



166166



G00002

- 1 -

2 April 2002

POLYFUNCTIONAL CYANATE RESIN COMPOSITION AND RESIN-ENCAPSULATED TYPE SEMICONDUCTOR DEVICE

BACKGROUND OF THE INVENTION

Technical Field of the Invention

The present invention relates to a cyanate resin composition which is useful as an adhesive, a coating material, electric and electronic materials such as insulation materials and laminated plates, especially for the encapsulating an electronic device, and a resin-encapsulated type semiconductor device using the same.

Description of the Related Art

In recent years, for electronic instruments, characteristics such as small size, light weight, excellent performance and high speed are still required.

In connection with this, a semiconductor package which is yet smaller and suitable for high-density mounting has become necessary. Due to such requirements, various forms of semiconductor packages are proposed. Among them, BGA (Ball Grid Array) packages with its easy formation of large number of pins and its easy mounting, have attracted much attention, and have thus been widely studied.

About the encapsulating resin for this BGA, there has been

a problem in that warpage arises from the mismatch of the thermal expansion coefficients between an encapsulating resin and a substrate. As a means to solve this problem, resins having a high heat resistant property and a low thermal expansion coefficient have been required, and a development focusing on an epoxy resin has been conducted. However, there is a limit in the performance of an epoxy resin, and a fully satisfactory resin has not been obtained.

On the one hand, it is known that a polyfunctional cyanate resin has an excellent high heat resistant property and a low thermal expansion property, and it is also hitherto known that the resin is used for an encapsulating material in combination with an epoxy resin (U.S. patent No. 5132778).

However, when combining with an epoxy resin of a low melting point or softening point, the softening point of a cyanate resin composition becomes low, the blocking resistance of the resin compounds falls remarkably and the resin compounds themselves become easy to adhere, thus there has been a big problem in preservation stability.

SUMMARY OF THE INVENTION

The object of the present invention is to provide a composition, which has a high heat resistant property, a low thermal expansion coefficient, and an excellent blocking

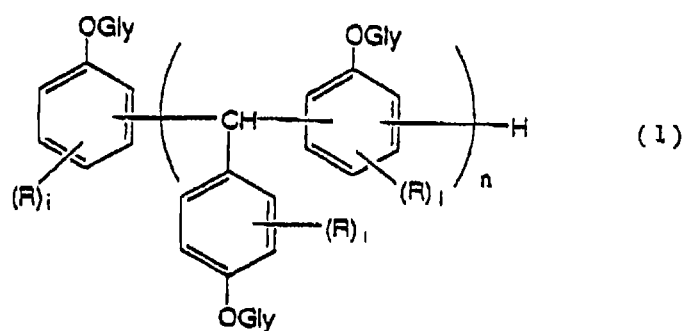
- 3 -

resistance of a resin compound, and a resin-encapsulated type semiconductor device using the same.

In view of such a situation, the present inventors have made extensive studies, and found that the above problem can be solved by combining a cyanate resin and/or its prepolymer with a specific epoxy resin, and thus, completed the invention.

That is, the present invention is as follows.

- (1) A polyfunctional cyanate resin composition comprising (A) a polyfunctional cyanate resin having a functional number of 2 or more or its prepolymer, (B) an epoxy resin having a softening point or melting point of 75°C or more, and (C) a curing catalyst as indispensable components, wherein, the epoxy resin is an epoxy resin represented by the following general formula (1),



in the formula, n represents an average repeating number of 0-10; R represents each independently either hydrogen atom, an alkyl group having 1 to 10 carbon atoms, a cycloalkyl group having 5 to 7 carbon atoms or a hydrocarbon group having 6 to 20 carbon atoms containing a cycloalkyl group having 5 to 7 carbon atoms; the symbol i is each independently an integer of 1-4; when i is two or more, R may be the same, or may differ from each other; and Gly represents glycidyl group.

- (2) The polyfunctional cyanate resin composition comprising the polyfunctional cyanate resin composition described in (1), and (D) an inorganic filler as indispensable

components.

(3) The polyfunctional cyanate resin composition described in (1) or (2), wherein the polyfunctional cyanate resin is a cyanate resin derived from bisphenol A.

(4) A resin-encapsulated type semiconductor device, wherein a semiconductor element
5 is encapsulated using the polyfunctional cyanate resin composition described in (1), (2), or (3).

DETAILED DESCRIPTION OF THE INVENTION

The polyfunctional cyanate resin having a functional number of 2 or more which is a component (A) used in the present invention can be obtained by conducting a
10 dehydrohalogenation reaction of a phenol as a raw material with a cyanogen halide such as cyanogen chloride and cyanogen bromide in a suitable organic solvent.

