

Description

The present invention relates to a resin composition. More particularly, the invention relates to a resin composition with improved resistance to heat and crack, for use as an insulating material, laminate sheet material and/or resin sealing material for electric and electronic parts and semiconductors. Most particularly, the invention relates to a resin composition having solder crack resistance, which is suitable for sealing semiconductor devices.

Resin compositions having excellent heat resistance and crack resistance have recently been required in the field of electric and electronic parts and semiconductors. For example, in the field of electric and electronic parts, and semiconductors in particular, increasing part density on a substrate fitted with the parts tends to be accompanied by miniaturization and thickness reduction of the apparatus and equipment where these parts are to be fitted. The parts themselves have a tendency to diversify their function. As to the materials for sealing the parts, there has been a strong desire to develop resin compositions which have excellent resistance to high temperature solder during soldering to the substrate.

Conventionally, the resin compositions primarily employed for this purpose, i.e. so-called semiconductor-sealing resin compositions, mainly comprise an epoxy resin of the o-cresol type, phenolic novolak resin as a hardener and silica. Such compositions are excellent in moldability and reliability. However, the resin-sealed types of semiconductor devices are changing to surface-mounted types as a result of a trend towards the above-mentioned high density mounting. The surface-mounted type of semiconductor device differs from conventional inserted types of semiconductor devices. The whole of the semiconductor device is exposed to a soldering temperature of 200 °C or more during soldering to the substrate.

In the soldering step, cracks have occurred in the sealing resin and caused the problem of seriously decreasing reliability in semiconductor devices. The cracks develop due to absorption of moisture during storage of the semiconductor devices, followed by explosive expansion of the moisture at temperatures of 200 °C or more, causing stress which exceeds the strength of the resin. In such a case, the stress on the resin is approximately indicated by the following equation:

$$\sigma = k.p.a^2/t^2,$$

where σ is the stress on the resin, k is a constant, a is the length of a short side of a die pad, and t is the thickness of the resin in the bottom part of the die pad.

Accordingly, imide-based resins have been considered, in order to provide sufficient resin strength to overcome the stress of moisture expansion by increasing the glass transition temperature of the sealing resin. However, imide resin-cured products tend to suffer from increased moisture absorption and hence, in view of the above equation, the stress on the resin increases and this inhibits utilization of the high strength which is normally a characteristic of an imide-based resin. Therefore, to inhibit crack development it would be useful to decrease moisture absorption and to lower moisture vapor pressure during the soldering step.

JP-A-1 213 335 describes a semiconductor-sealing resin composition comprising a maleimide resin and a phenol aralkyl resin and/or resorcinol aralkyl resin.

JP-A-2 045 554 describes a semiconductor-sealing resin comprising a polymaleimide of a specific formula, again together with a phenol aralkyl resin and/or resorcinol aralkyl resin.

JP-A-1 045 426 discloses a semiconductor-sealing resin composition comprising a maleimide resin which contains certain specific maleimide components, together with a phenol aralkyl resin as a hardener and an organic phosphine compound as a curing catalyst.

EP-A-O 354 033 also describes a semiconductor-sealing resin composition, the composition comprising a silicone-modified epoxy resin, a hardening agent, an inorganic filler and a polymaleimide of a specific structure. The hardener may be, inter alia, a novolak-type phenol resin, a phenol aralkyl resin or a resorcinol aralkyl resin.

US-A-5 041 507 discloses a resin composition comprising a polymaleimide and a modified phenol novolak resin, optionally with an epoxy resin.

JP-A-3 140 555 discloses a semiconductor-sealing resin composition which preferably comprises a maleimide compound, an epoxy resin such as of the phenol novolak type and an alkenylphenol and/or alkenylphenol ether.

It is desirable that embodiments of the present invention should provide a resin composition which has excellent heat resistance and crack resistance and which can also be applied to a resin-sealed type of semiconductor device required to have solder crack resistance during the mounting step.

Embodiments of the present invention preferably also provide a resin composition which can improve the heat resistance and crack resistance of insulating materials and laminate sheet materials and can be

widely applied to electric and electronic parts.

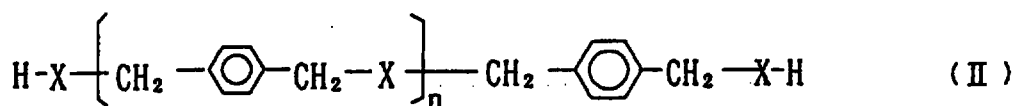
As a result of an intensive investigation the present inventors have succeeded in remarkably enhancing the strength of a sealing resin without increasing its moisture absorption, by using a polymaleimide which can be cured at relatively low temperatures in polyimide resin and further by simultaneously using a phenolic aralkyl resin having low moisture absorption. Thus the present invention has been completed

One aspect of the present invention is a resin composition comprising an organic component containing a polymaleimide represented by the formula (I) and a phenolic aralkyl resin represented by the formula (II); and an inorganic filler. The organic component may also contain an epoxy resin.

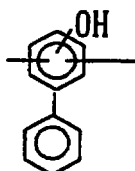
More particularly, this aspect of the present invention provides a resin composition comprising an organic component (A) containing (a) a polymaleimide compound represented by the formula (I):



wherein R_1 is a m -valent organic group having two or more carbon atoms and m is an integer of two or more and (b) a phenolic aralkyl resin represented by the formula (II):



wherein X is a divalent group having the formula



or



, and n is an integer of from 0 to 100, or containing a mixture of the phenolic aralkyl resin and a phenol, and component (B) containing an inorganic filler; or a resin composition comprising an organic component (A) containing the above polymaleimide compound (a) and the phenolic aralkyl resin (b), or a mixture of the phenolic aralkyl resin and a phenol and further containing an epoxy resin (C), with a component (B) containing an inorganic filler.

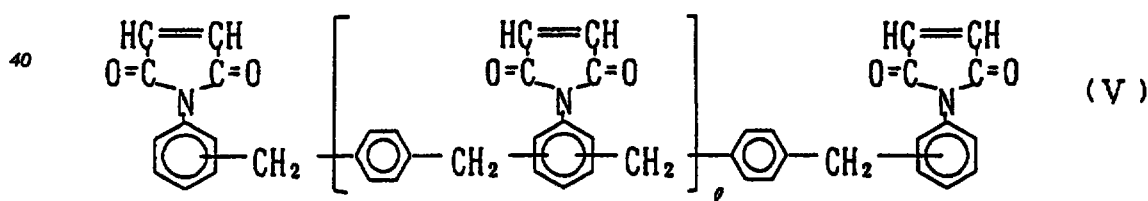
This resin composition is particularly excellent in solder crack resistance and is suitable for use in semiconductor sealing.

