

EPOXY RESIN COMPOSITION FOR SEMICONDUCTOR SEALING AND SEMICONDUCTOR DEVICE

FIELD OF THE INVENTION

The present invention relates to an epoxy resin compound used for sealing of semiconductor devices, which consist of a well disperse raw materials especially fine filler and consequently provided an excellent flowability epoxy resin compound.

RELATED ART STATEMENT

Electronic parts such as diodes, transistors, integrated circuits and the like have been sealed with a thermosetting resin. In integrated circuits, in particular, there is used as such a thermosetting resin, an epoxy resin having excellent heat resistance and moisture resistance, obtained by curing an o-cresol novolak epoxy resin with a novolak type phenolic resin.

However epoxy resins cannot act as encapsulants themselves due to their high coefficient of thermal expansion (CTE) and low thermal conductivity. Many other additives, such as inorganic filler, coloring agent, stress-relief agent, accelerator and etc are employed with epoxy resin to enhance the performance of epoxy resin compound. Yet, some of those additives, especially the fine inorganic fillers are colloidal in nature and easy to agglomerate and aggregate together during mixing, consequently affect the homogeneity of the epoxy resin compound.

Fillers are employed in epoxy resins for many reasons. The main functions of filler are to control the viscosity, reduce the mold shrinkage and coefficient of thermal expansion. However due to the aggregation of the fine fillers, the epoxy resin compound materials are not well mixed and are not well dispersed as a result affect the uniformity of the compound and the consistency of the compound properties.

In recent years, with higher integration of integrated circuits, chips have becomes larger and surface-mounted have been gradually switched from DIP (Dual Inline Package) to small thin flat packages such as SOP (Small Outline Package), SOJ (Small Outline J-leads), PLCC (Plastic Leaded Chip Carrier) and the like. This is followed by the industrial trend towards more condensed packages such as the BGAs, Chip Size Packages (CSP), Flip Chip (FC), non-lead packages and the like. Thus, large chips are sealed in a small thin package. This, however, produces problems such as generation of cracks caused by stress, reduction in moisture resistance caused by said cracks, and the like.

In the soldering step, in particular, the package is suddenly exposed to high temperature of 200°C or above, which invites cracking of the package or separation of sealing resin from chips, which causes reduction in moisture resistance.

Hence, it is necessary to improve the homogeneity of epoxy resin compound for better quality and consistent performance and it is also desired to develop a resin composition which can be suitably used for sealing of large chips at high reliability.

OBJECT AND SUMMARY OF THE INVENTION

The objective of this invention is to provide an epoxy resin compound consists of the well dispersed of raw materials, especially those raw materials which are in fine powder form and hereby given homogenous compound with consistent performance and even better flowability.

According to a first aspect of the present invention, there is provided an epoxy resin composition used for sealing of semiconductor devices, comprising:
an inorganic filler, with an amount of 75% or above and less than 95% by weight based on the total resin composition;
an epoxy resin,
a phenolic resin curing agent,
a curing accelerator,
a ammonia type of humic acid as a dispersing agent which is present in an amount of 0.01% or above and less than 1% by weight based on total epoxy resin composition.

According to a second aspect of the present invention, there is provided a semiconductor device which has been manufactured using the epoxy resin composition as defined above.

DETAILED DESCRIPTION OF THE INVENTION

Coarse particles, for example in the size of 1-5 mm, has negligible attractive forces between two particles compared to the weight of a particles. However, when the size of particles is reduced, the weight of the particle drops more rapidly then the attractive force between particles, and at some points the particles will start to stick to each other.

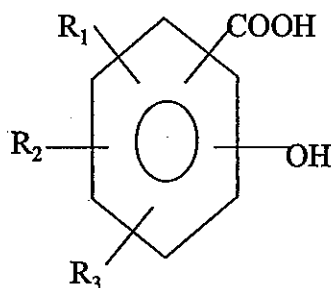
A well disperse raw materials of epoxy resin compound is essential for obtaining a homogeneous compound which leads to consistent of compound properties. The epoxy resin compound can content inorganic filler which has an average size 10-30 μm or even smaller from 70% up to 95% by weight. In view of the small size of filler, filler has the tendency of agglomeration during mixing which might be due to the following interparticle forces; electrostatic forces, Van der Waals force and forces caused by moisture.

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The humic acid supplied from Telmite Co., Ltd. which is a group of aromatic acids with high molecular weight and can be obtained from soil, peat or brown coal has the following formulation, $(C_6H_6)R_1R_2R_3(COOH)(OH)$, where R_1 , R_2 and R_3 can be any organic functional group. Ammonia type of humic acid has

size about 10nm, it will attach to particle and has the capability of increasing the electrical change on particle surface. Due to the increase of particle's surface electrical change, the particle and particle will repulse each other and hence to prevent agglomeration.

