

SEMICONDUCTOR DEVICES CONTAINING EPOXY MOULDING COMPOSITIONS AND THE COMPOSITIONS PER SE

FIELD OF THE INVENTION

The present invention relates to semiconductor devices sealed with resin composition (preferably an epoxy resin composition or epoxy molding compound (EMC)) which is an environmental friendly material ("green plastic") without (or at least a reduced amount of) bromine, antimony, boron, phosphorus and/or their compounds as flame retardant ingredients. Instead the flame retardancy is provided at least to a substantial extent by another existing component in the EMC. It also demonstrates excellent thermal conductivity and soldering stress resistance performance during surface mounting of said semiconductor devices.

RELATED ART STATEMENT

Electronic parts such as diodes, transistors, integrated circuits and the like have been sealed with an epoxy resin composition, modified by additives. In line with the semiconductor industry trend to use environmental friendly or "Green" materials, the thermosetting encapsulation resin used for sealing of semiconductor devices, would require usage of suitable types of the various environmental friendly ingredients without (or with a reduced amount of) bromine, antimony, boron, phosphorus and/or their compounds as flame retardant agent.

OBJECT AND SUMMARY OF THE INVENTION

The object of this invention is to provide an environmental friendly epoxy resin composition, which shows high thermal conductivity, and good solder cracking resistance or at least provides the public with a useful choice.

In accordance with a first aspect the invention provides a semiconductor device sealed with a resin composition preferably an epoxy resin which contains as a flame retardant a material comprising aluminum nitride, preferably aluminum nitride particles coated with silicon oxide, more preferably particles having a maximum size of 150 microns.

In a further aspect of the invention there is provided an epoxy resin composition used for sealing semiconductor devices comprising an epoxy resin, a resin curing agent, a filler material comprising as a flame retardant aluminum nitride, optionally together with silica oxide, and a curing accelerator preferably in which the amounts of aluminum nitride and silica in relation to the total resin content and the amount of aluminum nitride in relation to the total

filler content is selected so that the resin composition meets the Under-water Laboratory (USA) requirement for V-0 in the UL-94 flammability test.

As such, new and environmental friendly EMC uses inorganic aluminum nitride and/or silica fillers. These fillers double as flame retardants have been utilised in this invention. Inclusion of aluminum nitride can yield good flame retardant performance in EMC. In addition, the resulting aluminum nitride filled EMC possesses excellent heat dissipation ability compared to conventional silica filled EMC.

Epoxy resins and epoxy curing agents are superior in flammability (low flame- ability or good fire resistance) in comparison to other resins and curing agents due to higher concentration of aromatic hydrocarbon. Hence widening the “green” boundary of resulting EMC containing as inorganic fillers - aluminum nitride and/or silica.

The resulting EMC is an environmental friendly (green) compound with good flame retardant performance, high thermal conductivity, lower moisture absorption and higher soldering stress resistance.

In a further aspect of the invention there is provided an epoxy resin composition used for sealing semiconductor devices comprising a naphthalene tetra-functional type represented by formula II as herein described, a curing agent, a filler material comprising silica as a flame retardant optionally together with aluminium nitride, and a curing accelerator.

The present series of environmental friendly epoxy resin composition consists of some candidates with very high heat dissipation capability as well as soldering stress resistance at 260°C (for robust IC packages).

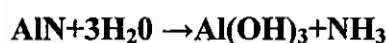
DETAILED DESCRIPTION OF THE INVENTION

In most cases polymer resins or other organic based materials in the EMC initiate or help propagate fire. These materials decompose to volatile combustible products and release flammable vapors when they are exposed to heat. Hence flame retardant agents are added into the EMC to fulfil the legal requirements. Conventional flame retardants for EMC include brominated epoxies, antimony, boron, phosphorus and/or their compounds.

The type and content of ceramic fillers, type of the organic resin as well as the curing agent, etc. determines the flame retardancy performance of an EMC. In order to obtain maximum flame retardancy of the present invention without adding any other flame retardant, aluminum nitride (thermal conductivity of about 30W/mK) is selected as the main filler instead of the conventional fused silica (thermal conductivity of about 1.3W/mK) for its newly discovered flame retardancy behavior. The absence of those hazardous conventional undesirable flame

retardant systems is a preferred feature of the invention as it renders it the most environmental friendly epoxy resin composition. The invention does allow the addition of small amounts of conventional flame retardants where necessary to produce acceptable flame retardancy at a lower level than when such flame retardants are used alone.

Aluminium nitride does hydrolyse in the presence of moisture to form aluminium hydroxide and ammonia. Methods can be developed to minimise the amount of moisture in the environment of the aluminium nitride. Alternatively it is desirable to control the rate of this reaction as discussed below. Suitable methods currently known are to coat the aluminium nitride with a protective coating such as silicon dioxide (silica) as described in Knudsen and Howard (Arne K. Knudsen and Kevin. E. Howard, "High performance Molded Packages using SCAN — Silica Coated Aluminum Nitride", The Dow Chemical Company internal publication 1998.). Despite the silica coating aluminum nitride (SCAN) (Howard, K. E., US Patent Number: 5,589,714, Dec 1996) will still react to some extent according to the Rxn 1:



Rxn 1

Enthalpy (heat of reaction) involved, $\Delta H = -260 \text{ kJ/mol}$

According to Knudsen and Howard (supra) the extent of hydrolysis of SCAN needs to be within stipulated limits according to the two tests as followed:

Boiling Water Test (20hrs, 100deg C)

NH₃ (ppm)

Standard AlN (without coating)

>100,000

Silica coated AlN (SCAN)

<150

Pressure Cooker Test (20hrs, 120deg C)

NH₃ (ppm)

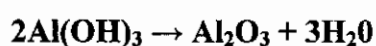
Standard AlN (without coating)

>80,000

Silica coated AlN (SCAN)

<2,500

Consequently the aluminum hydroxide generated, is an established flame retardant as it liberates water (to stop heat transfer) at elevated temperature according to Rxn 2. During a heating or burning process, metal hydroxides such as aluminum hydroxide undergo an endothermic reaction to shed its water content and revert to aluminum oxide. By so doing, it "draws" the heat (from burning) away from the organic resin network and help prevents a potential fire in the EMC.



Rxn 2

Enthalpy (heat of reaction) involved, $\Delta H = -298 \text{ kJ/mol}$

The combined effect of Rxn 1 and Rxn 2 enables the abovementioned coated AlN to act as a flame retardant in the present epoxy resin composition. (It is important to realize that the flame retardant effect is not the original design intent of silica coated aluminum nitride. Knudsen and Howard (as referred to above) solely taught its use for heat dissipation because of its high thermal conductivity). The control over the extent of hydrolysis described in Rxn 1 is important as excessive NH_3 can lead to circuit failure of the IC chips under high temperature and high humidity conditions. Some reliability tests can be used to indicate the stability of the coating: high temperature storage life test (HTSL) and pressure cooker test (PCT). The detailed test methods will be described with examples in subsequent sections.

By virtue of the above-mentioned mechanism, in the preferred form of the invention the present epoxy resin composition does not contain a conventional flame retardant agent such as brominated epoxy (hexa-bromo type) resin, antimony trioxide or pentaoxide. But within the broader aspects of the invention small amounts of these agents can be added. The outcome is a more environmentally friendly epoxy resin composition. Among the abovementioned advantages, this may render the expensive aluminum nitride filled epoxy resin composition recyclable and possess high thermal conductivity for certain niche IC packages that require good heat dissipation.

Flame retardant effects are measured by the UL-94 (Underwriter Laboratory - USA)'s V-0 flammability requirement adopted by the IC packaging industry. In the current invention the amounts of aluminium nitride and/or silica can be tested in order to meet that requirement.

Different types of epoxy resins and curing agents have different flammability characteristics because of variations in bulkiness, solidity of structure, aromatic and aliphatic carbon content. Hence "boundary" lines with minimum amount of AlN filler (as a percentage of the total filler content by weight — vertical axis) in the EMC with respect to total filler content by weight (as a percentage of the EMC) that is able to meet the V-0 flammability requirement can be plotted as shown in figure 1. The equation of the boundary line illustrated in figure 1 is drawn by joining the compositions (represented by points) that can meet the UL-94 V-0 requirement:

$$Y \geq -0.077X + 6.385$$

Eq. 1

Where,

Y = Ratio of aluminum nitride filler to total filler content (in % by weight)

From 0 to 1.0,

X = Total filler content - from 70% to 83% by weight,

100-X = corresponding resin content.

Higher filler content also increases resistance to flow of EMC. Hence there is the upper limit of how much can be added. This is plotted in Figure I between points C & D and is given in the following equation:

The mixture on the straight line CD are given by the following equation:

$$Y = -0.2X + 18.0$$

Where,

Y = Ratio of aluminium nitride filler to total filler content (in % by weight) is from 0 to 1.0,

X = Total filler content is from 90% to 95% by weight,

100-X = corresponding resin content,

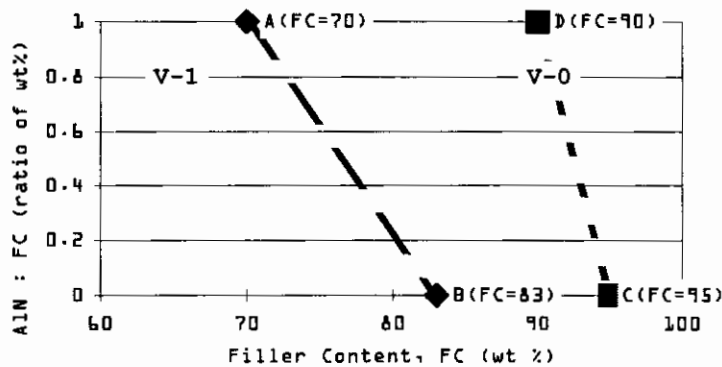


Figure 1: UL (V-0) flammability limits (1/8 inch thick test piece)
 Straight line AB (left of which will fail UL);
 Flowability Limits – straight line CD – Filler configurations right of line CD will not flow well

In accordance with the present invention, the epoxy resin composition consists of an epoxy resin represented either by formula (I) or formula (II) or combinations thereof, preferably formula (II) which is a naphthalene tetra-functional type epoxy resin, having a rigid naphthalene skeleton with high symmetry and high density aromatic rings providing high melting point and combustion temperature. This epoxy resin can provide one of the highest Tg levels among epoxy resins, excellent curability and relatively lower moisture absorption. These features are desirable in order to achieve good flammability; low warpage and good solder cracking resistance, all important requirements of the new generation IC packaging materials.