The ingredient (a) used in the organic component (A) of the composition of the present invention is a polymaleimide compound represented by the formula (I). The polymaleimide compound of the formula (I) has two or more maleimide groups in each module.

Exemplary polymaleimide compounds which can be used include

N,N'-ethylenebismaleimide,
N,N'-hexamethylenebismaleimide,
N,N'-(1,3-phenylene)bismaleimide,

- N,N'-(1,4-phenylene)bismaleimide,
 bis(4-maleimidophenyl)methane,
 bis(4-maleimidophenyl)ether,
 bis(3-chloro-4-maleimidophenyl)methane,
 5 bis(4-maleimidophenyl)sulfone,
 bis(4-maleimidocyclohexyl)methane,
 1,4-bis(4-maleimidophenyl)cyclohexane,
 1,4-bis(maleimidomethyl)cyclohexane,
 1,4-bis(maleimidomethyl)benzene,
 10 1,3-bis(4-maleimidophenoxy)benzene,
 1,3-bis(3-maleimidophenoxy)benzene,
 bis [4-(3-maleimidophenoxy)phenyl] methane,
 bis [4-(4-maleimidophenoxy)phenyl] methane,
 1,1-bis [4-(3-maleimidophenoxy)phenyl] ethane,
 15 1,1-bis [4-(4-maleimidophenoxy)phenyl] ethane,
 1,2-bis [4-(3-maleimidophenoxy)phenyl] ethane,
 1,2-bis [4-(4-maleimidophenoxy)phenyl] ethane,
 2,2-bis [4-(3-maleimidophenoxy)phenyl] propane,
 2,2-bis [4-(4-maleimidophenoxy)phenyl] propane,
 20 2,2-bis [4-(3-maleimidophenoxy)phenyl] butane,
 2,2-bis [4-(4-maleimidophenoxy)phenyl] butane,
 2,2-bis [4-(3-maleimidophenoxy)phenyl] -1,1,1,3,3,3-hexafluoropropane,
 2,2-bis [4-(4-maleimidophenoxy)phenyl] -1,1,1,3,3,3-hexafluoropropane,
 4,4'-bis(3-maleimidophenoxy)biphenyl,
 25 4,4'-bis(4-maleimidophenoxy)biphenyl,
 bis [4-(3-maleimidophenoxy)phenyl] ketone,
 bis [4-(4-maleimidophenoxy)phenyl] ketone,
 bis [4-(3-maleimidophenoxy)phenyl] sulfide,
 bis [4-(4-maleimidophenoxy)phenyl] sulfide,
 30 bis [4-(3-maleimidophenoxy)phenyl] sulfoxide,
 bis [4-(4-maleimidophenoxy)phenyl] sulfoxide,
 bis [4-(3-maleimidophenoxy)phenyl] sulfone,
 bis [4-(4-maleimidophenoxy)phenyl] sulfone,
 bis [4-(3-maleimidophenoxy)phenyl] ether,
 35 bis [4-(4-maleimidophenoxy)phenyl] ether,
 polymaleimidophenylmethylenes and a polymaleimide compound represented by the formula (V):



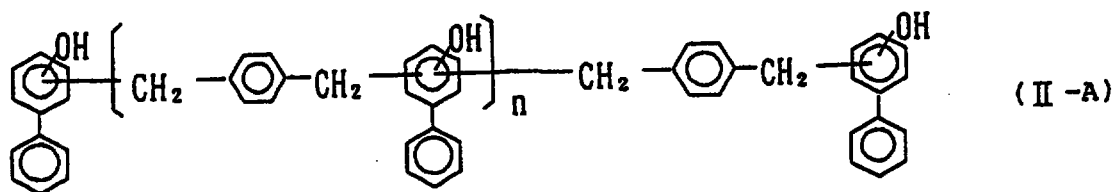
wherein l is on average from 0 to 10.

These polymaleimide compounds can be used singly or as a mixture.

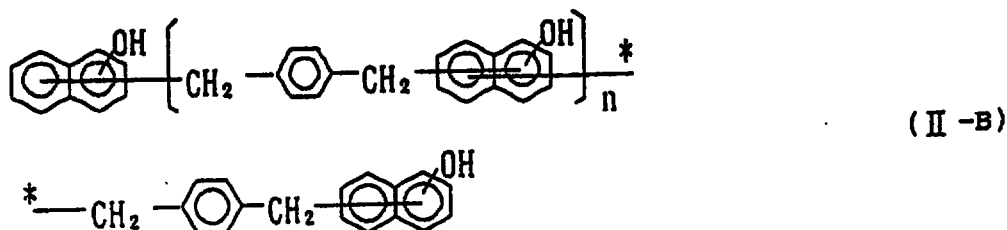
The ingredient (b) which is used in component (A) of the composition of the invention is a phenolic aralkyl resin represented by the formula (II), or a mixture of the phenolic aralkyl resin with a phenol. The phenolic aralkyl resin of the formula (II) may be used alone or in combination with a compound having two or more phenolic hydroxyl groups per molecule.

The phenolic aralkyl resin represented by the formula (II) is either a phenylphenol aralkyl resin represented by the formula (II-A):

55



10 wherein n is an integer of from 0 to 100, or a naphthol aralkyl resin represented by the formula (II-B):



25 wherein n is an integer of from 0 to 100. A phenolic aralkyl resin in which n is an integer of from 0 to 5 is preferred, since it has a low softening point and excellent fluidity.

These phenolic aralkyl resins can be prepared by reacting an aralkyl alcohol derivative represented by the formula (VI):



35 wherein R₄ is a hydrogen atom or an alkyl group having 4 or fewer carbon atoms, with phenylphenol or naphthol having the formula (VII):



45 in the presence of an acid catalyst.

Representative aralkyl alcohol derivatives which can be used include, for example:

α,α' -dihydroxy-p-xylene,

α,α' -dimethoxy-p-xylene,

α,α' -diethoxy-p-xylene,

45 α,α' -di-n-propoxy-p-xylene,

α,α' -diisopropoxy-p-xylene,

α,α' -n-butoxy-p-xylene,

α,α' -di-sec-butoxy-p-xylene and

α,α' -diisobutoxy-p-xylene.