Humic Acid



Wherein R_1 , R_2 and R_3 are the same or different group with the structure of C_nH_{2n+1} , where n is an integer from 1 to 20.

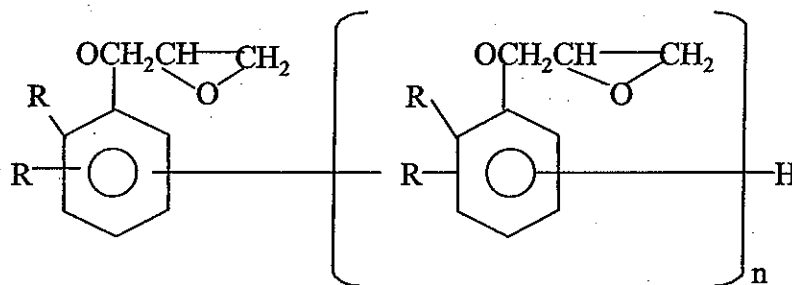
Filler is able to breakup after mixing with additional 0.1-0.5% ammonia type of humic acid as a dispersion agent. This can be shown on the "acetone insoluble" test, or so-called UPA test, the amount of insoluble particle in percentage was reduced with the additional of 0.1-0.5% ammonia type of humic acid. Because of the well disperse of the filler, the flowability of epoxy molding compound showed improvement. The spiral flow length of sample with 0.1-0.5% ammonia type of humic acid showed longer than the compound without it. And also due to better dispersing of raw material, samples with dispersing agent showed less bleeding out of epoxy resin and showed stronger adhesion strength to copper material surface. However, if more than 0.5% of humic acid was added into the compound, the electrical properties of compound will be affected which can be shown on the electric conductivity (EC).

According to this invention, at the package level it also showed not changed in anti-solder crack performance and even better highly accelerated stress test (HAST) performance.

When another epoxy resin is used in combination with the biphenyl type epoxy resin of formula (I) or (II) or (III), the other epoxy resin is an ordinary polymer

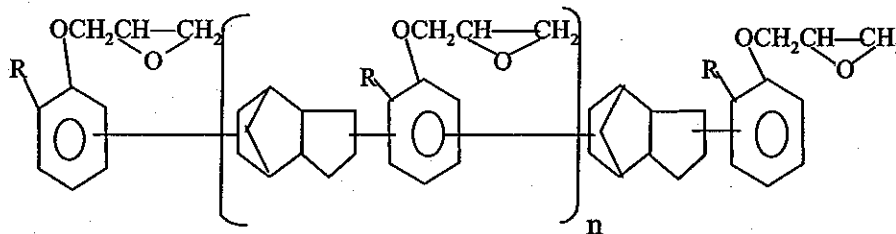
having epoxy groups. There are cited, for example, bisphenol type epoxy resins, phenol novolac type epoxy resins, trifunctional epoxy resins (e.g., triphenolmethane type epoxy resins, and alkylmodified triphenolmethane type epoxy resins) and triazine nucleus-contained epoxy resins.

Formulation (I)



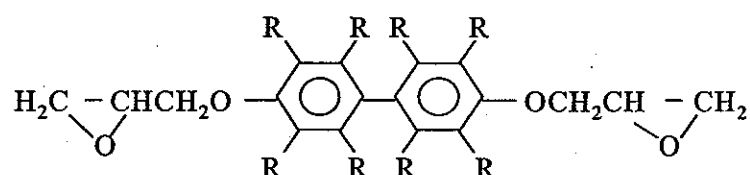
Wherein n is an integer of 0-5 and each R is independently an atom or group selected from hydrogen atom, a halogen atom and an alkyl group.

Formulation (II)



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

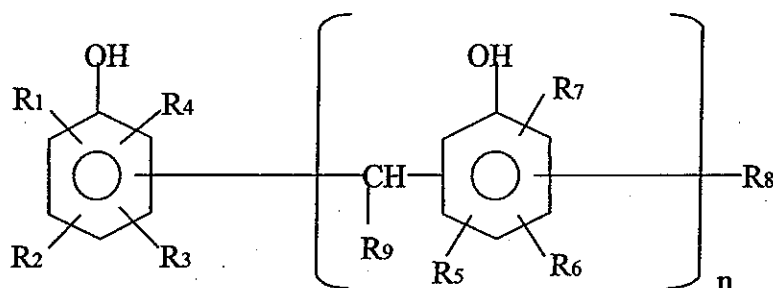
Formulation (III)



Wherein R is independently an atom or group selected from hydrogen, halogens and alkyl group.

