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LIQUID EPOXY RESIN POTTING MATERIAL
TECHNICAL FIELD OF THE INVENTION

The present invention relates to a liquid epoxy resin potting material which is used for potting semiconductors.

5 PRIOR ART

The lower cost and higher integration trends in semiconductor packaging have changed the packaging form used from the conventional transfer molding DIP (dual inline package) to COB (chip on board), PPGA
10 (plastic pin grid array), and the like. A liquid potting material is used for potting the PPGA-type semiconductor, but it is not satisfactory in reliability compared to a ceramic-based hermetic potting type. The causes for this include, for example, moisture
15 penetrating through the package-fabricated organic printed circuit boards. Moreover, unlike transfer molding DIPs, a liquid potting material under no pressure, when allowed to flow and be molded, results in residual gas bubbles which lead to cracks when subjected
20 to thermal stresses. Furthermore, when the potting material has a different coefficient of linear expansion from that of the semiconductor chip or the organic baseboard, a delamination occurs at the interface when

subjected to a thermal stress, which facilitates moisture penetration.

OBJECT AND SUMMARY OF THE INVENTION

Intensive study of a way to solve the prior art problems has led to the finding that a composition comprising a specific epoxy resin, aromatic diamine, and elastomer, along with an inorganic filler, provides a potting material with substantially improved semiconductor reliability in an accelerated test such as the PCT (pressure-cooker test) or T/C (cold-heat cycle test), and the like, resulting in the present invention.

The present invention provides a liquid epoxy resin potting material mainly comprising (A) a liquid epoxy resin, (B) a liquid alkylated diaminodiphenylmethane, (C) an epoxidized polybutadiene, and (D) an inorganic filler, wherein the ratios of the individual components in weight ratios are:

$$(A)/[(A)+(B)] = 0.65 - 0.80$$

$$(C)/[(A)+(B)] = 0.01 - 0.05$$

and

$$(D)/[(A)+(B)+(C)+(D)] = 0.50 - 0.80.$$

This potting material can substantially improve the reliability of the PPGA-type semiconductor that uses an organic printed circuit board.

DETAILED DESCRIPTION OF THE INVENTION

At least 50% by weight of the liquid epoxy

resin component used in this invention preferably has a viscosity at 25°C of not more than 8Pa·s. If at least 50% by weight of the epoxy resin component is not a low-viscosity epoxy, the viscosity of the composition will increase, tending to entrain gas bubbles or to not completely fill to the corner edges when the PPGA package is potted by allowing the liquid potting material to flow, leading to undesirable decreases in reliability. The method for measuring the viscosity of the epoxy resin involves a measurement using an E-type viscometer (manufactured by Toki Sangyo KK) at 25°C if the sample is liquid at room temperature, and a measurement at 150°C using a high temperature cone plate viscometer if the sample is solid at room temperature.

Any epoxy resin can be used as long as it meets the above requirements and these are not particularly limited, but they are specifically, for example, bisphenol-A diglycidyl ether-type epoxy resin, bisphenol-F diglycidyl ether-type epoxy resin, bisphenol-S diglycidyl ether-type epoxy resin, 3,3',5,5'-tetramethyl-4,4'-dihydroxybiphenyl diglycidyl ether-type epoxy resin, 1,6-dihydroxynaphthalene diglycidyl ether-type epoxy resin, phenol novolak-type epoxy resin, cresol novolak-type epoxy resin, brominated bisphenol-A diglycidyl ether-type epoxy resin, brominated cresol novolak-type epoxy resin, and the like, which may be used singly or in mixtures thereof.

The liquid alkylated diaminodiphenylmethane used in this invention is a diaminodiphenylmethane where 1, 2, or more of the hydrogen atoms of the benzene rings are substituted by an alkyl group such as methyl, ethyl, 5 or the like; having no such alkyl group with 4 or fewer carbon atoms is not preferred because the composition will have a higher viscosity, which tends to entrain gas bubbles or to not completely fill to the corner edges when the package is potted by allowing the liquid 10 potting material to flow in, leading to reduced reliability.