50 The phenylphenols which can be used are o-phenylphenol, m-phenylphenol and p-phenylphenol.

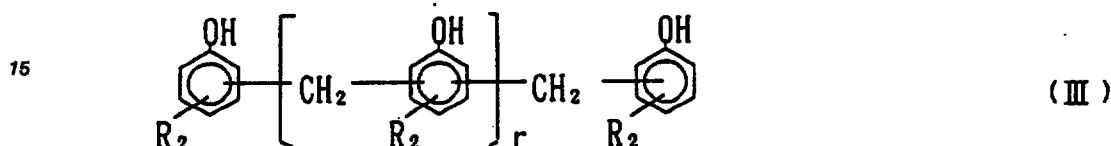
Naphthols of the formula (VII) which can be used in the invention are α -naphthol and β -naphthol.

55 The reaction of the aralkyl alcohol derivative with naphthol or phenylphenol is carried out using naphthol or phenylphenol in a range of usually from 1.3 to 20 moles, preferably from 1.5 to 10 moles, per mole of the aralkyl alcohol derivative, in the presence of an acid catalyst and at a temperature of 110 °C or more, preferably from 130 to 180 °C. Useful acid catalysts are inorganic or organic acids, for example, a single compound or a mixture of compounds selected from mineral acids such as hydrochloric acid, sulphuric acid and phosphoric acid; Friedel-Crafts type catalysts such as zinc chloride, aluminium chloride, stannic chloride and ferric chloride; organic sulphonc acids such as methanesulphonic acid and p-toluenesulphonic

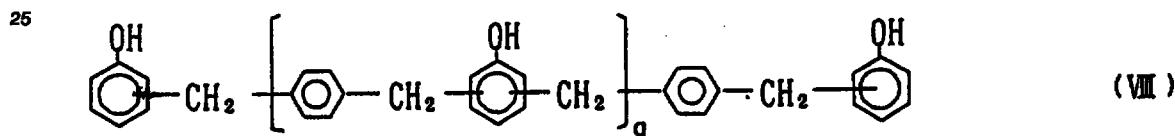
acid; sulphate esters such as dimethyl sulphate and diethyl sulphate; and ultra strong acids such as trifluoromethanesulphonic acid and boron trifluoride. The amount of catalyst used is usually from 0.0001 to 10 % by weight, preferably from 0.001 to 1 % by weight, for the total weight of naphthol / phenylphenol and aralkyl alcohol derivative.

- 5 As the reaction progresses, hydrogen halide, water or alcohol are formed and are distilled out of the reaction system. After finishing the reaction, unreacted naphthol or phenylphenol is removed by vacuum distillation or other suitable methods.

In the composition of the present invention, the phenol compound which has two or more phenolic hydroxyl groups per molecule and which can be used in combination with the phenolic aralkyl resin represented by the formula (II) is most preferably a phenolic novolak resin which is a reaction product of phenol and/or substituted phenol with an aldehyde and is represented by the formula (III):

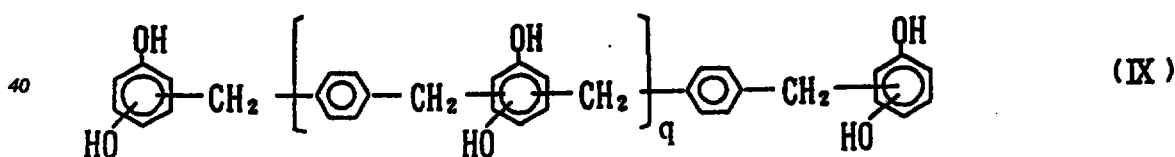


- 20 wherein R₂ is a hydrogen atom, hydroxyl group or alkyl group having from 1 to 9 carbon atoms, and r is an integer of 1 or more. Other phenol compounds include, for example, aralkyl resins having the formula (VIII) or (IX):



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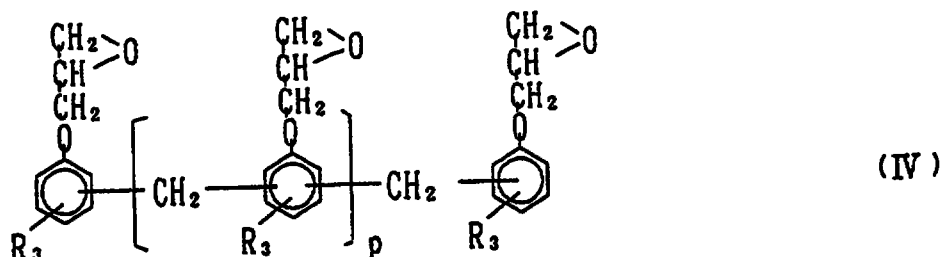


- 45 wherein q is an integer of from 0 to 100, and polyhydric phenols such as trihydroxyphenylmethane, tetrahydroxyphenylethane and alkanetetraakisphenol. An aralkyl resin in which q is an integer of from 0 to 5 is preferred due to its low softening point and excellent fluidity.

When the phenolic aralkyl resin is used in combination with the above type of phenol compound, their relative proportions are preferably in the range of from 0 to 100 parts by weight of the latter to 100 parts by weight of the former.

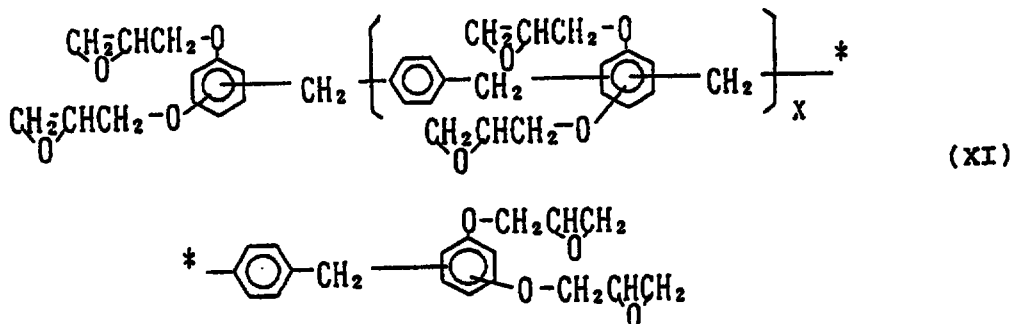
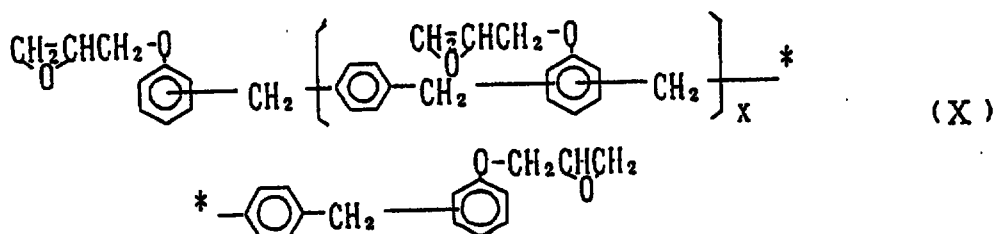
When the component (A) contains ingredient (c), the epoxy resin which is preferably used as ingredient (c) is, in view of heat resistance and electrical properties, derived from a phenolic novolak resin which is a reaction product of phenol and/or substituted phenol with an aldehyde, and is represented by the formula (IV):