Examples of a polyfunctional cyanate resin include bifunctional cyanate resins, such as 2,2-bis(4-cyanatephenyl)propane, bis(4-cyanatephenyl)ethane, bis(4-cyanate-3,5-dimethylphenyl)methane, 1,3-bis(4-cyanatephenyl-1-(methyl ethylidene))benzene, bis(4-cyanatephenyl)thioether, bis(4-cyanatephenyl)ether; and polyfunctional cyanate resins derived from, such as phenol novolak and cresol novolak.

The polyfunctional cyanate resin which is a component(A) used in the present invention can be employed appropriately according to requirements. In order to attain the object of the present invention, especially a cyanate resin derived from bisphenol A is suitable from the point of reactivity and heat-resistance.

The polyfunctional cyanate resin used in the present invention may be used as a monomer, and may be also used as a prepolymer.

The prepolymer can be obtained by heating a cyanate resin at 50 - 200°C in a solvent or in bulk as alone or as a mixture of two or more. It can be also obtained by heating to 50 - 200°C in a solvent or in bulk with the curing catalyst which is the below-mentioned component(C).

The epoxy resin having a softening point or melting point of 75 °C or more which is the component (B) used in the present

invention can be obtained, for example, by glycidyl etherification of a phenol, that is, reaction of a phenol with an epihalohydrin in the presence of alkali, such as sodium hydroxide. In order to obtain a highly pure compound, a reaction in an aprotic solvent described in JP-A-60-31517 is applicable.

The softening point or melting point of the epoxy resin used in the present invention is 75°C or more, further suitably 80°C or more.

Examples of these epoxy resins include polyfunctional epoxy resins derived from, such as cresol novolak, naphthalene novolak, and 1,1,2,2-tetra(4-hydroxyphenyl)ethane; bifunctional epoxy resins derived from, such as bisphenol S, dihydroxy stilbene, and tetramethyl dihydroxy biphenyl; and the epoxy resins represented by the above general formula (1), without being limited thereto.

Examples of the alkyl group having 1 to 10 carbon atoms of R in the above general formula (1) include, methyl group, ethyl group, propyl group, butyl group, hexyl group, nonyl groups, or isomers thereof. Example of the cycloalkyl group having 5 to 7 carbon atoms include cyclopentyl group, cyclohexyl group, etc. Furthermore, examples of the hydrocarbon group having 6 to 20 carbon atoms containing cycloalkyl group having 5 to 7 carbon atoms include benzyl group, phenetyl group, styryl group, mesityl group, etc., without being limited thereto.

Among them, especially the epoxy resin represented by the above-mentioned general formula (1) is favorable in order to attain the object of the present invention.

The polyfunctional cyanate resin and the epoxy resin having a softening point or melting point of 75 °C or more which are used in the present invention can be formulated in appropriate compounding ratios. In order to attain the object, the formulation amount of the polyfunctional cyanate resin is suitably 20% - 90%, more suitably 30% - 70%. When the formulation amount of a polyfunctional cyanate resin becomes low, the heat resistance of a cured product will fall. When the formulation amount becomes high, the blocking resistance of a resin compound will fall.

The curing catalyst which is the component (C) used in the present invention is a curing catalyst for a cyanate resin, and known catalysts can be used. Examples are, proton acids represented by hydrochloric acid and phosphoric acid; Lewis acids represented by aluminum chloride, a boron trifluoride complex, and zinc chloride; aromatic hydroxy compounds represented by phenol, pyrocatechol, and dihydroxy naphthalene; metal organic salts such as zinc naphthenate, cobalt naphthenate, tin octylate, cobalt octylate, etc.; metal organic complexes such as copper acetylacetonate, aluminum acetylacetonate, etc.; tertiary amines such as triethyl amine,

tributyl amine, quinoline, isoquinoline, diazabicyclo[2, 2, 2]octane, etc.; quaternary ammonium salts represented by tetraethylammonium chloride and tetraethylammonium bromide; imidazoles; and sodium hydroxide, sodium methyllate, triphenyl phosphine, or these mixtures.

Among these curing catalysts, metal organic salts such as zinc naphthenate, cobalt octylate and tin octylate, metal organic complexes such as copper acetylacetonate, imidazoles, phenols, or these mixed catalysts are suitably exemplified.

The curing catalyst used in the present invention can be used in appropriate amount. As for encapsulating use, it is usually formulated so that the gel time of a composition becomes 10 seconds - 10 minutes at a setting temperature of 100°C - 250°C.

Examples of the inorganic filler which is the component(D) used in the present invention include silica, alumina, titanium white, aluminum hydroxide, talc, clay, glass fiber, etc., and silica and alumina are preferable. These can be used as a mixture of those having various forms (spherical or crushed) or various sizes, and can be also used with increasing the filling amount.