In accordance with the present invention, the epoxy resin composition also contains an epoxy curing agent represented either by formula (III) or formula (IV) or formula (V) or combinations thereof but preferably formula (V) that is a naphthalene tri-functional type resin curing agent which has a rigid naphthalene skeleton and the high density aromatic rings providing high melting point and combustion temperature. The weight fraction of hydrogen atoms is lower compared to both the phenolic resin curing agent represented by formula (III) and the paraxylene-modified phenolic resin curing agent (xyloc) represented by formula (IV). Hence structure (V) possesses relatively highest flame retardancy among these three resin curing agents and others.

With the above naphthalene type epoxy resin (II) and naphthalene type resin curing agent (V) composition, it allows lower filler loading of the epoxy resin composition to meet UL-94 V 0 requirement without additional flame retardant agent. The minimum filler content was found to be 70% (aluminum nitride alone) and 83% (silica alone) by weight based on the weight of the total epoxy resin composition containing aluminum nitride and silica as the only filler. This is calculated from equation I, (referring to example 1 — 3 as described hereafter) as depicted in figure 1.

The flame retardant performance of compositions of the invention is illustrated in Table 2 hereinafter.

When the total amount of filler is less than 70% by weight of aluminum nitride or 83% by weight of silica respectively as the only filler type in the EMC, the resulting compositions will have inadequate flame retardancy performance (Comparative Examples: CE1 and CE2). Also in the region to the left and below the line A-B where the ratio of aluminum nitride to total filler content by weight is lower than those points on line A-B, could not achieve UL-94 V-0 (CE3) without additional flame retardant agents.

The use of additional flame retardant agents such as brominated epoxyresin and antimony to achieve UL-94 V-0 requirement is given in (CE4). Different flame retardancy of different resins and resin curing agents used are illustrated by CE5 (biphenyl type epoxy resin), CE6 (Phenolic resin curing agent) and CE7 (Paraxylene-modified phenolic resin curing agent). These compositions also need additional flame retardant agents.

In Table 2 the terminology “comparative examples” illustrates compositions which do not meet UL-94 requirements for V-0 without additional flame retardants being added. These compositions fall within the scope of the current invention provided that at least some aluminium nitride is present.

When another epoxy resin is used in combination with the naphthalene tetra-functional type epoxy resin of formula (II), this other epoxy resin can be for example bisphenol type epoxy resins, cresol novolac type epoxy resins, phenol novolac type epoxy resins, tri- functional epoxy resins (e.g., triphenolmethane type epoxy resins, and alkyl modified triphenolmethane type epoxy resins) and tri-azine nucleus-containing epoxy resins.

The blending ratio of the total epoxy resin by weight to the total resin curing agents (I) and/or (II) by weight is generally in an amount of about 0.8 to about 1.3 epoxy equivalents per hydroxyl group equivalent of the total amount of resin curing (III) and/or (IV) and/or (V). It is typically observed that the physical properties such as humidity resistance tend to deteriorate outside of this range.

In the present invention, the filler particle size distribution should be between $D_{10}=1.5-2.0\mu m$, $D_{50}=10-20\mu m$, $D_{90}=70-80\mu m$ for pure silica, and $D_{10}=2-8\mu m$, $D_{50}=15-25\mu m$, $D_{90}=40-55\mu m$ for pure aluminum nitride, where D_{XX} refers to a diameter at XX% by weight based on the cumulative filler particle size distribution. Fine fillers (below D_{10}) serve as lubricating 'bearings' that promote flowability as well as minimizing air-vent flashes during transfer molding. Too much or too little of such filler can render these functions ineffective.

Higher sphericity of fillers and wider filler particle size distribution are necessary to maintain good flowability and processibility for EMC with higher filler content. Spherical fillers can also help to reduce abrasiveness and the flexural modulus of the resin composition.

The curing accelerator used in the present composition can be any material as long as it can accelerate the reaction between the epoxy group of the component (A) and the hydroxyl group of the component (B). Curing accelerators generally used in sealing materials are suitable, such as diazabicycloundecene (DBU), triphenylphosphine (TPP), benzyldimethylamine (BDMA), 2-methylimidazole (2-MZ) and the like. These compounds can be used alone or in combination of two or more.

The curing accelerator is preferably used in an amount of 0.1 to 1.0% by weight of the total epoxy resin composition. If the amount is less than 0.1% by weight, hardness of the resulting molded product decreases and mold release characteristics tend to deteriorate. In an amount more than 1.0% by weight, the reaction proceeds undesirably fast and fluidity tends to decrease.

The present epoxy resin composition used for sealing comprises, as essential components, an epoxy resin, a curing agent, an inorganic filler and a curing accelerator. The resin composition may further comprise, if necessary, various additives such as silane coupling agent, releasing

agent (e.g., natural wax or synthetic wax), stress-reducing additive (e.g., silicone oil or rubber), and the like.

In producing the present epoxy resin composition for sealing as a molding material, an epoxy resin, a curing agent, a curing accelerator, a filler and other additives are mixed sufficiently and uniformly using a mixer or the like; then, the mixture is melt kneaded using hot rolls, a kneader or the like; and the kneaded product is cooled and ground. The molding material thus obtained can be used for sealing, coating, insulation, etc. of electronic parts or electric parts

According to the present invention, there can be obtained an environmental friendly resin composition having high thermal conductivity, high flame retardancy, low thermal expansion and low moisture absorption, among others.

DESCRIPTION OF PREFERRED EMBODIMENTS

The present invention is hereinafter described specifically by way of Examples. In the Examples, the amount of each component used in compounding is parts by weight.

EXAMPLE 1

The following components of the following proportions are mixed at room temperature using a mixer a biaxial roll, cooled and ground to obtain a molding material. Naphthalene epoxy resin of formula (II), (softening point: 68°C, epoxy equivalent:

167g/eq)	13.6 parts by weight
Naphthalene epoxy resin curing agent of formula (V), (softening point: 87°C, hydroxyl group equivalent: 210 g/eq)	14.8 parts by weight
Silica coated Aluminum Nitride (SCAN) filler*	70.0 parts by weight
Fused silica filler	0.0 parts by weight
Triphenylphosphine (TPP)	0.2 part by weight
Silane coupling agent	0.6 part by weight
Carbon black	0.3 part by weight
Releasing agent	0.5 part by weight

* According to Knudsen and Howard [the extent of reaction of SCAN hydrolysis are controlled to be in stipulated limits according to the two tests as followed:

<u>Boiling Water Test (20hrs, 100deg C)</u>	<u>NH₃ (ppm)</u>
Standard AlN (without coating)	>100,000

Silica coated AlN (SCAN)	<150
<u>Pressure Cooker Test (20hrs, 120deg C)</u>	NH ₃
Standard AlN (without coating)	>80,000
Silica coated AlN (SCAN)	<2,500

AlN and coated AlN are compared. In the boiling water test, 25g of powder is suspended in 100ml of de ionized water for 20hours at 100deg C. In the pressure cooker test, 1g of powder is placed in 40ml of de ionized water for 20hours at 120deg C. the extent of hydrolysis is measured by analyzing the ammonia content of the water after the tests.

For epoxy resin composition flame retardant performance testing, UL-94, developed by Underwriters Laboratories, is one of the most widely used. It begins with pellet preparation, then mold into test piece with size at 125mm x 13mm x 3.2mm thickness. The molded test piece is then put into a chamber with temperature control at 23+/-2 °C and 50+/-5°C relative humidity for at least 48hrs. After pre-treatment test piece is ready for burning test, which follows ASTM D5207. In the test, the specimens are clamped vertically. A small ¾ in. high blue flame is applied to the bottom of the specimen for 10sec. It is then withdrawn, and reapplied for an additional 10 sec; the duration of flaming and glowing is noted as soon as the specimen has extinguished. A layer of cotton is placed beneath the specimen to determine whether dripping materials will ignite it during the test period. Five test pieces are needed for every sample. If the total flaming time of five test pieces is less than 50 seconds, the epoxy resin composition is considered to pass UL-94 test and is classified as V-0. On the other hand, if total flaming time is more than 50 seconds, the sample is considered to fail UL-94 test and is classified as V-1 and V-2.

The materials are classified V-2, the least stringent classification, or V-1 or V-0, which are the most stringent classification for the test. Table 1 below summarizes the requirements for each classification.

Performance testing, at the package level, begins with pellet preparation into various sizes. Depending on test purposes, it can be molded into 14x20mm Quad-Flat-Package (QFP) with 100 external leads on a Copper lead frame at a temperature of 175°C, 80- 120kgf/cm and 60-120sec. Subsequently the packages with chip in it (7.5x7.5mm, polyimide (PI) coated) are exposed to an atmosphere of 60°C/60% RH for 120hrs. Thereafter the packages are sent through a varying temperature profile according to the JEDEC standard with peak temperature 255°C in an infrared (IR) oven. Thereafter, cracks present at the surfaces of the devices are observed using a microscope. In addition, the packages are also scanned using CSAM (C-

mode Scanning Acoustic Microscope) for delaminated interfaces with focus on the chip top and the substrate-mold compound (iii) with these chips to obtain devices for solder cracking test.

