resin in an amount of up to about 50%, by weight of the total weight of the composition, preferably, from about 5% to about 20%, by weight. This composition is a thermosetting resin that contains a dihydrobenzoxazine ring that is formed by the reaction depicted below:



This component and its process of manufacture is further described in U.S. Patent No. 5,945,222 (at Col. 2, line 59 to Col. 3, line 62), which is incorporated herein by reference.

The next additional optional component of the composition of the present invention is a co-curing agent for the aforementioned resin component(s). Mixtures of compatible co-curing agents can be used. This co-curing agent will be present at from about 0% to about 20%, by weight of the total weight of the composition, preferably from about 5% to about 15%, by weight. Representative co-curing agents include, phenol-formaldehyde, cresol-formaldehyde, novolac, novolac/melamine, phosphorylated novolac, triazine-modified novolac resins, dicyandiamide, and the like.

The compositions of the present invention also contain one or more inorganic filler material(s) at from about 10% to about 50%, by weight. The filler material or materials can be selected from such known fillers as: talc, silica, alumina, aluminum hydroxide, magnesium hydroxide, zinc borate, and the like. A preferred material for use herein is alumina trihydrate.

While PCT Published Patent Application No. WO 03/029258 teaches that epoxy resins can contain a hydroxy-terminated oligomeric phosphonate as a flame retardant, that PCT application generally shows that the level of such phosphonate needs to be in the neighborhood of from about 20% to about 30%, by weight of the epoxy resin, or higher for acceptable results. No use of filler in such compositions is mentioned. In accordance with the present invention, the additional presence of filler has allowed for the use of lower amounts of the phosphonate additive. In Table I, which is given below, Example 7 illustrates that only 10% of the phosphonate was needed. The use of the filler allows for the production of a

sufficiently flame retarded epoxy composition, despite the use of lower amounts of phosphonate flame retardant, while still producing a product having good physical properties (such as, higher T_g, better hydrolytic stability, etc).

Each of the foregoing components of the present composition are individually known to persons of ordinary skill in the art as potential components for epoxy compositions of the present type, and they have been employed in various combinations heretofore, as exemplified by the aforementioned Japanese Patent Publication No. 2001/302,879.

The reactive phosphonate curing agent that forms a novel and essential additive herein, as compared to prior art approaches that relied upon varying combinations of the previously described components, is present at from about 3% to about 40%, by weight of the total weight of the composition, preferably from about 5% to about 20%, by weight. This flame retardant curing agent, as more fully described in PCT International Patent Publication No. WO 03/029258, is an oligomeric phosphonate comprising the repeating unit -OP(O)(R)-O-Arylene- and has a phosphorus content of greater than about 12%, by weight. The phosphonate species in the composition comprise those containing -OH end groups as well, possibly, of those not containing -OH end groups. The preferred R group is methyl, but can be any lower alkyl group.

By "Arylene" is meant any radical of a dihydric phenol. The dihydric phenol preferably should have its two hydroxy groups in non-adjacent positions. Examples include the resorcinols; hydroquinones; and bisphenols, such as bisphenol A, bisphenol F, and 4,4'-biphenol, phenolphthalein, 4,4'-thiodiphenol, or 4,4'-sulfonyldiphenol. The Arylene group can be 1,3-phenylene, 1,4-phenylene, or a bisphenol diradical unit, but it is preferably 1,3-phenylene.

This component for the epoxy resin composition of this invention can be made as described in PCT Patent Application 03/029258 by any of several routes: (1) the reaction of an $RPOCl_2$ with HO-Aryl-OH or a salt thereof, where R is lower alkyl, preferably methyl; (2) the reaction of diphenyl alkylphosphonate, preferably methylphosphonate, with HO-Arylene-OH under transesterification conditions; (3) the reaction of an oligomeric phosphite with repeating units of the structure -OP(OR')-O-Arylene- with an Arbuzov rearrangement catalyst, where R' is lower alkyl, preferably methyl; or (4) the reaction of an oligomeric phosphite with the repeating units having the structure -OP(O-Ph)-O-Arylene with trimethyl phosphite and an Arbuzov catalyst or with dimethyl methylphosphonate with, optionally, an Arbuzov catalyst-. The -OH end groups, if attached to Arylene can be produced by having a controlled molar excess of the HO-Arylene-OH in the reaction media. The -OH end groups, if acid type (P-OH), can be formed by hydrolytic reactions. It is preferred that the end groups of the oligomers be mainly -Arylene-OH types.