Any of alkylated diaminodiphenylmethanes which satisfy the above requirements can be used with no particular limitation and they are specifically, for 15 example, 3,3'-diethyl-4,4'-diaminodiphenylmethane, 3,3',5,5'-tetramethyl-4,4'-diaminodiphenylmethane, 3,3',5,5'-tetraethyl-4,4'-diaminodiphenylmethane, and the like, which may be used singly or in mixtures thereof.

20 It is preferred for the compounding ratio of the liquid epoxy resin (A) and liquid alkylated diamino-diphenylmethane (B) by weight to be in the range of $(A)/[(A)+(B)] = 0.65 - 0.80$. If the ratio $(A)/[(A)+(B)]$ exceeds 0.80, this results in an increased number of 25 unreacted epoxy groups, which decreases the heat resistance such as the glass transition temperature and the like, and which causes an undesirable reduction in reliability in the cold-heat cycle test. On the

other hand, a ratio below 0.65 is not preferred due to decreased storage life for the composition.

The epoxidized polybutadiene (C) used in this invention preferably has a number average molecular weight of 1,000 to 5,000. It is not preferred for it to be less than 1,000 due to a decreased flexibilizing effect while a level exceeding 5,000 increases the viscosity and decreases the workability, which is not preferable. The epoxy group content (mole% fraction incorporated into the main chain) is preferably 3% to 10%. A mole fraction less than 3% is not preferred because the epoxidized polybutadiene will lack compatibility with the liquid epoxy resin (A), while a level exceeding 10% is not preferred because this will result in epoxy group's cross-linking with a hardening agent, and failing to take on a "sea-island" structure with no prospect of reducing stress, thereby reducing the flexibilizing effect. Using the epoxidized polybutadiene (C) in the range of a compounding weight ratio of $(C)/[(A)+(B)] = 0.01 - 0.05$, provides a relaxation effect against thermal stresses, which occur during the cold-heat cycle test. A ratio less than 0.01 is not preferred due to a meager effect of improving stress relaxation, nor is a level exceeding 0.05 preferred, because that will give a cured product with a decreased glass transition temperature, a rise in composition viscosity, and a reduced compatibility, and cause a blooming to the surface of the cured product.

The inorganic filler (D) includes fused silica, crystalline silica, and the like. It is available, in general, in spherical form, ruptured form, and the like, but a spherical form filler is most preferred in order to permit incorporating a large amount of filler to reduce the coefficient of linear expansion. It is preferred for the inorganic filler (D) in a weight compounding ratio to be in the range of $(D)/[(A)+(B)+(C)+(D)] = 0.50 - 0.80$. A level below 0.50 is not preferred because of its small effect of reducing the coefficient of linear expansion, nor is a level exceeding 0.80 preferred, because it will increase the viscosity of the composition, thereby decreasing workability. In general, a small-particle-size filler increases the viscosity of the resin composition, resulting in decreased flow and in gas bubble entrainment and insufficient fillings. On the other hand, a large-particle-size filler tends to undergo a sedimentation, which results in nonuniform filler distribution. The nonuniform filler distribution will give portions of the composition with different coefficients of linear expansion, and top portions having lower amounts of filler tending to experience more crack formation. If the largest particle size is greater than a wire interval, there will be a tendency to insufficiently fill underneath the wires and a short-circuiting problem due to wire distortion.

A study of the way to solve the above problems has led to the finding that compounding (a) a spherical silica of an average particle size of 0.1 - 3.0 μm and a maximum particle size not more than 10 μm , and (b) a
5 spherical silica of an average particle size of 4 - 10 μm and a maximum particle size not more than 50 μm at a weight ratio of $(a)/(a)+(b)] = 0.05 - 0.50$ enables suppression of sedimentation without losing flow characteristics. Any silica which satisfies these
10 requirements can be used without limitations. Each of (a) and (b) may be used singly or in blends of two or more kinds.

The particle size distribution and average particle size were measured by a laser-type method
15 (Horiba LA-500), where the average particle size was based on a median size.

The liquid potting material of this invention, as needed, in addition to the above essential components may contain other resins, a catalyst for promoting the
20 reaction, a diluent, a pigment, a coupler, a leveling agent, a defoamer, or the like. The liquid potting material is prepared by dispersing and kneading each of these components and additives and the like, using a three-roll mill followed by vacuum-defoaming.