55



10 wherein R_3 is a hydrogen atom or an alkyl group having from 1 to 9 carbon atoms and p is an integer of 1 or more. Other compounds having two or more epoxy groups per molecule can also be used.

Exemplary epoxy resins include an epoxy resin derived from compounds having two or more active hydrogens per molecule, for example, an epoxy resin obtained by reacting polyhydric phenols such as bisphenol A, bisphenol F, resorcinol, bishydroxydiphenyl ether, bishydroxybiphenyl, tetrabromobisphenol A, trihydroxyphenylmethane, tetrahydroxyphenylethane and alkanetetraakisphenol; polyhydric alcohols such as ethylene glycol, neopentyl glycol, glycerol, trimethylolpropane, pentaerythritol, diethylene glycol and polypropylene glycol; amines such as ethylenediamine, aniline and bis(4-aminophenyl)methane; and polycarboxylic acids such as adipic acid, phthalic acid and isophthalic acid, with epichlorohydrin or 2-methylepichlorohydrin, and other epoxy resins represented by the formula (X) or (XI):



45 wherein x is an integer of from 0 to 100. An epoxy resin in which x is an integer of from 0 to 5 is preferred in view of its low softening point and excellent fluidity. These epoxy resins may be used singly or as a mixture.

The above epoxy resins can be modified with an oily or rubbery silicone compound. For example, Japanese Laid-Open Patent SHO 62-270617(1987) and 62-273222(1987) disclose silicone modified epoxy resins prepared by dispersing fine particles of silicone polymer into a reaction product of an epoxy resin and a vinyl polymer.

50 In component (A) of the composition of the invention, the amount of ingredient (a), i.e. the polymaleimide compound of formula (I), and of ingredient (b), i.e. the phenolic aralkyl resin of formula (II) or a mixture of the resin with phenol(s), is usually in the range of from 10 to 500 parts by weight, preferably from 25 to 300 parts by weight, of ingredient (b) for 100 parts by weight of ingredient (a).

55 When component (A) contains ingredient (c), i.e. the epoxy resin, the amounts of ingredients (a), (b) and (c) are usually in the range of from 10 to 500 parts by weight, preferably from 25 to 300 parts by weight of the sum of ingredients (b) and (c), for 100 parts by weight, of ingredient (a), and in the range of from 0.1 to

10 equivalents, preferably from 0.5 to 2.0 equivalents, of ingredient (c) per equivalent of ingredient (b).

According to the invention, the resin composition can be formulated and kneaded by conventional methods. The polymaleimide compound can be pre-dissolved in the whole or a portion of ingredient (b) or in a mixture of ingredients (b) and (c). A prepolymer, obtained by reacting these ingredients, can also be used.

The inorganic fillers which can be used as component (B) in the composition of the invention are preferably in the form of a powder or fiber. Representative inorganic fillers include, for example, crystalline silica, fused silica, alumina, silicon nitride, silicon carbide, talc, calcium silicate, calcium carbonate, mica, clay, titanium white and other inorganic powders; and glass fiber, carbon fiber and other inorganic fibers. Crystalline or fused silica powder is preferred in view of its heat expansion coefficient and thermal conductivity. Spherical silica powder, or a mixture of spherical silica powder and irregularly shaped silica powder, is preferred in view of its flowability during molding.

The amount of component (B), i.e. the inorganic filler is desirably from 100 to 900 parts by weight, more preferably from 200 to 600 parts by weight, to 100 parts by weight of the sum of the ingredients (a) and (b) or of the sum of ingredients (a), (b) and (c).

The above inorganic filler is preferably used in combination with a coupling agent in order to improve adhesion to the resin and enhance mechanical strength and heat resistance. The coupling agents which can be used are silane based, titanate based, aluminate based and zircon aluminate based coupling agents. Silane based coupling agents are preferred, in particular a silane based coupling agent having reactive groups.

Exemplary silane based coupling agents include:

vinyltrimethoxysilane, vinyltriethoxysilane,
N-(2-aminoethyl)-3-aminopropylmethyldimethoxysilane,
N-(2-aminoethyl)-3-aminopropyltrimethoxysilane,
3-aminopropyltriethoxysilane,
3-anilinopropyltrimethoxysilane,
3-glycidoxypropyltrimethoxysilane,
3-glycidoxypropylmethyldimethoxysilane,
2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane,
3-methacryloxypropyltrimethoxysilane, and
3-mercaptopropyltrimethoxysilane.

These coupling agents may be used singly or in combination.

They are preferably fixed on the surface of the inorganic fillers in advance by adsorption or reaction.

The curing of the resin composition of the invention is preferably carried out in the presence of a curing accelerator.

Useful curing accelerators include, for example:

2-methylimidazole, 2-methyl-4-ethylimidazole,
2-heptadecylimidazole and other imidazoles;
triethanolamine, triethylenediamine,
N-methylmorpholine and other amines;
tributylphosphine, triphenylphosphine,
tritolyphosphine and other organic phosphines;
tetraphenylphosphonium tetraphenylborate,
triethylammonium tetraphenylborate and other tetraphenylborates;
and 1,8-diazabicyclo (5, 4, 0) undecene and its derivatives.

These curing accelerators can be used singly or as a mixture and can also be used, if desired, in combination with organic peroxides or azo compounds.

The amount of curing accelerator used is in the range of from 0.01 to 10 % by weight of the total amount of ingredients (a) and (b), or of the total amount of ingredients (a), (b) and (c).