When another phenolic resin curing hardener is used in combination with the phenolic resin curing hardener represented by formula (IV), the other phenolic resin curing hardener is an ordinary polymer having hydroxyl groups.

Formulation (IV)



Wherein n is an integer of 1-6 and each R_1 - R_8 are the same or different atoms or group selected from hydrogen, halogen and alkyl groups, R_9 is a group selected from phenyl, naphthyl, anthracenyl and alkyl groups.

There can be cited, for example, dicyclopentadiene-modified phenolic resins, copolymers between dicyclopentadiene-modified phenolic resin and phenol novolac resin and/or cresol resin, and paraxylene-modified phenolic resins.

As the inorganic filler used in the present epoxy resin composition, there can be cited fused silica powder; spherical silica powder; crystalline silica powder; secondary agglomerated silica powder; porous silica powder; silica powder obtained by grinding secondary agglomerated silica powder or porous silica powder; alumina, etc. Fused silica powder, spherical silica powder and mixture of above two silica powders are preferable. The amount of the inorganic filler in the present composition is preferably 70-90% by weight in view of balance between the soldering stress resistance and moldability of the 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). There can be widely used those curing accelerators generally used in sealing materials, 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 0.4 wt % in the

total epoxy resin composition. In an amount less than 0.1 wt %, hardness of the resulting molded product decreases and mold release characteristics tend to deteriorate. In an amount more than 0.4 wt %, 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, flame retardant (e.g. brominated epoxy resin, antimony trioxide or hexabromobenzene), coloring agent (e.g., carbon black or red iron oxide), 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, filler and other additives are mixed sufficiently and uniformly 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 part or electric parts.

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:

o-Cresol novolak type of epoxy compound (softening point: 55-62°C, epoxy equivalent: 196g/eq) represented by formulation (I)

11.4 parts by weight.

Phenol novolak resin curing agent (softening point: 80 -100°C, hydroxyl equivalent =104) represented by formulation (IV)

4.6 parts by weight

Triphenylphosphine (TPP)

0.2 parts by weight

Fused silica powders (average particle size of 20 μ)

82.7 parts by weight

Ammonia type Humic Acid (Telmite Co., Ltd, #CH-07)

0.2 parts by weight

Carbon Black

0.3 parts by weight

Wax

0.6 parts by weight

The mixed powder was kneaded at 70-100°C, using a bi-axial roll, cooled and ground to obtain a molding material.

About 100g of the mixed powder was collected from the mixed powder before the kneading was started. About 200ml of acetone was added into a bottle together with the collected powder. The bottle was being shake for 20 minutes with a vibrator. After shaking, the mixture was poured onto a 212 micron m sieve. The sieve was washed with acetone until only the insoluble particles remain and was dry in an oven at 80-100°C for about 5 minutes then the insoluble particles was transferred onto a waxed paper and was weighted. The acetone insoluble content is calculated as follows:

Acetone Insoluble Content(wt%)

$$=(\text{Weight of Insolubles from 212 m sieve} / 100\text{g}) \times 100\%$$

A certain amount of molding material which shall give a cull thickness of $3 \pm 0.3\text{cm}$ was weighted. A spiral flow mold die was placed in the molding machine and was heated up to 175°C. When the temperature reaches 175°C, the certain amount of molding material was poured into the transfer pot and plunger was lower. The material was molded for 120sec then the mold press was opened, the spiral flow length (up to the lustrous tip) was measured after the mold die was taken out from the molding machine.

The molding material was also molded into a 5mm X 20mm test pieces under the conditions of 175°C, 70kg/cm² and 120sec using a 30ton transfer molding machine. The molded test pieces were subjected to 4 hours post-mold cured at 175°C and then were milled into powder. 3 grams of the powder was weighted. 3ml of ethanol and 40 ml of distillation water were added into the sample and then subjected to an oven set at 125°C for another 20 hours. Finally, the electric conductivity(EC) of the sample was tested by conductivity meter.

The results of the above-mentioned tests are shown in Table 1.

EXAMPLE 2-3

According to the formulation shown in Table 1, the components were blended and resin compositions were obtained and the tests were obtained in the same manner as in Example 1. The test results obtained are shown in Table 1.

Comparative Example 1-2

According to the formulation shown in Table 1, the components were blended and resin compositions were obtained and the tests were obtained in the same manner as in Example 1. The test results obtained are shown in Table 1.