25 EXAMPLES OF THIS INVENTION

The present invention is now specifically described by the following examples of this invention:

Example 1

The following ingredients were dispersed and kneaded on a three-roll mill and vacuum-defoamed to give a liquid epoxy resin potting material. The resultant
5 epoxy resin potting material was used to pot a PPGA package, followed by oven-curing for three hours at 165°C to give a semiconductor package. The following methods of evaluation were used to confirm the delamination, if any, between the semiconductor chip and print
10 baseboard; the presence, if any, of cracks; and filler sedimentation, and the results are given in Table 1.

- Bisphenol-F-type epoxy resin: 100 parts by weight
(Epoxy equivalent 161; viscosity at 25°C, 1.5 Pa.s)
- 15 • 3,3'-diethyl-4,4'-diaminodiphenylmethane: 40 parts by weight
- Epoxidized polybutadiene: 6 parts by weight
(Number average molecular weight: 1800; epoxy equivalent 250)
- 20 • Spherical fused silica (1): 340 parts by weight
(Average particle size 6 μm ; maximum particle size 48 μm)
- Spherical fused silica (2): 40 parts by weight
(Average particle size 0.5 μm ; maximum
25 particle size 2 μm)
- Composition viscosity:
E-type viscometer, 2.5 rpm, 25°C

- Ease of filling into packages:

The sample was dispensed into a PPGA package at 80°C to confirm the condition of filling in the cavities 5 minutes later.

- 5 • Confirming of delamination or cracks

(1) Normal conditions (after curing)

(2) PCT (pressure cooker test) treatment at 125°C/2.3 atm for 168 hours

10 (3) T/C (cold-heat cycle test) treatment under
-65°C/30 minutes ↔ 150°C/30 minutes, 1,000 cycles

After subjecting the above sample to the above conditions (1), (2) or (3) separately, the delamination between the semiconductor chips and print baseboard and
15 crack formation were confirmed using scanning acoustic tomograph (hereinafter abbreviated as SAT).

- Filler sedimentation:

A cured package was cut across and observed for the cross-section using a scanning electron
20 microscope (hereinafter abbreviated as SEM) to measure the extent of sedimentation from the top of the cured product.

The sample of Example 1 showed no delamination or cracks but slight filler sedimentation, which
25 indicates good reliability. The number of packages used for each evaluation were 10. The results are summarized in Table 1.

Examples 2-6

Comparative Examples 1-6

Liquid epoxy resin potting materials were obtained in a manner similar to that of Example 1, except for using the compounding recipes shown in Table 1 and Table 2, thereby potting the PPGA package to evaluate the reliability of these samples. The results are given in Tables 1 and 2.

The following ingredients were used in Example 1 and other examples:

- Bisphenol-F-type epoxy resin: (manufactured by Dainippon Ink Kagaku Kogyo KK, EXA-830LVP, epoxy equivalent 161; viscosity at 25°C 1.5 Pa·s)
- Bisphenol-A-type epoxy resin: (1): (manufactured by Dainippon Ink Kagaku Kogyo KK, EXA-850CRP, epoxy equivalent 171; viscosity at 25°C 4.5Pa·s)
- Bisphenol-A-type epoxy resin: (2): (manufactured by Yuka Shell Epoxy KK; Epikote 1001, epoxy equivalent 470, solid)
- 1,6-dihydroxynaphthalene-type resin: (manufacture by Dainippon Ink Kagaku Kogyo KK, HP-4032D, epoxy equivalent 140, viscosity at 25°C 25 Pa·s)
- 3,3'-diethyl-4,4'-diaminodiphenylmethane; (manufactured by Nippon Kayaku KK, Kayahard A-A)
- 3,3'-5,5'-tetramethyl-4,4'-diaminodiphenylmethane; (manufactured by Nippon Kayaku K.K., Kayabond C-200)
- Epoxidized polybutadiene: (manufactured by Nippon Sekiyu Kagaku KK, E-1800-6.5, number average

molecular weight 1800, epoxy equivalent 250)