The tablets are also made into 16p DIPs (16-pin Dual-Inline Packages) packages for HTSL test at 150°C, after which circuit resistance are examined for values exceeding 1.0 (value of electrical resistance after mold is typically $<0.8\Omega$. During prolong exposure to high temperature, free ions present within the encapsulant material, especially bromide and antimony can corrode the gold ball bond to form for example Kirkendall void which in turn leads to higher electrical resistance). The results are expressed by average life.

The 16p DIPs are also used in the PCT test. The packages are subjected to soaking conditions of 125°C and 100% relative humidity (RH) for extended period of time. The circuitries are tested at regular interval for open-circuit or closed-circuit failure caused by possible corrosion of the wire bonding pads within the circuitries.

For thermal conductivity measurement of the epoxy resin composition, it is first made into tablets and then into the cylindrical blocks with diameter 40mm by height 25 ± 5 mm at the temperature of 175°C, 150kgf/cm² and 300sec using a low pressure transfer molding machine.

Table 1 :Summary of UL 94 Vertical Burning Test for Classification Materials V-0, V-1, V-2

Criteria	Classification		
	V-2	V-1	V-0
Number of specimens	5	5	5
Number of Ignitions	2	2	2
Maximum flaming time per specimen per flame application (sec)	30	30	10
Total flaming time, five specimens, 2 ignitions (sec)	250	250	50
Flaming drips ignite cotton	Yes	No	No
Maximum afterflow time, per specimen (sec)	60	60	30
Burn to holding clamp	No	No	No

Examples 1-3

Epoxy resin compositions are compounded according to recipes of the invention shown in Table 2, and subjected to the same procedures as in Example 1 to obtain molding materials. Test results for these epoxy resin compositions were obtained in the same maimer as in Example 1. The results are shown in Table 2.

Comparative Examples 1-7

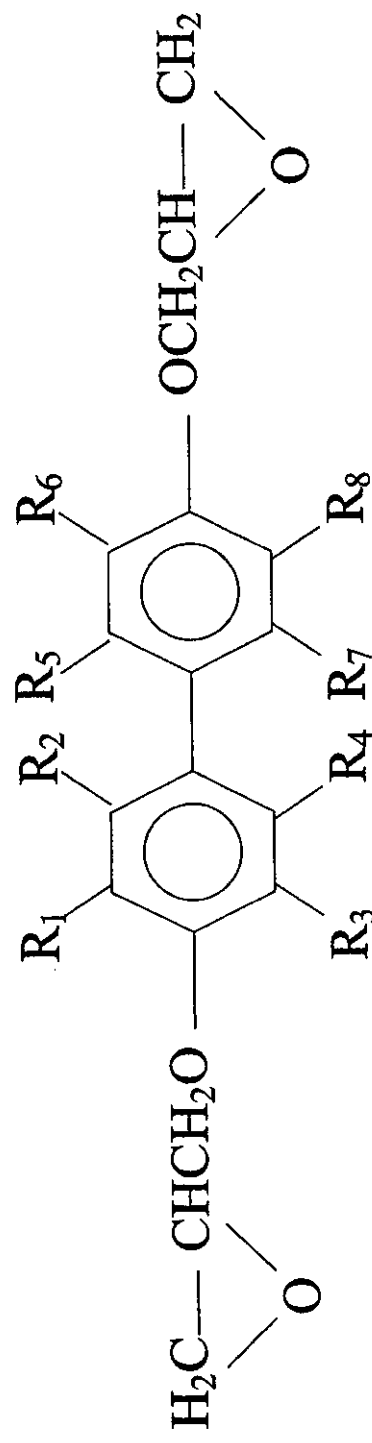
As discussed above additional epoxy resin compositions are compounded based on recipes outside the region defined above in Figure 1 and labeled comparative examples in Table 2. These epoxy resin compositions are subjected to the same procedures as in Example 1 to obtain molding materials. Test results for these molding materials were obtained in the same manner as in Example 1. The results are shown in Table 2.

Table 2: Comparison of examples on claimed boundaries w.r.t. comparative ones outside

	Examples			Comparative Examples						
COMPOSITIONS:	1	2	3	CE1	CE2	CE3	CE4	CE5	CE6	CE7
Aluminum nitride filler	70	0	18	68	0	16	68	70	70	70
Fused silica filler	0	83	62	0	80	64	0	0	0	0
Naphthalene epoxy resin (II)	13.6	6.6	9.1	14.2	8.8	8.8	13.6		16	14.2
Biphenyl epoxy resin (I)								13.6		
Naphthalene resin curing agent (V)	14.8	8.8	9.3	16.2	9.5	9.6	14.8	14.8		
Phenol Novolac resin curing agent (III)									12.4	
Paraxylene-modified phenolic resin curing agent (IV)										14.2
Triphenylphosphine (TPP)	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Silane coupling agent	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
Carbon black	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Releasing agent (waxes, etc)	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Antimony trioxide	0	0	0	0	0	0	0.6	0	0	0
Brominated epoxy resin	0	0	0	0	0	0	1.4	0	0	0
Aluminum nitride filler : FC*	1.00	0.00	0.23	1.00	0.00	0.20	1.00	1.00	1.00	1.00
PROPERTIES:										
Thermal conductivity (W/mK)	1.5	0.9	1.0	1.4	0.8	1.0	1.4	1.5	1.5	1.5
UL-94 / 3.2mm (V-0/V-1)	V-0	V-0	V-0	V-1	V-1	V-1	V-0	V-1	V-1	V-1
Soldering crack test (QFP-100L/PI/n=6)	0/6	0/6	0/6	0/6	0/6	0/6	1/6	0/6	0/6	0/6
Delamination check (QFP-100LPI/n=6)	0/6	0/6	0/6	1/6	0/6	0/6	1/6	0/6	0/6	0/6
HTSL at 150°C (hr to 1 st failure)	1000	1000	1000	100 0	100 0	100 0	100 0	100 0	100 0	100 0
PCT at 125°C/100%RH (hr to 1 st failure)	800	800	800	700	800	800	700	800	800	800

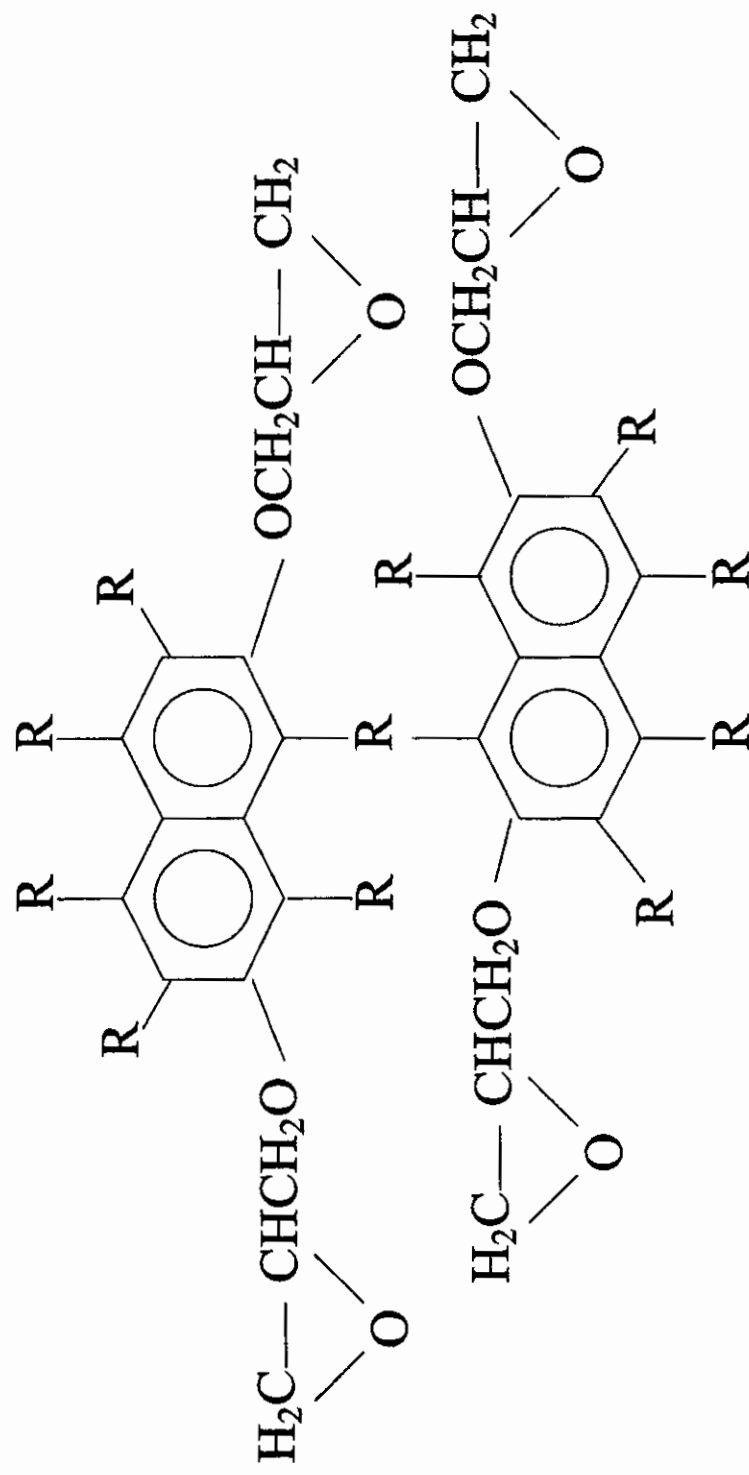
* : the ratio of Aluminum nitride filler in % by weight to total filler content (FC) in % by weight

Formula (I)