Table 1:

	Example			Comparative Example	
	1	2	3	1	2
Formulation					
o-cresol novolak type epoxy resin	11.4	11.4	11.4	11.4	11.4
Phenol novolak resin	4.6	4.6	4.6	4.6	4.6
Fused silica powder	82.4	82.7	82.8	82.9	81.9
Ammonia type humic acid (Telmite Co., Ltd. Grade name: CH-07)	0.5 <i>0.2 x 0.5 = 0.1</i>	0.2 <i>0.04</i>	0.1 <i>0.02</i>	0	1.0
TPP	0.2	0.2	0.2	0.2	0.2
Carbon Black	0.3	0.3	0.3	0.3	0.3
Wax	0.6	0.6	0.6	0.6	0.6
Physical Properties					
Spiral Flow, cm	105	105	110	100	90
Acetone Insoluble Content, %	1.6	1.2	2.2	4.6	4.0
Electric Conductivity, micro s/cm	85	50	50	70	110

Example 4-5

Epoxy resin compositions are compounded in the respective recipes shown in Table 2, and subjected to the same procedures as in Example 1 to obtain molding materials.

The molding material was made into tables and then into chips of 7.5 mm X 7.5 mm under the conditions of 175°C, 70kg/cm² and 120sec using a low pressure transfer molding machine. 100L QFP (100-pin Quad flatpack) packages were sealed with these chips to obtain devices for solder cracking test. The tablets were also made into chips of 3 mm X 6 mm, and 16L PDIP (16-pin plastic dual-in-line) were sealed with the chips to obtain devices for solder moisture resistance test.

The devices for test purposes were subjected to the following solder cracking test highly accelerated stress test (HAST). The results are showed in Table 2.

Solder cracking test

The devices for solder cracking test were allowed to stand in an atmosphere of 85°C and 60% R. H. for 48 hours and 168 hours. Then, the devices were

passed through the IR reflow oven of 220°C as peak temperature for 10seconds. Thereafter, the cracks present at the surfaces of the devices were observed using a microscope. The result is expressed by the number of cracked devices/ total number.

Highly Accelerated Stress Test

The devices were subjected to a pressure cooker test (125°C, 100% RH. 2atm and 20V), after which circuit opening was examined. The results are expressed by average life (hr).

Comparative Examples 3-4

Epoxy resin compositions are compounded in the respective recipes shown in Table 2, and subjected to the same procedures as in Example 1 to obtain molding materials. Devices for test purposes are prepared using these molding materials and subjected to the solder cracking test and HAST test. The results are shown in Table 2.

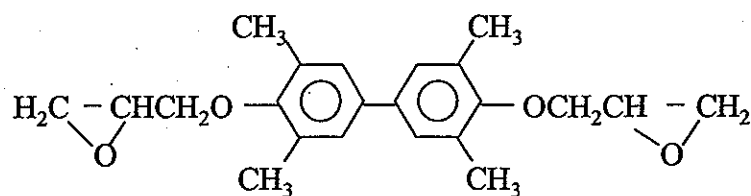
Table 2:

	Example		Comparative Example	
	4	5	3	4
Formulation				
Bi-Phenyl type Epoxy Resin represented by formulation (VII)	0	2.9	0	2.9
<i>o</i>-cresol novolak type epoxy resin represented by formulation (V)	0	3.4	0	3.4
Di-cyclopentadiene type Epoxy Resin represented by formulation (VI)	11.4	0	11.4	0
Phenol novolak resin	4.5	3.1	4.5	3.1
Fused silica powder	82.6	89.1	82.9	89.4
Ammonia type humic acid (Telmite Co., Ltd. Grade name=CH-07)	0.3	0.3	0	0
TPP	0.2	0.4	0.2	0.2
Carbon Black	0.4	0.3	0.4	0.4
Wax	0.6	0.5	0.6	0.6
Physical Properties				
Spiral Flow, cm	112	84	74	81
Acetone Insoluble Content, %	1.04	1.41	2.41	2.18
Soldering crack resistance test @	3/12	5/6	2/12	5/6

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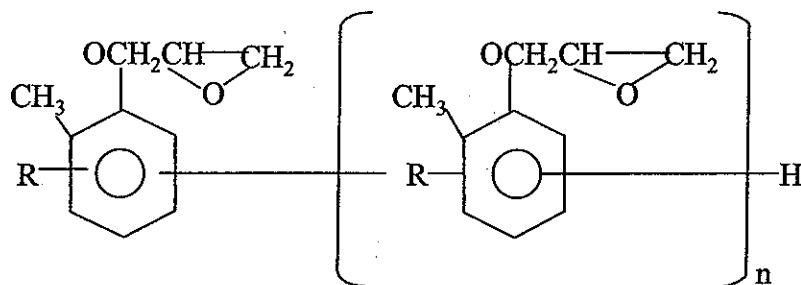
85°C, 60%RH, 168hrs				
HAST on 16LPDIP @ 125°C, 100% RH, 20 V	>200 hrs	>200 hrs	80 hrs	70 hrs
Average life (hrs)				