The filling amount of the inorganic filler is 25-92 % by weight in the whole resin composition, and suitably 70-90 % by weight. When the amount is little, a problem will occur in moisture absorption characteristics, such as the solder heat resistance after moisture absorption, or the volume resistivity

after moisture absorption. Moreover, when exceeding 92%, a problem in moldability will occur.

In the resin composition of the present invention, a mold lubricant such as a natural wax, a synthetic wax, a higher fatty acid and its metal salts, and a paraffin; or a colorant like carbon black; a surface treatment agent like a silane coupling agent etc. further may be added according to requirements. Moreover, flame retardants, such as antimony trioxide, a phosphorous compound, and a brominated epoxy resin, may be added.

In order to lower the stress, various elastomers can be added, optionally with having reacted beforehand. Examples of the elastomers include polybutadiene, butadiene-acrylonitrile copolymer, silicone rubber, and silicone oil, or a reactive type elastomer.

In order to encapsulate an electronic device such as a semiconductor and to produce a resin-encapsulated type semiconductor device with using the resin composition of the present invention, cure molding can be carried out by a well-known molding method such as transfer molding, compression molding, or injection molding.

In the resin composition of the present invention, other thermosetting resins can be used together within the range which does not injure the purpose. For example, bismaleimides, the

addition polymerization products of bismaleimide with diamine; alkenylaryl ether or amine resins such as a bis-vinylbenzylether compound of bisphenol A, and vinylbenzyl compounds of diaminodiphenylmethane; alkynylether or amine resins such as a dipropargylether of bisphenol A, and a dipropargyl compound of diaminodiphenylmethane. In addition to these, phenol resins, resol resins, allylether type compounds, allylamine type compounds, isocyanates, triallylisocyanurates, triallylcyanurates, vinyl group containing polyolefin compounds, etc. are exemplified. It is possible to also add a thermoplastic resin. For example, polyphenylene ether, polystyrene, polyethylene, polybutadiene, polyimides, polycarbonates, polyacrylates, poly methacrylates, and modifications thereof are exemplified. These resins can be mixed in the cyanate resin composition, and also can be used with having reacted beforehand.

EXAMPLES

Examples of the present invention are shown below, but the present invention cannot be limited to these.

Synthetic Example 1

This example is a synthetic example of a cyanate resin prepolymer used in the present invention.

2,2-bis(4-cyanatephenyl)propane 2000g was charged into a

3 liter flask equipped with a thermometer and a reflux condenser. This was heated to melt in an oil bath, and after the inner temperature reached to 150°C, mechanical stirring was conducted for 15 hours and a cyanate prepolymer was obtained.

Synthetic Example 2

This example is a synthetic example of an epoxy resin used in the present invention.

Into a reactor equipped with a thermometer, a stirrer, and a condenser having a separation tube, 2-t-butyl-5-methylphenol 328g, p-hydroxybenzaldehyde 122g, and toluene 450g were charged. Then 0.95g of p-toluenesulfonic acid (monohydrate) was charged. By azeotropically distilling toluene and water at 113-120°C under atmospheric pressure, condensation reaction was carried out for 8 hours, while returning only a toluene layer to the system. After neutralization with sodium hydroxide, toluene and the unreacted monomer were distilled off, and a polyhydric phenol was obtained.

Then, the polyhydric phenol (1 equivalent amount of phenolic hydroxy group) was charged into a reaction container equipped with a thermometer, a stirrer, a dropping funnel, and a condenser having a separation tube, and was dissolved in epichlorohydrin 462.6g and dimethyl sulfoxide 231.3g.

40% sodium hydroxide aqueous solutions 100g was added dropwise continuously for 5 hours, maintaining the reaction

system at 45 Torr. In the meantime, the cooling liquefaction of azeotropically boiled epichlorohydrin and water was carried out, with maintaining the temperature at 45°C, and returning the organic layer to the reaction system.

After the reaction, unreacted epichlorohydrin was removed by vacuum distillation. The glycidylether containing by-produced salts and dimethylsulfoxide was dissolved in methylisobutylketone, then the by-produced salt and dimethyl sulfoxide were removed by washing with water. Furthermore methylisobutylketone was removed by vacuum distillation and the desired epoxy resin was obtained. The softening point of the resultant epoxy resin was 83°C, and the average repeating number was 1.7.

Example 1

Various compositions described in Table 1 were compounded with the formulation ratio described in the table, and heat-kneading was carried out with using a two roll mill (the temperatures of the rolls were set to 110 °C and 50 °C, respectively). Then, transfer molding was carried out at 175°C, finally after-cure was performed for 180°C x 5 hours in an oven, and a cured product was obtained. The physical properties of the resultant cured product are shown in Table 1.

Details of the components are as follows.