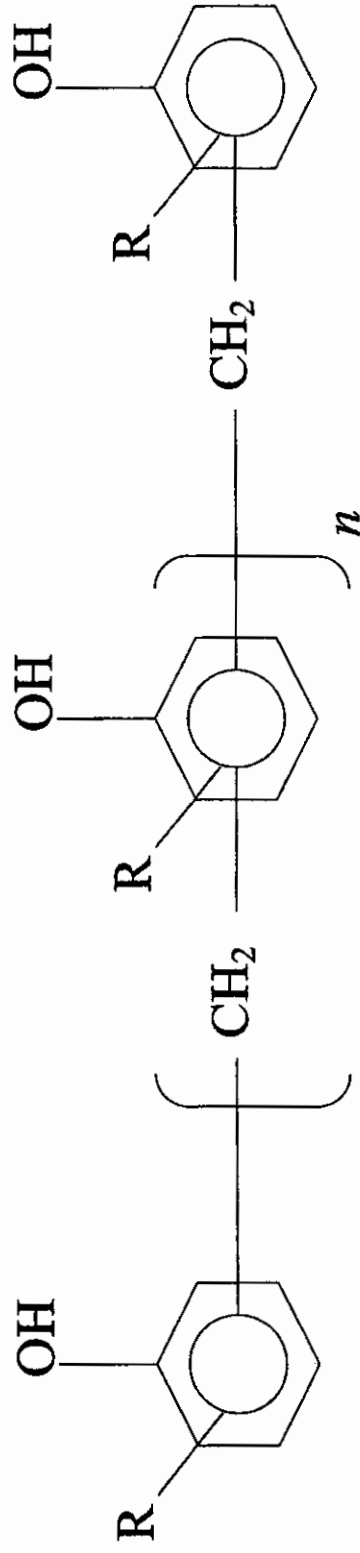
Wherein R_1 to R_8 is independently an atom or group selected from hydrogen atom, a halogen and an alkyl group

Formula (II)



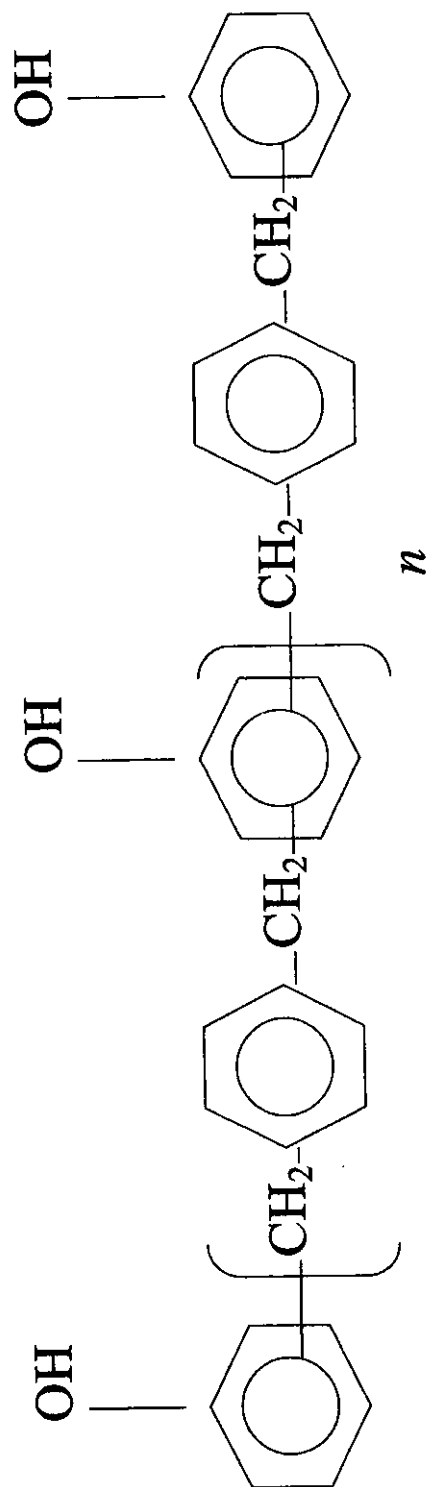
Wherein R is independently an atom or group selected from hydrogen atom, a halogen and an alkyl group

Formula (III)

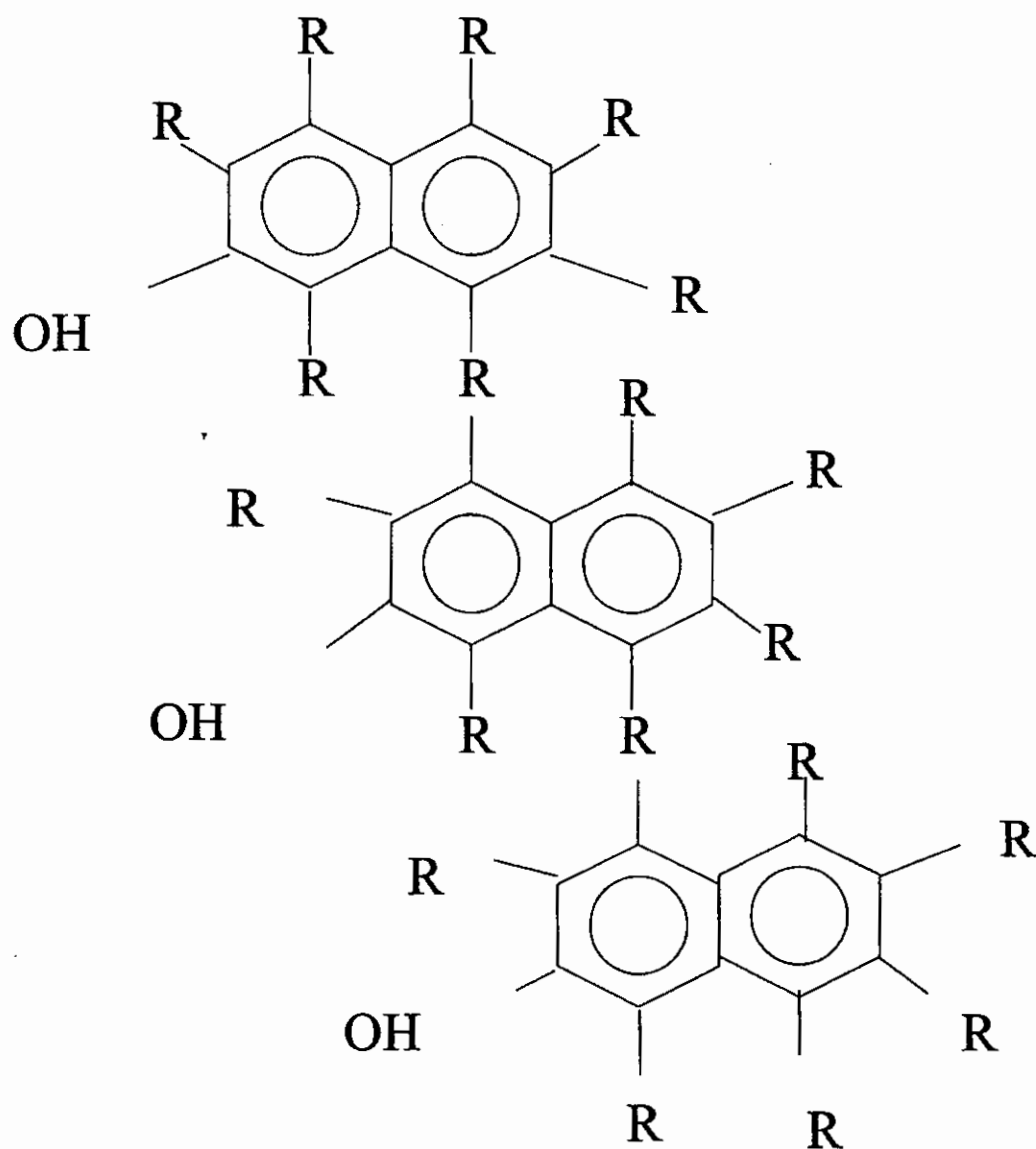


Wherein n is an integer of 0-5 and each R is independently an atom or group selected from hydrogen atom, a halogen and an alkyl group

Formula (IV)



Wherein n is an integer of 0-5 and
 $n=0$ (7%), $n=1$ (25%), $n=2$ (38%), $n=3$ (14%), $n=4$ (12%) and $n=5$ (4%)
 Result from GPC: Gel Permeation Chromatography

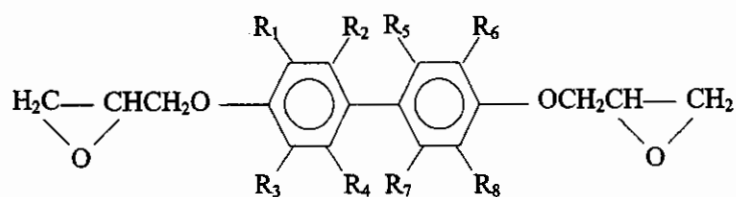


Wherein R is independently an atom or group selected from hydrogen atom, a halogen and an alkyl group

What we claim is:

1. The use of a flame retardant composition comprising aluminum nitride to impart flame retardancy to a semiconductor device sealed with a resin composition.
2. The use as claimed in claim 1 in which the flame retardant composition comprises aluminum nitride treated to inhibit hydrolysis.
3. The use as claimed in claim 1 or claim 2 in which the resin is an epoxy resin.
4. The use as claimed in claim 3 in which the epoxy resin is selected from the group consisting of naphthalene type resins, phenol novolac resins, cresol novolac resins, copolymers between dicyclopentadiene modified phenolic resins and phenol novolac resins and/or cresol novolac resins, biphenyl type epoxy resins, tri- or multi-functional type epoxy resins and/or paraxylene-modified phenolic resins.
5. The use as claimed in claim 3 in which the resin is a biphenyl (aralkyl modified) type represented by formula (I):