The epoxy resin composition of the present invention can contain optional additives as well including the following types of materials: fiber and/or cloth reinforcing additives; release agents; colorants; and the like.

Examples

Materials

Epoxy - bisphenol A type epoxy resin

Novolac - phenol-formaldehyde resin (novolac type) (auxiliary curing agent)

Melamine-novolac - copolymer of phenol, melamine and formaldehyde (auxiliary curing agent)

Phosphor-novolac - phosphorylated phenol-formaldehyde resin (auxiliary curing agent)

ATH - aluminum trihydrate

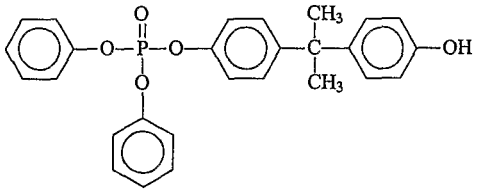
Phosphonate - reactive phosphonate curing agent where "arylene" is resorcinol

DICY - dicyandiamide (auxiliary curing agent)

AMI-2 - 2-methylimidazole (catalyst)

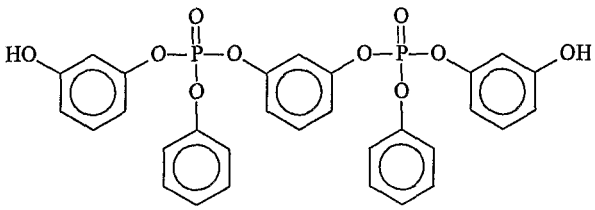
BDP - bisphenol A bis(diphenyl phosphate) Akzo Nobel brand FYROLFLEX BDP

BDP(OH) - Bisphenol A diphenylphosphate



made as described in U.S. Patent No. 3,090,799.

$RDP(OH)_2$ resorcinol bis(phenylresolcinyl phosphate)



made as described in U.S. Patent No. 5,508,462.

Experimental

T_g - glass transition temperature measured in TMA experiments as described in IPC-TM-650 protocol.

UL 94 - flammability rating according to UL 94 vertical protocol (V-0, V-1, V-2)

PCT - time of exposure to steam in Pressure Cooker Test according to IPC-TM-650 protocol. Water absorption was measured after removal of the specimen from the autoclave.

Delamination - measured in TMA experiments at 260 or 288°C as described in IPC-TM-650 protocol

CTE - coefficient of thermal expansion measured in TMA experiments at the temperatures below and above glass transition ($<T_g$ and $>T_g$ respectively). IPC-TM-650 protocol was followed.

Tables I and II that are reproduced below sets forth a number of formulations that represent embodiments of the present invention. Table III shows set of comparative formulations.

Table I

Example	1	2	3	4	5	6	7	8
Component								
Epoxy, wt. %	45	45	40	40	40	40	40	40
Novolac, wt. %	10	10	5	5				
ATH, wt. %	25	25	35	35	35	30	50	50
Phosphonate, wt. %	20	20	20	20	25	30	10	9
DICY								1
AMI-2, wt. %	0.25	0.5	0.25		0.25	0.1	0.25	0.25
Physical property								
T_g, °C	130	130	110	120	140	110	120	130
UL-94, rating	Fail	Fail	V-1	V-0	Fail	Fail	V-0	V-0
PCT, time (min)/pass (fail)	60/F	60/F	30/F	60/F	60/F	60/P	30/P	30/F
water absorption, %	0.4	0.4	0.3	0.3	0.1		0.2	0.3
Delamination at 260°C, min			>60					
288°C, min			>60	>60	>60	>60	>60	
CTE, < T_g, 10^6 mm			50	40	40		30	40
> T_g, 10^6 mm			250	250	200		160	195