The resin composition of the invention can, if desired, be blended with reactive diluents such as diallyl phthalate, triallyl isocyanurate, and o,o'-diallylbisphenol A which are commonly used for imide resins; various silicone oils; release agents such as fatty acids, fatty acid salts and waxes; flame retardants such as bromine compounds, antimony and phosphorous; and colorants such as carbon black. The blend thus obtained is kneaded to prepare molding materials.

The present invention will hereinafter be illustrated in detail by way of examples. In the examples, the properties of the resin compositions were measured using the following methods.

- Glass transition temperature:

According to TMA method

- Flexural strength and Flexural modulus:

According to JIS K-6911

- Moisture absorption:

A specimen for the Flexural test was used. The specimen was allowed to stand at 65 °C, 95% RH for 168 hours in a thermohygrostat and thereafter its weight increase was measured.

- VPS test:

Semiconductor devices to be tested were allowed to stand at 65 °C, 95% RH for 168 hours in a thermohygrostat and immediately thrown into a molten solder bath at 260 °C. The number of semiconductor devices which developed cracks was counted and indicated as follows.

Number of cracked semiconductor devices

Number of semiconductor devices tested

Synthesis Example 1 (o-Phenylphenol aralkyl resin)

To a reaction vessel equipped with a stirrer, thermometer, Deanstall azotropic trap and reflux condenser, 332 g (2.0 moles) of α,α' -dimethoxy-p-xylene, 550 g (3.0 moles) of o-phenylphenol and 2.1 g (0.25 %) of methanesulfonic acid were charged and reacted with stirring at 150-160 °C for 4 hours. The methanol formed was removed from the reaction system by the trap.

After finishing the reaction, unreacted o-phenylphenol and methanesulfonic acid were removed by distillation under reduced pressure, to obtain 595 g of o-phenylphenol aralkyl resin.

The resin composition, measured by high performance liquid chromatography, was 20.1 % of $n=0$, 16.9 % of $n=1$, 13.3 % of $n=2$, 10.8 % of $n=3$, and 38.9 % of $n\geq 4$. The resin had a hydroxyl equivalent of 283.8 g/eq and a softening point of 94 °C.

Synthesis Example 2 (p-Phenylphenol aralkyl resin)

To the same reaction vessel as used in Synthesis Example 1, 207.3 g (1.5 moles) of α,α' -dihydroxy-p-xylene, 510 g (3.0 moles) of p-phenylphenol and 0.35 g (0.05 %) of methanesulfonic acid were charged and reacted with stirring at 150-160 °C for 4 hours. The methanol formed was removed from the reaction system by the trap.

After finishing the reaction, unreacted P-phenylphenol and methanesulfonic acid were removed by distillation under reduced pressure, to obtain 395 g of p-phenylphenol aralkyl resin.

The resin composition, measured by high performance liquid chromatography, was 22.3 % of $n=0$, 18.3 % of $n=1$, 15.4 % of $n=2$, 11.7 % of $n=3$, and 32.3 % of $n\geq 4$. The resin had a hydroxyl equivalent of 299.0 g/eq and a softening point of 105 °C.

Synthesis Example 3 (α -naphthol aralkyl resin)

To the same reaction vessel as used in Synthesis Example 1, 249 g (1.5 moles) of α,α' -dimethoxy-p-xylene, 1080 g (7.5 moles) of α -naphthol and 4.65 g (0.05 %) of methanesulfonic acid were charged and reacted with stirring at 150-160 °C for 4 hours. The methanol formed was removed from the reaction system by the trap.

After finishing the reaction, unreacted α -naphthol and methanesulfonic acid were removed by distillation under reduced pressure, to obtain 470 g of α -naphthol aralkyl resin.

The resin composition, measured by high performance liquid chromatography, was 61.5 % of $n=0$, 18.2 % of $n=1$, 8.7 % of $n=2$, and 11.6 % of $n\geq 3$. The resin had a hydroxyl equivalent of 207.2 g/eq and a softening point of 72 °C.

Synthesis Example 4 (β -naphthol aralkyl resin)

To the same reaction vessel as used in Synthesis Example 1, 207.3 g (1.5 moles) of α,α' -dihydroxy-p-xylene, 2160 g (15 moles) of β -naphthol and 1.18 g (0.05 %) of methanesulfonic acid were charged and reacted with stirring at 150-160 °C for 4 hours. The methanol formed was removed from the reaction

system by the trap.

After finishing the reaction, unreacted β -naphthol and methanesulfonic acid were removed by distillation under reduced pressure, to obtain 438 g of β -naphthol aralkyl resin.

The resin composition, measured by high performance liquid chromatography, was 83.4 % of $n=0$, 9.2 % of $n=1$, 4.6 % of $n=2$, and 2.8 % of $n\geq 3$. The resin had a hydroxyl equivalent of 202.6 g/eq and a softening point of 42 °C.

Examples 1-16 and Comparative Examples 1-4

The compositions (parts by weight) illustrated in Table 1 and Table 2 were mixed in a Henschel mixer and melt-kneaded with hot rolls at 100-130 °C for 3 minutes.

The mixtures were cooled, crushed and tabletted to obtain molding resin compositions.

The following raw materials were used in Table 1 as well as the raw materials prepared in Synthesis Examples 1-4.

- Phenol compound:
Phenolic novolak PN-80 (Trade Mark of Nippon Kayaku)
- Epoxy resin:
o-Cresol novolak type epoxy resin EOCN-1020 (Trade Mark of Nippon Kayaku)
- Inorganic filler:
A mixture composed of 50 parts by weight of spherical, fused silica, HALIMIX SCO (Trade Mark of Micron) and 50 parts by weight of irregular, fused silica FUSEREX RD-8 (Trade Mark of Tatsumori)
- Silane coupling agent:
SZ-6083 (Trade Mark of Toray Dow Corning Silicone)

The molding resin compositions thus obtained were transfer molded at 180 °C under a pressure of 2.9 MPa (30 kg/cm²) for 3 minutes to prepare specimens for the testing of physical properties. Semiconductor devices were prepared for the tests by mounting a test element having dimensions of 10×10 mm on the element installing portion of a lead frame for a flat package type semiconductor device, and then subjecting the lead frame to transfer molding at 180 °C under a pressure of 2.9 MPa (30 kg/cm²) for 3 minutes.

These test pieces, thus molded, were post cured at 180 °C for 6 hours before carrying out each test.

The results are illustrated in Table 3 and Table 4.

As illustrated by the examples and comparative examples, the resin compositions of the invention can efficiently provide heat resistance in an imide resin, without impairing moisture absorption.