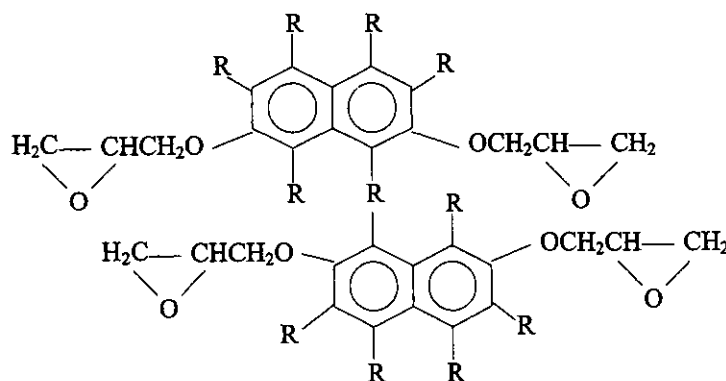
Formula (I)



wherein R₁ to R₈ is independently an atom or group selected from hydrogen atom, a halogen and an alkyl group;

or a naphthalene tetra-functional type represented by formula (II):

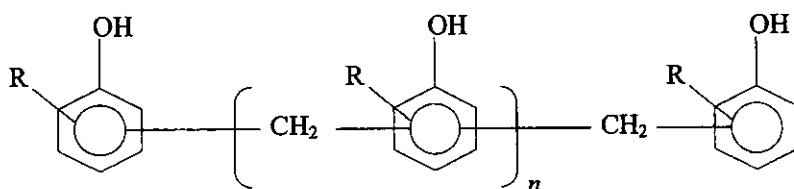
Formula (II)



wherein each R is independently an atom or group selected from hydrogen atom, a halogen and an alkyl group

6. The use as claimed in claim 5 in which the resin is the naphthalene tetra-functional type presented by formula (II).
7. The use as claimed in any one of the preceding claims in which an epoxy resin is used and as a curing agent a resin curing agent selected from the group consisting of naphthalene type resin curing agent, phenolic type resin curing agent and /or para-xylene modified (para-xylene glycol dimethyl ether) phenolic resin curing agent.
8. The use as claimed claim 7 wherein the curing agent is selected from a phenolic resin curing agent represented by formula (III);

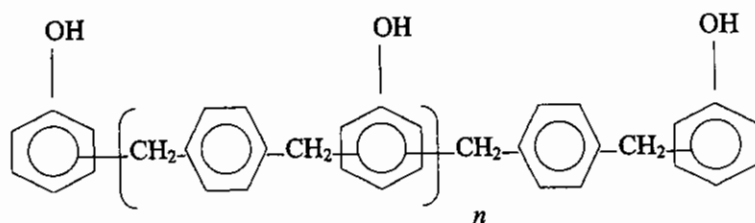
Formula (III)



wherein n is an integer of 0-5 and each R is independently an atom or group selected from hydrogen atom, a halogen and an alkyl group

a paraxylene-modified phenolic resin curing agent represented by formula (IV)

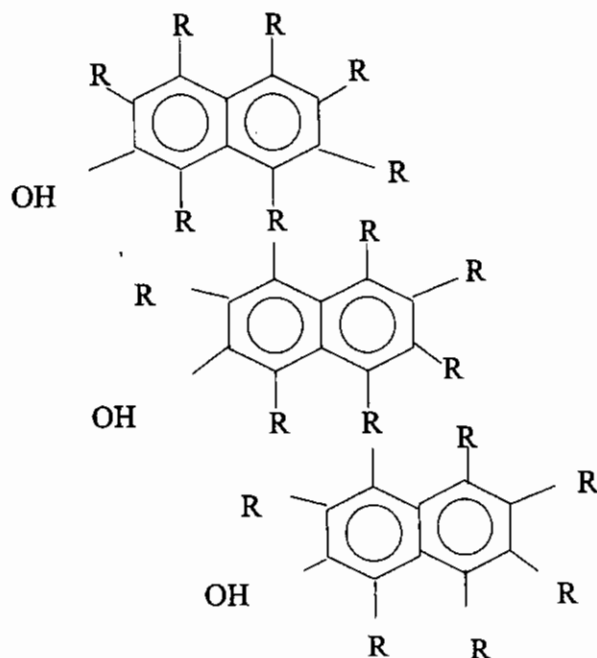
Formula (IV)



wherein n is an integer of 0-5

and a naphthalene resin curing agent represented by formula (V):

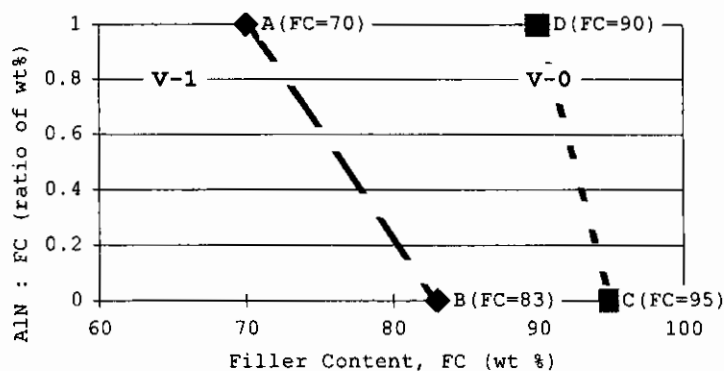
Formula (V)



wherein each R is independently an atom or group selected from hydrogen atom, a halogen and an alkyl group.

9. The use as claimed in claim 8 wherein the curing agent is a resin curing agent represented by formula V.
10. The use as claimed in any one of claims 3 to 9 wherein the epoxy resin is used in an amount of from 0.8 to 1.3 times the epoxy equivalents per hydroxyl group equivalent of said resin curing agent.

11. The use as claimed in any one of the preceding claims wherein the flame retardant composition comprises aluminum nitride together with fused silica, crystalline silica and/or aluminum oxide.
12. The use as claimed in any one of the preceding claims in which the flame retardant composition is particles of aluminum nitride together with silica having a maximum size not exceeding 150 microns.
13. The use as claimed in claim 12 wherein the filler particle size distribution lies between that of D10=1.5-2.0um, D50=10-20um, D90=70-80um for pure silica, and D10=2-8um, D50=15-25um, D90=40-55um for pure aluminum nitride, where DXX refers to diameter at XX% by weight based on the cumulative filler particle size distribution.
14. The use as claimed in any one of the preceding claims in which the semiconductor device contains as a sealing material a cured epoxy resin composition comprising an epoxy resin of the formula II, an epoxy resin curing agent of the formula V, a mixture of inorganic aluminum nitride filler and silica oxide fillers, curing accelerator, wherein the amount of fillers is between the following straight lines AB-BC-CD-DA drawn on a graph as shown in Figure 1:



15. The use as claimed in any one of the preceding claims wherein the aluminum nitride is coated with silica.
16. The use claimed in claim 15 in which the silica coated aluminum has the following limits of hydrolysis:

Boiling Water Test (20hrs, 100deg C).

NL (ppm)

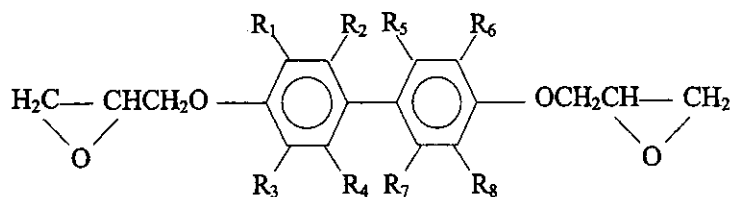
Standard AlN (without coating)

>100,000

Silica coated AlN (SCAN)	<150
<u>Pressure Cooker Test (20hrs, 120deg C)</u>	<u>N (ppm)</u>
Standard AlN (without coating)	>80,000
Silica coated AlN (SCAN)	<2,500

17. The use as claimed in any one of the preceding claims wherein a curing accelerator is present in an amount of from 0.05 to 1% by weight based on the total resin composition.
18. The use of a flame retardant composition comprising aluminium nitride as a filler to impart flame retardancy to an epoxy resin composition used for sealing semiconductor devices the epoxy resin composition further comprising an epoxy resin, a resin curing agent optionally together with silica oxide and a curing accelerator.
19. The use as claimed in claim 18 in which the amounts of aluminum nitride and silica in relation to the total resin content and the amount of aluminum nitride in relation to the total filler content is selected so that the resin composition meets the Under Water Laboratory (USA) requirement for V-0 in the UL-94 flammability test, optionally with the addition of one or more conventional flame retardants.
20. The use as claimed in claim 18 or 19 in which the aluminum nitride particles are coated with silica.
21. The use as claimed in claim 18, 19 or 20 in which the epoxy resin is selected from the group consisting of naphthalene type resins, phenol novolac resins, cresol novolac resins, copolymers between dicyclopentadiene modified phenolic resins and phenol novolac resins and/or cresol novolac resins, biphenyl type epoxy resins, tri- or multi-functional type epoxy resins and/or paraxylene-modified phenolic resins.
22. The use as claimed in any one of the preceding claims 18 to 21 in which the resin is a biphenyl (aralkyl modified) type represented by formula (I):

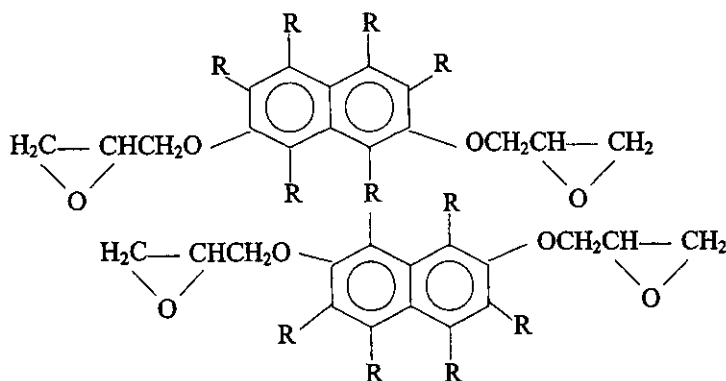
Formula (I)



wherein R_1 to R_8 is independently an atom or group selected from hydrogylhydrogen atom, a halogen and an alkyl group;

or a naphthalene tetra-functional type represented by formula (II):