Formulation (VII)



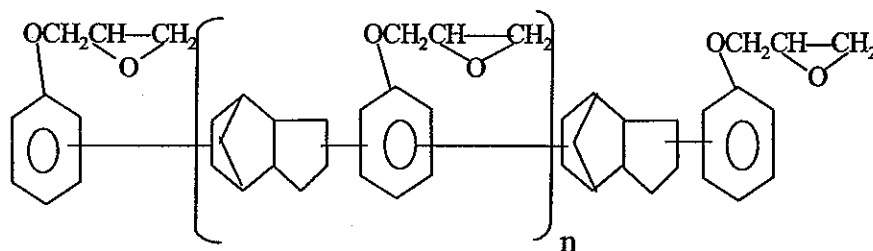
Wherein n is an integer of 0-5,

Formulation (V)



Wherein n is an integer of 0-5,

Formulation (VI)

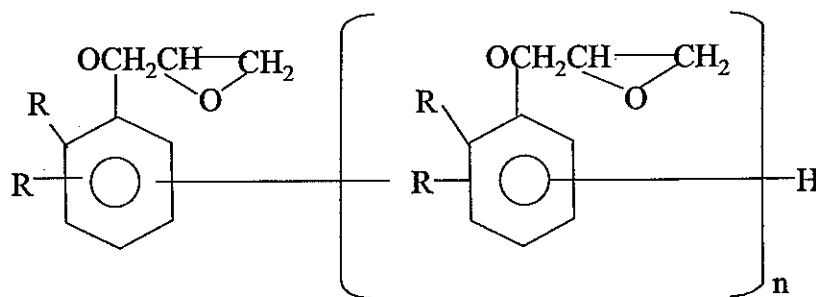


Wherein n is an integer of 0-5.

Claims:

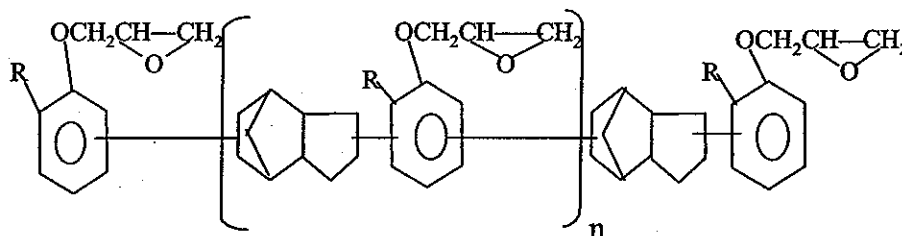
1. An epoxy resin composition used for sealing of semiconductor devices comprising:
 an inorganic filler with an amount of 75% or above and less than 95% by weight based on the epoxy resin composition;
 an epoxy resin;
 a phenolic resin;
 a curing accelerator; and
 an ammonia type of humic acid as a dispersing agent which is present in an amount of 0.01% or above and less than 1% by weight based on the epoxy resin composition.
2. An epoxy resin composition of claim 1 wherein the inorganic filler has an average size 10-30 μm .
3. An epoxy resin composition of claim 1 or 2 wherein said epoxy resin is represented by formulation (I), (II) or (III), or mixtures thereof.

Formulation (I)



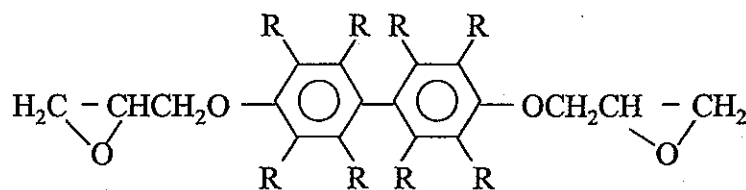
Wherein n is an integer of 0-5 and each R is independently an atom or group selected from hydrogen atom, a halogen atom and an alkyl group

Formulation (II)



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

Formulation (III)



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

4. An epoxy resin composition of any one of the preceding claims wherein a curing accelerator is present in an amount of 0.05-1% by weight based on the epoxy resin composition.

5. A semiconductor device which has been manufactured using the epoxy resin composition of any one of the preceding claims.