Table II

Example	9	10	11	12	13	14	15	16
Component								
Epoxy, wt. %	30	20	20	20	40	35	20	20
Novolac, wt. %	10	10	5	5				
Melamine-novolac, wt. %					15	10	10	5
PBZ, wt. %	15	15	15	15			15	15
ATH, wt. %	25	35	50	50	25	35	35	50
Phosphonate, wt. %	20	20	10	10	20	20	20	10
AMI-2, wt. %	0.25	0.25	0.25		0.25	0.25	0.25	0.25
Physical property								
T_g, °C		140	150	190	130	120	160	
UL-94, rating	Fail	V-1	V-0	V-0	Fail	V-1	V-1	V-0
PCT, time (min)/pass (fail)	60/P	90/P	90/P	90/F	120/P	120/P	90/P	90/F
water absorption, %	0.8	1.2	0.3	0.5	1.0	0.9	1.2	0.2
Delamination at 260°C, min					5	5		
288°C, min		>60		>60			>60	
CTE, < T_g, 10^6 mm		30	30	30	40	35	40	
> T_g, 10^6 mm		160	130	160	160	200	165	

Table III (comparative)

Example	17	18	19	20	21
Component					
Epoxy, wt. %	40	35	35	35	35
Phosphor-novolac, wt. %	15	10			
Melamine-novolac, wt. %			10	10	10
BDP, wt. %			20		
BDP(OH), wt. %				20	
$RDP(OH)_2$, wt. %					20
Phosphonate, wt. %	20	20			
ATH, wt. %	25	35	35	35	35
AMI-2, wt. %	0.25	0.25	0.25	0.25	0.25
Physical property					
T_g, °C		100	115	120	120
UL-94, rating	Fail	V-1	Fail	Fail	Fail
PCT, time (min)/pass (fail)	60/F	60/F	30/F	60/F	120/P
water absorption, %	0.4	0.4	0.2	0.3	0.6
Delamination at 260°C, min		>60			
288°C, min		20	>60	>60	>60
CTE, $< T_g$, 10^6 mm		50	50	65	60
$> T_g$, 10^6 mm		230	240	210	200

We Claim:

1. An epoxy resin composition comprising an epoxy resin; a reactive phosphonate curing agent; an inorganic filler; an optional polybenzoxazine resin; and an optional co-curing agent.

2. A composition as claim in Claim 1 wherein the epoxy resin comprises from about 10% to about 50%, by weight of the total weight of the composition.

3. A composition as claim in Claim 1 wherein reactive phosphonate curing agent comprises from about 5% to about 30%, by weight, by weight of the total weight of the composition.

4. A composition as claim in Claim 1 wherein the polybenzoxazine resin comprises up to about 50%, by weight of the total weight of the composition.

5. A composition as claim in Claim 1 wherein co-curing agent comprises from about 5% to about 20%, by weight of the total weight of the composition.

6. A composition as claim in Claim 1 wherein the inorganic filler comprises from about 10% to about 50%, by weight, by weight of the total weight of the composition.

7. A composition as claim in Claim 1 wherein the epoxy resin comprises from about 10% to about 50%, by weight of the total weight of the composition, the reactive phosphonate curing agent comprises from about 5% to about 30%, by weight, by weight of the total weight of the composition, and the

inorganic filler comprises from about 10% to about 50%, by weight, by weight of the total weight of the composition. and the benzoxazine resin comprises up to about 50%, by weight of the total weight of the composition.

8. A composition as claim in Claim 7 further comprising a co-curing agent at from about 5% to about 20%, by weight of the total weight of the composition.

9. A composition as claim in any of Claims 1 to 6 and 8 wherein the co-curing agent is selected from the group consisting of novolac, melamine-novolac, and phosphor-novolac compositions.