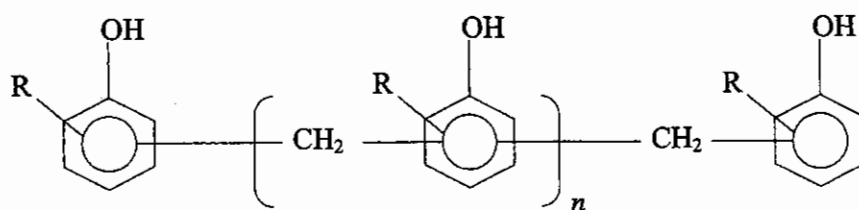
Formula (II)



wherein each R is independently an atom or group selected from hydrogen atom, a halogen and an alkyl group

23. The use as claimed in claim 22 in which the resin is the naphthalene tetra-functional type represented by formula (II).
24. The use as claimed in any one of the preceding claims 18 to 23 in which the curing agent is a resin curing agent selected from the group consisting of naphthalene type resin curing agent, phenolic type resin curing agent and /or para-xylene modified (para-xylene glycol dimethyl ether) phenolic resin curing agent.
25. The use as claimed in any one of the preceding claims 18 to 24 in which the curing agent is selected from a phenolic resin curing agent represented by formula (III):

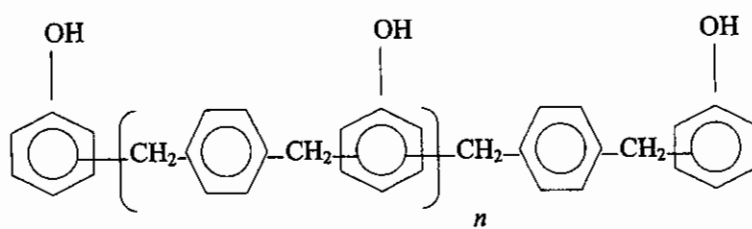
Formula (III)



wherein η is an integer of 0-5 and each R is independently an atom or group selected from hydrogen atom, a halogen and an alkyl group.

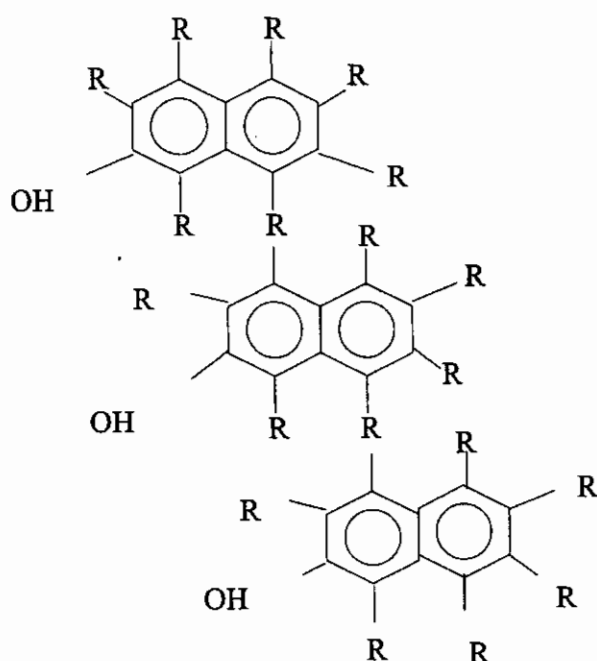
a paraxylene-modified phenolic resin curing agent represented by formula (IV):

Formula (IV)



wherein η is an integer of 0-5 and a naphthalene resin curing agent represented by formula (V):

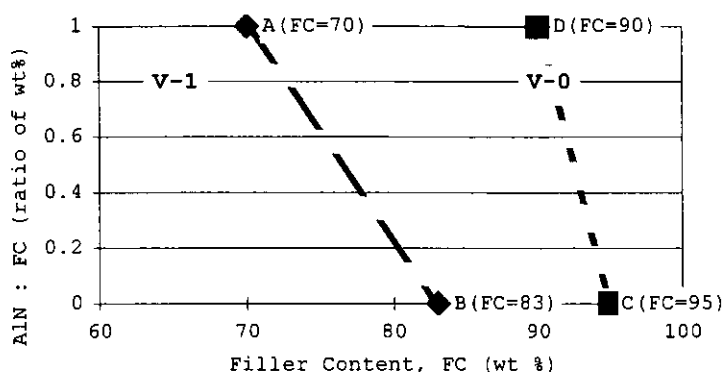
Formula (V)



wherein each R is independently an atom or group selected from hydrogen atom, a halogen and an alkyl group.

26. The use as claimed in any one of the preceding claims 18 to 25 in which the curing agent is a resin curing agent represented by formula V.
27. The use as claimed in any one of the preceding claims 18 to 26 in which the epoxy resin is used in an amount of from 0.8 to 1.3 times the epoxy equivalents per hydroxyl group equivalent of said resin curing agent.
28. The use as claimed in any one of the preceding claims 18 to 27 in which the flame retardant composition aluminum nitride together with fused silica, crystalline silica and/or aluminum oxide.
29. The use as claimed in any one of the preceding claims 18 to 28 in which the flame retardant composition is particles of aluminum nitride together with silica having a maximum size not exceeding 150 microns.
30. The use as claimed in any one of the preceding claims 18 to 29 in which the filler particle size distribution lies between that of D10=1.5-2.0um, D50=10-20um, D90=70-80um for pure silica, and D10=2- 8um, D50=15-25um, D90=40-55um for pure aluminum nitride, where DXX refers to diameter at XX% by weight based on the cumulative filler particle size distribution.

31. The use as claimed in any one of the preceding claims 18 to 30 wherein the amount of fillers is between the following straight lines AB-BC-CD-DA drawn on a graph as shown in Figure 1:



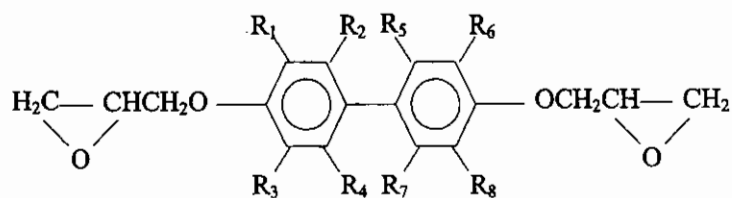
32. The use as claimed in any one of the preceding claims 18 to 31 in which the aluminum nitride is coated with silica.
33. The use claimed in any one of the preceding claims 18 to 32 in which the silica coated aluminum has the following limits of hydrolysis:

<u>Boiling Water Test (20hrs, 100deg C).</u>	<u>NL (ppm)</u>
Standard AlN (without coating)	>100,000
Silica coated AlN (SCAN)	<150
<u>Pressure Cooker Test (20hrs, 120deg C)</u>	<u>N (ppm)</u>
Standard AlN (without coating)	>80,000
Silica coated AlN (SCAN)	<2,500

34. The use as claimed in any one of the preceding claims 18 to 33 in which a curing accelerator is present in an amount of from 0.05 to 1% by weight based on the total resin composition.
35. The method of imparting flame retardancy to a semiconductor device sealed with a resin composition comprising incorporating in the resin composition a flame retardant composition comprising aluminum nitride.

36. The method as claimed in claim 35 in which the flame retardant composition comprises aluminum nitride treated to inhibit hydrolysis.
37. The method as claimed in claim 35 or claim 36 in which the resin is an epoxy resin.
38. The method as claimed in claim 35 in which the epoxy resin is selected from the group consisting of naphthalene type resins, phenol novolac resins, cresol novolac resins, copolymers between dicyclopentadiene modified phenolic resins and phenol novolac resins and/or cresol novolac resins, biphenyl type epoxy resins, tri- or multi-functional type epoxy resins and/or paraxylene-modified phenolic resins.
39. The method as claimed in claim 37 in which the resin is a biphenyl (aralkyl modified) type represented by formula (I):

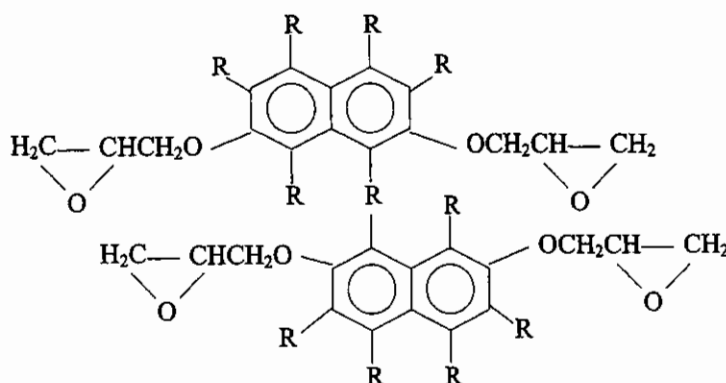
Formula (I)



wherein R₁ to R₈ is independently an atom or group selected from hydrogen atom, a halogen and an alkyl group;

or a naphthalene tetra-functional type represented by formula (II):

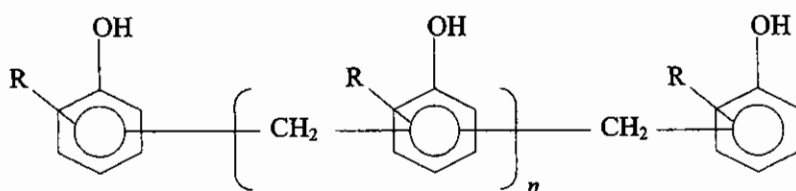
Formula (II)



wherein each R is independently an atom or group selected from hydrogen atom, a halogen and an alkyl group