Table 1

Raw material	Example								Comparative Example	
	1	2	3	4	5	6	7	8	1	2
4,4'-Bis(3-maleimidophenoxy)biphenyl	15	15	15	15	-	-	-	-	15	-
Bis(4-maleimidophenyl)methane	-	-	-	-	15	15	15	15	-	15
o-Phenylphenolaralkyl resin	10	-	7	-	5.9	-	3.8	-	-	-
t-Phenylphenolaralkyl resin	-	10	-	7	-	6.0	-	3.8	-	-
Phenolic novolak	-	-	3	3	-	-	1.2	1.3	10	4
Epoxy resin	-	-	-	-	4.1	4.0	5.0	4.9	-	6
Inorganic filler	75	75	75	75	75	75	75	75	75	75
Silane coupling agent	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
Triphenyl phosphine	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Triethylammonium tetraphenylborate	-	-	-	-	0.3	0.3	0.3	0.3	-	0.3
Carnauba wax	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45
Carbon black	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Antimony trioxide	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0

Table 2

Raw material	Example								Comparative Example	
	9	10	11	12	13	14	15	16	3	4
4,4'-Bis(3-maleimidophenoxy)biphenyl	15	15	15	15	-	-	-	-	15	-
Bis(4-maleimidophenyl)methane	-	-	-	-	15	15	15	15	-	15
α -Naphthol aralkyl resin	10	-	7	-	4.4	-	3.5	-	-	-
β -Naphthol aralkyl resin	-	10	-	7	-	4.4	-	3.5	-	-
Phenolic novolak	-	-	3	3	-	-	1.5	1.5	10	4
Epoxy resin	-	-	-	-	5.6	5.6	5.0	5.0	-	-
Inorganic filler	75	75	75	75	75	75	75	75	75	75
Silane coupling agent	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
Triphenyl phosphine	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Triethylammonium tetraphenylborate	-	-	-	-	0.3	0.3	0.3	0.3	-	0.3
Carnauba wax	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45
Carbon black	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Antimony trioxide	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0

Table 3

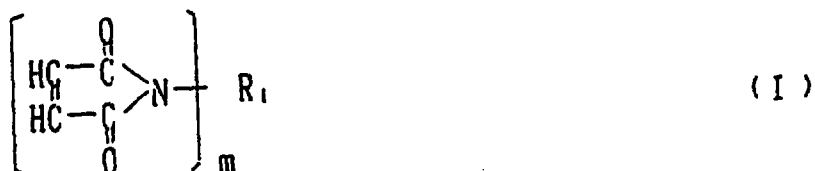
Property	Example								Compa- rative Example	
	1	2	3	4	5	6	7	8	1	2
Glass transition temperature (°C)	210	205	210	205	205	200	205	200	210	205
Flexural strength (kg/mm ²) room temperature 215°C	16.0 6.7	15.0 5.7	16.0 6.5	15.5 6.0	15.5 6.0	15.0 5.5	15.5 6.0	15.0 5.5	16.0 6.5	15.5 6.0
Flexural modulus (kg/mm ²)	1530	1550	1500	1500	1550	1530	1500	1500	1600	1600
Moisture absorption (%)	0.30	0.30	0.35	0.35	0.40	0.40	0.43	0.43	0.55	0.60
V.P.S test (the number of cracked specimens)	0/20	0/20	0/20	0/20	2/20	2/20	5/20	5/20	10/ 20	15/ 20
Flexural strength(MPa) room temperature 215°C	157 66	147 56	157 64	152 59	152 59	147 54	152 59	147 54	157 64	152 59
Flexural modulus(GPa)	15.0	15.2	14.7	14.7	15.2	15.0	14.7	14.7	15.7	15.7

Table 4

Property	Example								Compa- rative Example	
	9	10	11	12	13	14	15	16	3	4
Glass transition temperature (°C)	210	205	210	205	205	200	205	200	210	205
Flexural strength (kg/mm ²) room temperature 215°C	16.0 6.5	15.0 5.7	16.0 6.5	15.5 6.0	15.5 6.0	15.0 5.5	15.5 6.0	15.0 5.5	16.0 6.5	15.5 6.0
Flexural modulus (kg/mm ²)	1530	1550	1500	1500	1550	1530	1500	1500	1600	1600
Moisture absorption (%)	0.30	0.30	0.35	0.35	0.40	0.40	0.43	0.43	0.55	0.60
V.P.S test (the number of cracked specimens)	0/20	0/20	0/20	0/20	2/20	2/20	5/20	5/20	10/ 20	15/ 20
Flexural strength(MPa) room temperature 215°C	157 64	147 56	157 64	152 59	152 59	147 54	152 59	147 54	157 64	152 59
Flexural modulus(GPa)	15.0	15.2	14.7	14.7	15.2	15.0	14.7	14.7	15.7	15.7

Claims

1. A resin composition comprising an organic component (A) which contains (a) a polymaleimide compound represented by the formula (I):



wherein R₁ is a m-valent organic group having two or more carbon atoms and m is an integer of two or more, and component (B) which contains an inorganic filler, characterised in that

the organic component (A) also contains (b) a phenolic aralkyl resin represented by the formula (II):



Table 4

Property	Example								Compa- rative Example	
	9	10	11	12	13	14	15	16	3	4
Glass transition temperature (°C)	210	205	210	205	205	200	205	200	210	205
Flexural strength (kg/mm ²) room temperature 215°C	16.0 6.5	15.0 5.7	16.0 6.5	15.5 6.0	15.5 6.0	15.0 5.5	15.5 6.0	15.0 5.5	16.0 6.5	15.5 6.0
Flexural modulus (kg/mm ²)	1530	1550	1500	1500	1550	1530	1500	1500	1600	1600
Moisture absorption (%)	0.30	0.30	0.35	0.35	0.40	0.40	0.43	0.43	0.55	0.60
V.P.S test (the number of cracked specimens)	0/20	0/20	0/20	0/20	2/20	2/20	5/20	5/20	10/ 20	15/ 20
Flexural strength(MPa) room temperature 215°C	157 64	147 56	157 64	152 59	152 59	147 54	152 59	147 54	157 64	152 59
Flexural modulus(GPa)	15.0	15.2	14.7	14.7	15.2	15.0	14.7	14.7	15.7	15.7

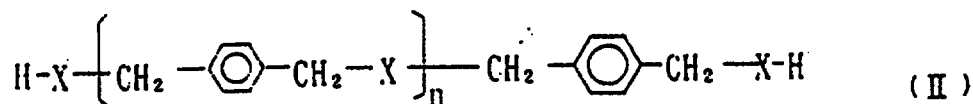
40 Claims

1. A resin composition comprising an organic component (A) which contains (a) a polymaleimide compound represented by the formula (I):

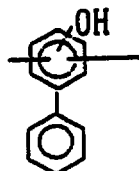


wherein R₁ is a m-valent organic group having two or more carbon atoms and m is an integer of two or more, and component (B) which contains an inorganic filler, characterised in that

the organic component (A) also contains (b) a phenolic aralkyl resin represented by the formula (II):



wherein X is a divalent group having the formula

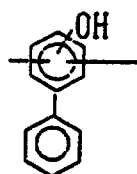


or



, and n is an integer of from 0 to 100, or contains a mixture of the phenolic aralkyl resin and a phenol.