ESCN-195: Epoxy resin (made by Sumitomo Chemical Co.,Ltd.,

softening point 65°C)

PSM-4261: Phenol novolak (made by Gun-ei Chemical Industry Co., Ltd.)

SH-6040: Coupling agent (made by Toray Dow Corning)

FB-60: Spherical silica (made by Denki Kagaku Kogyo K.K.)

FS-891: Crush silica (made by Denki Kagaku Kogyo K.K.)

Comparative Examples 1-3

Cured products were obtained in the same manner with Example 1, except that the formulation of the composition were as shown in Table 1. The physical properties of the resultant cured products are shown in Table 1.

The physical properties were measured by the following methods.

Glass Transition Temperature, and thermal expansion coefficient (α 1) : Determined from the inflection point of a thermal expansion curve using a thermal analyzer TMA120 made by Seiko Instruments Inc. α 1 is the average value from 50°C to 100°C

Blocking Resistance : Resin compositions kneaded by a roll were kept in 40°C oven, and observed the state of the compound. ○ means that there is no blocking of the compound, and × means that blocking of the compound occurs.

Softening Point : Determined by RING&BALL method.

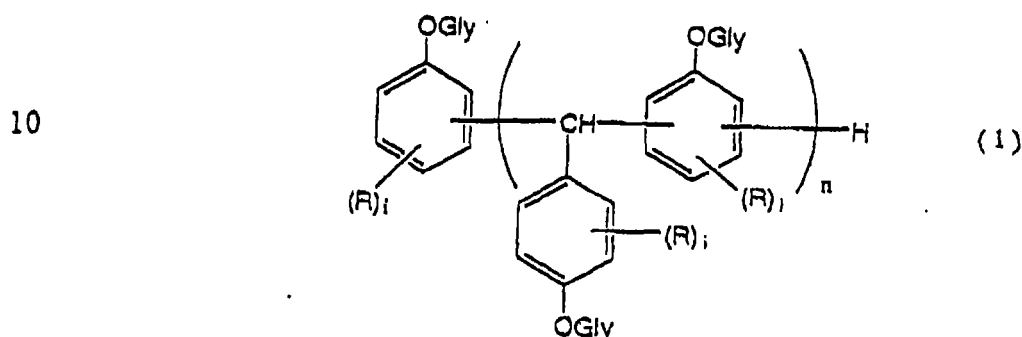
Table 1

	Example 1	Comparative Example 1	Comparative Example 2	Comparative Example 3
Cyanate prepolymer	49.61	49.61	—	—
Epoxy resin of synthetic example 2	49.61	—	66.53	—
ESCN-195	—	49.61	—	64.37
PSM-4261	—	—	32.80	34.99
Zinc naphthenate	0.40	0.40	—	—
Triphenyl phosphine	—	—	1.00	0.97
Carnauba wax	1.49	1.49	1.00	0.97
SH-6040	1.98	1.98	1.33	1.29
FB-60	317.52	317.52	317.87	317.94
FS-891	79.38	79.38	79.47	79.49
Filler content (%)	80	80	80	80
Tg (TMA method)	189	185	173	15.1
α 1(ppm/°C)	10.4	10.1	13.6	14.7
Blocking resistance	○	×	○	○

The polyfunctional cyanate resin composition of the present invention is excellent in a high heat resistant property or a low thermal expansion property. The blocking resistance of the resin compound is also still good. The resin-encapsulated type semiconductor device using this resin composition is useful as a BGA use for which high heat resistant property and low expansion property is required.

What is claimed is:

1. A polyfunctional cyanate resin composition comprising (A) a polyfunctional cyanate resin having a functional number of 2 or more or its prepolymer, (B) an epoxy resin having a softening point or melting point of 75°C or more, and (C) a curing catalyst as indispensable components, wherein, the epoxy resin is an epoxy resin represented by the following general formula (1),



15

- in the formula, n represents an average repeating number of 0-10; R represents each independently either hydrogen atom, an alkyl group having 1 to 10 carbon atoms, a cycloalkyl group having 5 to 7 carbon atoms or a hydrocarbon group having 6 to 20 carbon atoms containing a cycloalkyl group having 5 to 7 carbon atoms; the symbol i is each independently an integer of 1-4; when i is two or more, R may be the same, or may differ from each other; and Gly represents glycidyl group.
- 20

2. The polyfunctional cyanate resin composition comprising the polyfunctional cyanate resin composition described in claim 1, and (D) an inorganic filler as indispensable components.
- 25

3. The polyfunctional cyanate resin composition according to claim 1 or 2, wherein the polyfunctional cyanate resin is a cyanate resin derived from bisphenol A.

4. A resin-encapsulated type semiconductor device, wherein a semiconductor element is encapsulated using the polyfunctional cyanate resin composition described in claim 1, 2, or 3.
- 30