40. The method as claimed in claim 39 in which the resin is the naphthalene tetra-functional type presented by formula (II).
41. The method as claimed in any one of the preceding claims 35 to 40 in which an epoxy resin is used and as a curing agent a resin curing agent selected from the group consisting of naphthalene type resin curing agent, phenolic type resin curing agent and /or para-xylene modified (para-xylene glycol dimethyl ether) phenolic resin curing agent.
42. The method as claimed claim 41 wherein the curing agent is selected from a phenolic resin curing agent represented by formula (III);

Formula (III)



wherein n is an integer of 0-5 and each R is independently an atom or group selected from hydrogen atom, a halogen and an alkyl group

$$\text{HO-C}_6\text{H}_4\text{-}\left[\text{CH}_2\text{-C}_6\text{H}_4\text{-CH}_2\text{-C}_6\text{H}_4\right]_n\text{-CH}_2\text{-C}_6\text{H}_4\text{-CH}_2\text{-C}_6\text{H}_4\text{-OH}$$

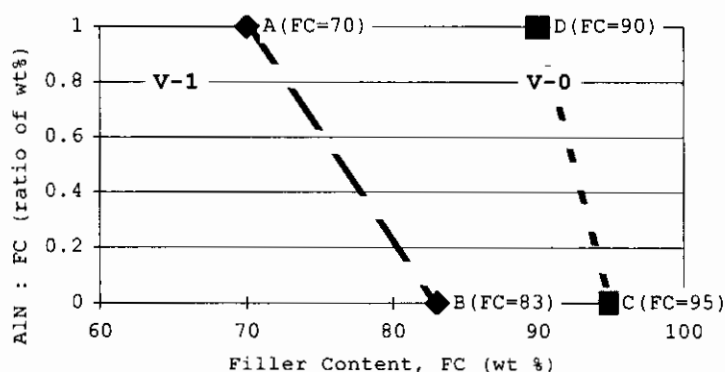
and a naphthalene resin curing agent represented by formula (V):

The image displays three chemical structures of bisphenol A derivatives, arranged vertically. Each structure consists of two phenyl rings connected by a central group. The rings are substituted with R groups and an OH group.

- Top structure:** 2,2-bis(4-hydroxyphenyl)propane (BPA). The central group is an isopropylidene group. The rings are substituted with R groups at the 2, 4, and 6 positions, and an OH group at the 1 position.
- Middle structure:** 2,2-bis(4-hydroxyphenyl)hexafluoropropane (BPF). The central group is a hexafluoroisopropylidene group. The rings are substituted with R groups at the 2, 4, and 6 positions, and an OH group at the 1 position.
- Bottom structure:** 2,2-bis(4-hydroxyphenyl)ether (BPE). The central group is an ether group. The rings are substituted with R groups at the 2, 4, and 6 positions, and an OH group at the 1 position.

43. The method as claimed in claim 42 wherein the curing agent is a resin curing agent represented by formula V.
44. The method as claimed in any one of claims 37 to 43 wherein the epoxy resin is used in an amount of from 0.8 to 1.3 times the epoxy equivalents per hydroxyl group equivalent of said resin curing agent.

45. The method as claimed in any one of the preceding claims 35 to 44 wherein the flame retardant composition comprises aluminum nitride together with fused silica, crystalline silica and/or aluminum oxide.
46. The method as claimed in any one of the preceding claims 35 to 45 in which the flame retardant composition is particles of aluminum nitride together with silica having a maximum size not exceeding 150 microns.
47. The method as claimed in claim 46 wherein the filler particle size distribution lies between that of D10=1.5-2.0um, D50=10-20um, D90=70-80um for pure silica, and D10=2- 8um, D50=15-25um, D90=40-55um for pure aluminum nitride, where DXX refers to diameter at XX% by weight based on the cumulative filler particle size distribution.
48. The method as claimed in any one of the preceding claims 3 to 47 in which the semiconductor device contains as a sealing material a cured epoxy resin composition comprising an epoxy resin of the formula II, an epoxy resin curing agent of the formula V, a mixture of inorganic aluminum nitride filler and silica oxide fillers, curing accelerator, wherein the amount of fillers is between the following straight lines AB-BC-CD-DA drawn on a graph as shown in Figure 1:



49. The method as claimed in any one of the preceding claims 35 to 48 wherein the aluminum nitride is coated with silica.
50. The method as claimed in claim 49 in which the silica coated aluminum has the following limits of hydrolysis:

Boiling Water Test (20hrs, 100deg C).

NL (ppm)

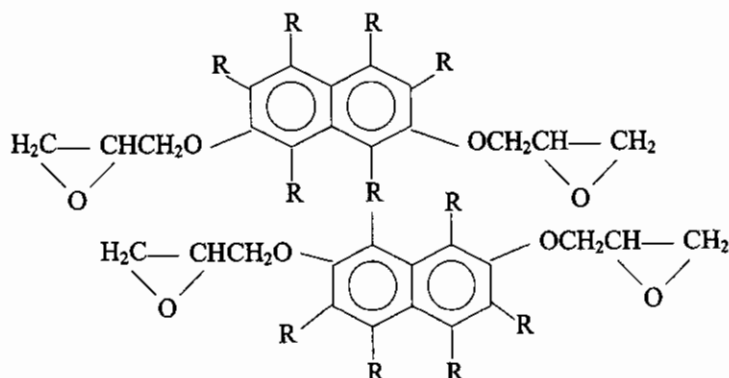
Standard AlN (without coating)

>100,000

Silica coated AlN (SCAN)	<150
<u>Pressure Cooker Test (20hrs, 120deg C)</u>	<u>N (ppm)</u>
Standard AlN (without coating)	>80,000
Silica coated AlN (SCAN)	<2,500

51. The method as claimed in any one of the preceding claims wherein a curing accelerator is present in an amount of from 0.05 to 1% by weight based on the total resin composition.
52. A semiconductor device sealed with an epoxy resin composition which contains as a flame retardant a material comprising aluminium nitride in which the resin is a naphthalene tetra-functional type presented by formula (II):

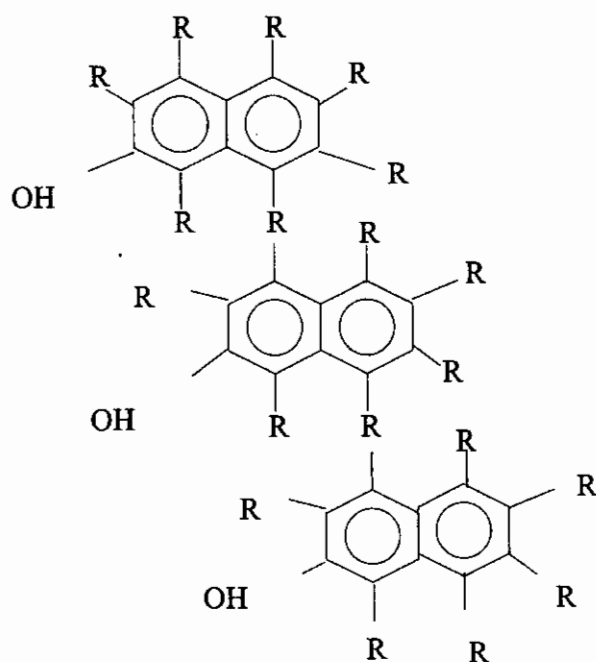
Formula (II)



wherein R_1 to R_8 is independently an atom or group selected from hydrogen atom, a halogen and an alkyl group;

53. A semiconductor device as claimed in claim 52 in which the flame retardant comprises aluminium nitride treated to inhibit hydrolysis.
54. A semiconductor device as claimed in claim 52 or 53 wherein as a curing agent a naphthalene resin curing agent represented by formula (V):

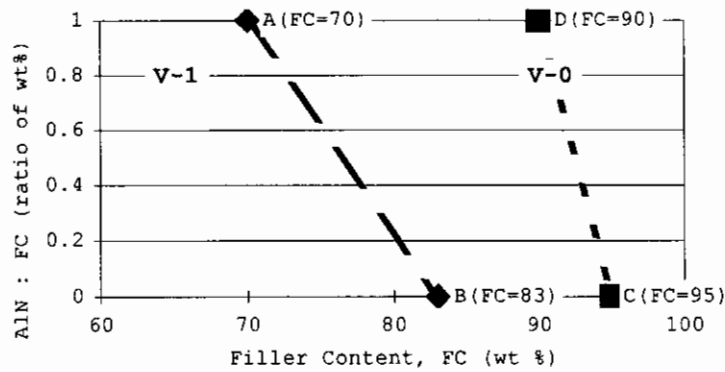
Formula (V)



wherein each R is independently an atom or group selected from hydrogen atom, a halogen and an alkyl group.