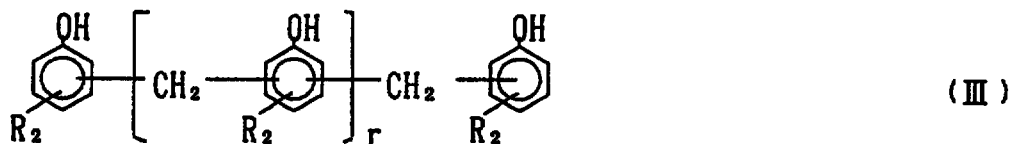
2. A resin composition according to claim 1, wherein the organic component (A) also contains (c) an epoxy resin.
3. The resin composition according to claim 1 or claim 2, wherein the phenolic aralkyl resin (b) is a phenylphenol aralkyl resin in which, in Formula (II), X is:



4. The resin composition according to claim 1 or claim 2, wherein the phenolic aralkyl resin (b) is a naphthol aralkyl resin in which, in Formula (II), X is:

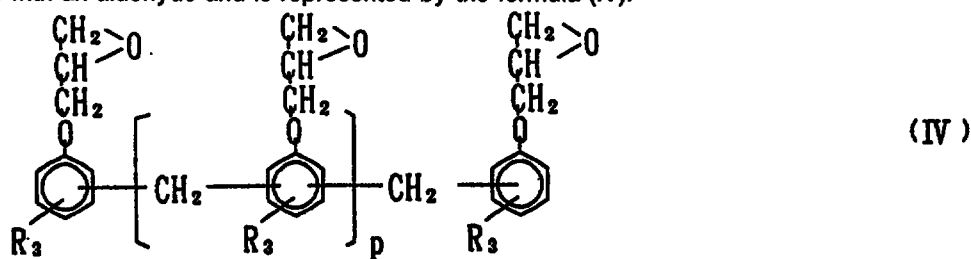


5. A semiconductor-sealing resin composition comprising a resin composition according to any one of claims 1-4.
6. A semiconductor-sealing resin composition according to claim 5, wherein the phenol which forms a mixture with the phenolic aralkyl resin in the ingredient (b) is a phenolic novolak resin which is a reaction product of phenol and/or substituted phenol with an aldehyde and is represented by the formula (III):



wherein R_2 is a hydrogen atom, hydroxyl group or alkyl group having from 1 to 9 carbon atoms, and r is an integer of 1 or more.

7. A semiconductor-sealing resin composition according to claim 5 or claim 6, wherein the epoxy resin (c) is derived from a phenolic novolak resin which is a reaction product of a phenol and/or substituted phenol with an aldehyde and is represented by the formula (IV):



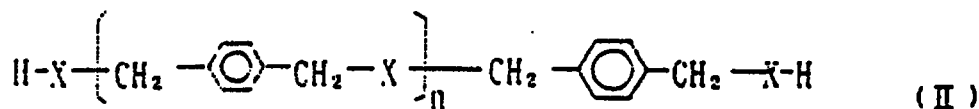
wherein R_3 is a hydrogen atom or alkyl group having from 1 to 9 carbon atoms and p is an integer of one or more.

Patentansprüche

1. Harzzusammensetzung, umfassend eine organische Komponente (A), die (a) eine Polymaleimid-Verbindung der Formel (I):



enthält, worin R_1 eine m -wertige organische Gruppe ist, die zwei oder mehr Kohlenstoffatome aufweist, und m eine ganze Zahl von 2 oder mehr ist, und Komponente (B), die einen anorganischen Füllstoff enthält, dadurch gekennzeichnet, daß die organische Komponente (A) auch (b) ein phenolisches Aralkylharz der Formel (II):



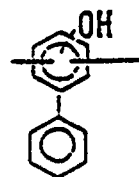
enthält, worin X eine zweiwertige Gruppe der Formel:



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oder

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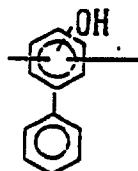
ist und n eine ganze Zahl von 0 bis 100 ist, oder ein Gemisch aus dem phenolischen Aralkylharz und einem Phenol enthält.

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2. Harzzusammensetzung nach Anspruch 1, worin die organische Komponente (A) auch (c) ein Epoxyharz enthält.

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3. Harzzusammensetzung nach Anspruch 1 oder 2, worin das phenolische Aralkylharz (b) ein Phenylphenol-Aralkylharz ist, in dem in Formel (II) X:



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ist.

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4. Harzzusammensetzung nach Anspruch 1 oder 2, worin das phenolische Aralkylharz (b) ein Naphthol-Aralkylharz ist, in dem in Formel (II) X



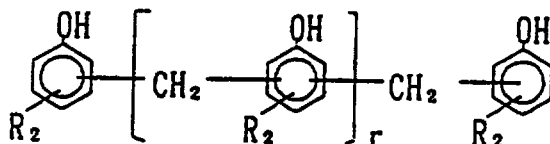
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ist.

5. Harzzusammensetzung zum Einsiegeln von Halbleitern, umfassend eine Harzzusammensetzung nach einem der Ansprüche 1 bis 4.