55. A semiconductor device as claimed in claim 54 wherein the epoxy resin is used in an amount of from 0.8 to 1.3 times the epoxy equivalents per hydroxyl group equivalent of said resin curing agent.
56. A semiconductor device as claimed in any one of claims 52 to 55 wherein the flame retardant comprises aluminum nitride together with fused silica, crystalline silica and/or aluminum oxide.
57. A semiconductor device as claimed in any one of claims 52 to 56 in which the flame retardant material is particles of aluminum nitride together with silica having a maximum size not exceeding 150 microns.
58. A semiconductor device as claimed in claim 57 wherein the filler particle size distribution lies between that of D10=1.5-2.0um, D50=10-20um, D90=70-80um for pure silica, and D10=2- 8um, D50=1 5-25um, D90=40-55um for pure aluminum nitride, where DXX refers to diameter at XX% by weight based on the cumulative filler particle size distribution.
59. A semiconductor device containing as a sealing material a cured epoxy resin composition comprising an epoxy resin of the formula II, an epoxy resin curing agent of the formula V, a mixture of inorganic aluminum nitride filler and silica oxide

fillers, curing accelerator, wherein the amount of fillers is between the following straight lines AB-BC-CD-DA drawn on a graph as shown in Figure 1:



60. A semiconductor device claimed in any one of claims 52 to 59 when the aluminum nitride is coated with silica.
61. A semiconductor device as claimed in claim 60 in which the silica coated aluminum has the following limits of hydrolysis:

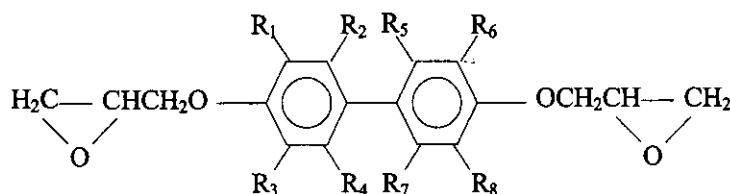
<u>Boiling Water Test (20hrs, 100deg C).</u>	<u>NL (ppm)</u>
Standard AlN (without coating)	>100,000
Silica coated AlN (SCAN)	<150
<u>Pressure Cooker Test (20hrs, 120deg C)</u>	<u>N (ppm)</u>
Standard AlN (without coating)	>80,000
Silica coated AlN (SCAN)	<2,500

62. A semiconductor device as claimed in any one of claims 52 to 61 wherein a curing accelerator is present in an amount of from 0.05 to 1% by weight based on the total resin composition.
63. An epoxy resin composition used for sealing semiconductor devices comprising an epoxy resin, a resin curing agent, a filler material comprising aluminum nitride as a flame retardant optionally together with silica oxide and a curing accelerator, in which the amounts of aluminum nitride and silica in relation to the total resin content and the amount of aluminum nitride in relation to the total filler content is selected so that the resin composition meets the Under Water Laboratory (USA) requirement for V-0 in

the UL-94 flammability test, optionally with the addition of one or more conventional flame retardants.

64. An epoxy resin composition as claimed in claim 63 in which the aluminium nitride particles are coated with silica.
65. An epoxy resin composition as claimed in claim 63 or 64 in which the epoxy resin is selected from the group consisting of naphthalene type resins, phenol novolac resins, cresol novolac resins, copolymers between dicyclopentadiene modified phenolic resins and phenol novolac resins and/or cresol novolac resins, biphenyl type epoxy resins, tri- or multi-functional type epoxy resins and/or paraxylene-modified phenolic resins.
66. An epoxy resin composition as claimed in any one of claims 63 to 65 in which the resin is a biphenyl (aralkyl modified) type represented by formula (I):

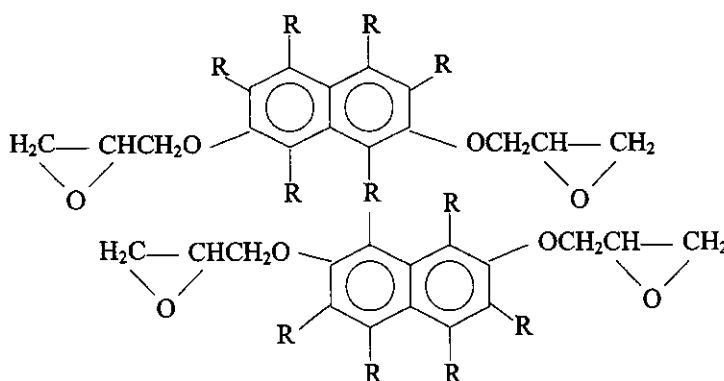
Formula (I)



wherein R_1 to R_8 is independently an atom or group selected from hydrogen atom, a halogen and an alkyl group;

wherein R_1 to R_8 , which may be the same or different, are each an atom or group selected from the group consisting of hydrogen atom and alkyl groups or a naphthalene tetra-functional type represented by formula (II):

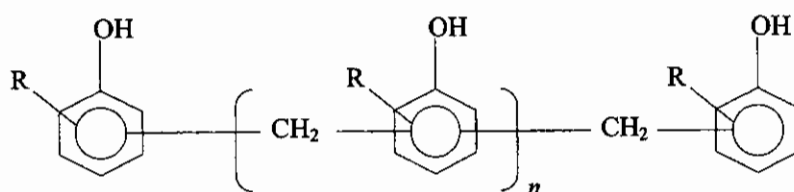
Formula (II)



wherein each R is independently an atom or group selected from hydrogen atom, a halogen and an alkyl group

67. An epoxy resin composition as claimed in any one of claims 63 to 66 in which the resin is the naphthalene tetra-functional type represented by formula (II).
68. An epoxy resin composition as claimed in any one of claims 63 to 67 in which the curing agent is a resin curing agent selected from the group consisting of naphthalene type resin curing agent, phenolic type resin curing agent and /or para-xylene modified (para-xylene glycol dimethyl ether) phenolic resin curing agent.
69. An epoxy resin composition as claimed in any one of claims 63 to 68 in which the curing agent is selected from a phenolic resin curing agent represented by formula (III):

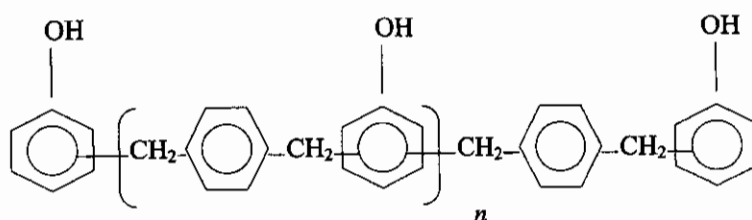
Formula (III)



wherein n is an integer of 0-5 and each R is independently an atom or group selected from hydrogen atom, a halogen and an alkyl group

a paraxylene-modified phenolic resin curing agent represented by formula (IV):

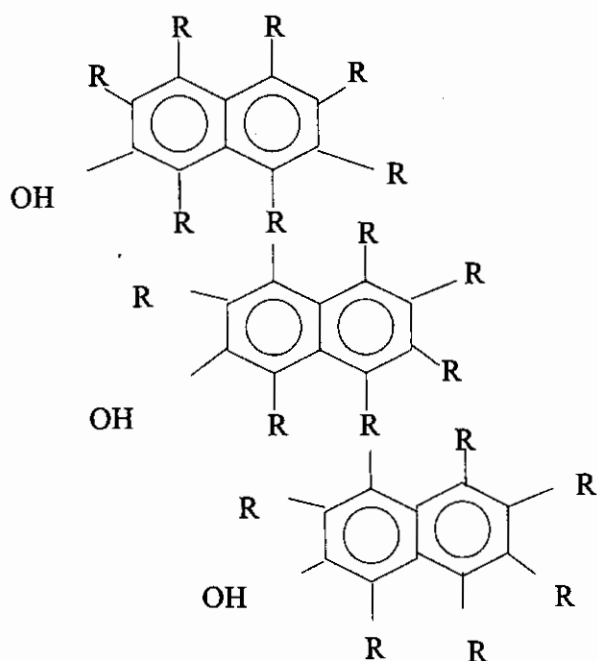
Formula (IV)



wherein n is an integer of 0-5

and a naphthalene resin curing agent represented by formula (V):

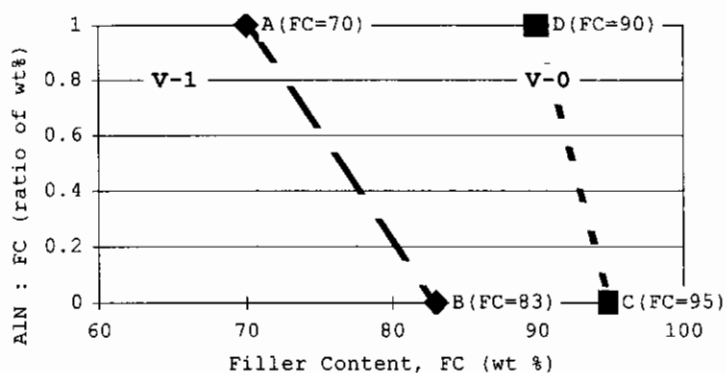
Formula (V)



wherein each R is independently an atom or group selected from hydrogen atom, a halogen and an alkyl group.

70. An epoxy resin composition as claimed in any one of claims 63 to 69 in which the curing agent is a resin curing agent represented by formula V.
71. An epoxy resin composition as claimed in any one of claims 63 to 70 in which the epoxy resin is used in an amount of from 0.8 to 1.3 times the epoxy equivalents per hydroxyl group equivalent of said resin curing agent.
72. An epoxy resin composition as claimed in any one of claims 63 to 71 in which the flame retardant comprises aluminum nitride together with fused silica, crystalline silica and/or aluminum oxide.
73. An epoxy resin composition as claimed in any one of claims 63 to 72 in which the flame retardant material is particles of aluminum nitride together with silica having a maximum size not exceeding 150 microns.
74. An epoxy resin composition as claimed in any one of claims 63 to 73 in which the filler particle size distribution lies between that of D10=1.5-2.0um, D50=10-20um, D90=70-80um for pure silica, and D10=2- 8um, D50=15-25um, D90=40-55um for pure aluminum nitride, where DXX refers to diameter at XX% by weight based on the cumulative filler particle size distribution.

75. An epoxy resin composition as claimed in any one of claims 63 to 74 wherein the amount of fillers is between the following straight lines AB-BC-CD-DA drawn on a graph as shown in Figure 1:



76. An epoxy resin composition as claimed in any one of claims 64 to 75 in which the silica coated aluminum has the following limits of hydrolysis:

<u>Boiling Water Test (20hrs, 100deg C).</u>	<u>NL (ppm)</u>
Standard AlN (without coating)	>100,000
Silica coated AlN (SCAN)	<150
<u>Pressure Cooker Test (20hrs, 120deg C)</u>	<u>N (ppm)</u>
Standard AlN (without coating)	>80,000
Silica coated AlN (SCAN)	<2,500

77. An epoxy resin composition as claimed in any one of claims 63 to 76 in which a curing accelerator is present in an amount of from 0.05 to 1% by weight based on the total resin composition.