6. Harzzusammensetzung zum Einsiegeln von Halbleitern nach Anspruch 5, worin das Phenol, das in Bestandteil (b) ein Gemisch mit dem phenolischen Aralkylharz bildet, ein phenolisches Novolakharz ist, das ein Reaktionsprodukt von Phenol und/oder substituiertem Phenol mit einem Aldehyd ist und durch Formel (III):

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(III)

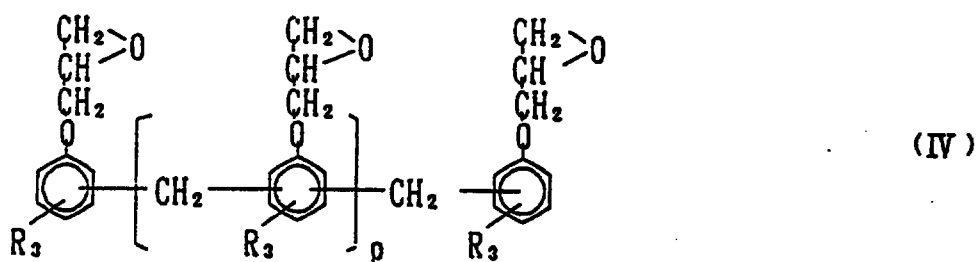
dargestellt wird, worin R₂ ein Wasserstoffatom, eine Hydroxylgruppe oder eine Alkylgruppe mit 1 bis 9 Kohlenstoffatomen ist und r eine ganze Zahl von 1 oder mehr ist.

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7. Harzzusammensetzung zum Einsiegeln von Halbleitern nach Anspruch 5 oder 6, worin das Epoxyharz (c) von einem phenolischen Novolakharz abgeleitet ist, das ein Reaktionsprodukt eines Phenols



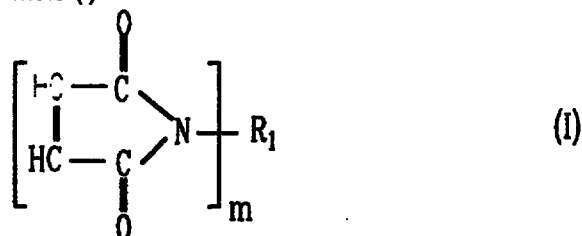
und/oder eines substituierten Phenols mit einem Aldehyd ist und durch die Formel (IV):



dargestellt wird, worin R_3 ein Wasserstoffatom oder eine Alkylgruppe mit 1 bis 9 Kohlenstoffatomen ist und p eine ganze Zahl von 1 oder mehr ist.

15 Revendications

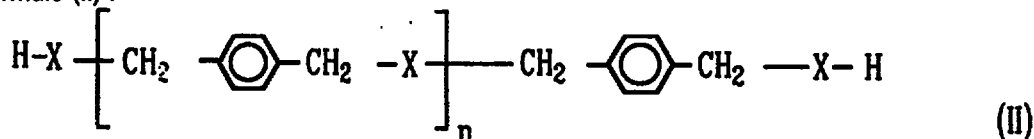
1. Composition de résine comprenant un composant (A) organique qui contient (a) un composé polymaléimide représenté par la formule (I) :



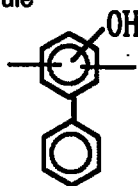
où R^1 est un groupe organique m -valent ayant deux ou plus atomes de carbone et m est un entier valant deux ou plus, et un composant (B) qui contient une charge inorganique,

caractérisée en ce que

le composant (A) organique contient également (b) une résine phénolique aralkyle représentée par la formule (II) :



où X est un groupe divalent ayant la formule



ou

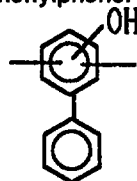


et n est un entier valant de 0 à 100, ou contient un mélange de résine aralkyle phénolique et un phénol.



2. Composition de résine selon la revendication 1, dans laquelle le composant (A) organique contient également (c) une résine époxy.

3. Composition de résine selon la revendication 1 ou la revendication 2, dans laquelle la résine (b) aralkyle phénolique est une résine aralkyle phénylphénol dans laquelle, dans la Formule (II), X est :

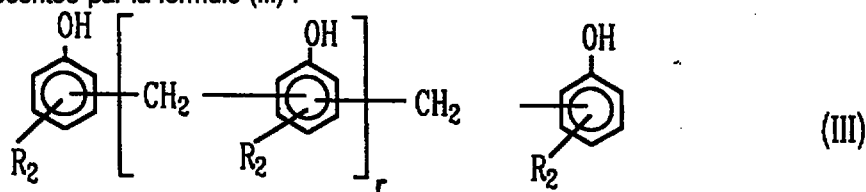


4. Composition de résine selon la revendication 1 ou la revendication 2, dans laquelle la résine (b) aralkyle phénolique est une résine aralkyl naphthol dans laquelle, dans la Formule (II), X est :



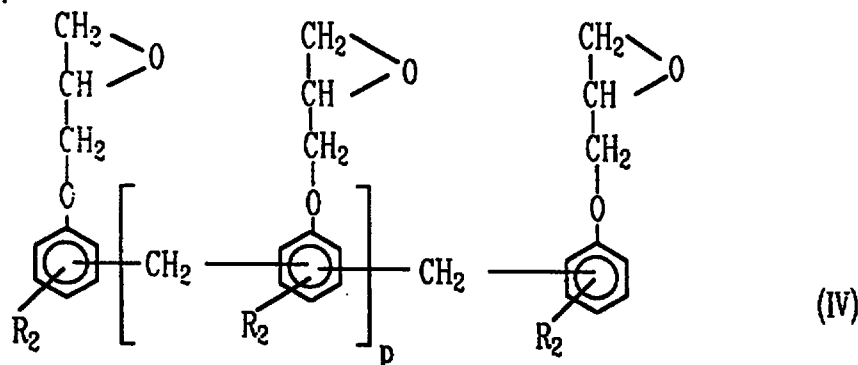
5. Composition de résine de scellement d'un semiconducteur comprenant une composition de résine selon l'une quelconque des revendications 1 à 4.

6. Composition de résine de scellement d'un semiconducteur selon la revendication 5, où le phénol qui forme un mélange avec la résine aralkyle phénolique dans l'ingrédient (b) est une résine novolaque phénolique qui est un produit de réaction d'un phénol et/ou d'un phénol substitué avec une aldéhyde qui est représentée par la formule (III) :



où R_2 est un atome d'hydrogène, un groupe hydroxyle ou un groupe alkyle ayant de 1 à 9 atomes de carbone, et r est un entier valant 1 ou plus.

7. Composition de résine de scellement d'un semiconducteur selon la revendication 5 ou la revendication 6, dans laquelle la résine (c) époxy est dérivée d'une résine novolaque phénolique qui est un produit de réaction d'un phénol et/ou d'un phénol substitué avec une aldéhyde et est représentée par la formule (IV) :



où R_3 est un atome d'hydrogène ou un groupe alkyle ayant de 1 à 9 atomes de carbone et p est un entier valant un ou plus.