- Spherical fused silica (1): (manufactured by Denki Kagaku Kogyo KK, FB-30, average particle size 6 μm , maximum particle size 48 μm)
- 5 • Spherical fused silica (2): (manufactured by Admatex KK, SO-25R, average particle size 0.5 μm , maximum particle size 2 μm)
- Spherical fused silica (3): (manufactured by Admatex KK, SO-32R, average particle size 2.0 μm , maximum particle size 8 μm)
- 10 • Spherical fused silica (4): (a blend [weight ratio 1:1] of the above spherical fused silicas (2) and (3); average particle size 1.0 μm , maximum particle size 8 μm)
- 15 • Spherical fused silica (5): (manufactured by Denki Kagaku Kogyo KK, FB-25S, average particle size 17.0 μm , maximum particle size 75 μm)

TABLE 1

		Examples					
		1	2	3	4	5	6
Compounding (parts by weight)							
Bisphenol-F-type epoxy resin		100	100	100		100	50
Bisphenol-A-type epoxy resin (1)					100		
1,6-dihydroxynaphthalene-type epoxy resin							50
3,3'-diethyl-4,4'-diaminodiphenylmethane		40	40	40	37	32	43
3,3'-5,5'-tetramethyl-4,4'-diaminodiphenylmethane						5	
Epoxidized polybutadiene		6	6	6	6	6	6
Spherical fused silica (1)		340	230	230	340	300	260
Spherical fused silica (2)		40	160		40		110
Spherical fused silica (3)						80	
Spherical fused silica (4)				160			
Physical Properties							
Composition viscosity (Pa·s)		20	17	18	30	19	35
Ease of package filling		good	good	good	good	good	good
Delamination	After Curing	0	0	0	0	0	0
	After PCT	0	0	0	0	0	0
	After T/C	0	0	0	0	0	0
Cracks	After Curing	0	0	0	0	0	0
	After PCT	0	0	0	0	0	0
	After T/C	0	0	0	0	0	0
Filler sedimentation (μm)		24	Not more than 3	Not more than 3	20	10	5

TABLE 2

		Comparative Examples					
		1	2	3	4	5	6
Compounding (parts by weight)							
Bisphenol-F-type epoxy resin		100	100	100	100	100	30
Bisphenol-A-type epoxy resin (2)							70
3,3'-diethyl-4,4'-diaminodiphenylmethane		40	40	40	40	40	40
Epoxidized polybutadiene		6	6		6	6	6
Spherical fused silica (1)		380	420	230	110		340
Spherical fused silica (2)			280	160	260		40
Spherical fused silica (5)						380	
Physical Properties							
Composition viscosity (Pa·s)		30	120	17	130	27	125
Ease of package filling		good	poor	good	poor	good	poor
Delamination	After Curing	0	-	0	-	0	-
	After PCT	0	-	8	-	0	-
	After T/C	3	-	0	-	4	-
Cracks	After Curing	0	-	0	-	0	-
	After PCT	0	-	3	-	0	-
	After T/C	5	-	0	-	8	-
Filler sedimentation (μm)		80	-	Not more than 3	-	100	-

As illustrated in the above Examples 1 - 6,
potting a semiconductor package with a liquid potting
material of this invention can provide a highly reliable
semiconductor package free of delamination or cracks in
5 a pressure cooker test or cold-heat cycle test without
adversely affecting flow or workability, thereby
providing much industrial advantage.



WHAT IS CLAIMED IS:

1. A liquid epoxy resin potting material comprising (A) a liquid epoxy resin, (B) a liquid alkylated diaminodiphenylmethane, (C) an epoxidized polybutadiene, and (D) an inorganic filler, wherein the ratios of the individual components in weight ratios are:

$$(A)/[(A)+(B)] = 0.65 - 0.80$$

$$(C)/[(A)+(B)] = 0.01 - 0.05$$

and

$$(D)/[(A)+(B)+(C)+(D)] = 0.50 - 0.80.$$

2. A liquid epoxy resin potting material, as set forth in claim 1, in which at least 50% by weight of the (A) liquid epoxy resin has a viscosity not higher than 8 Pa·s/25°C.

3. A liquid epoxy resin potting material, as set forth in claim 1, wherein the (D) inorganic filler comprises (a) a spherical silica having an average particle size of 0.1 μm to 3.0 μm and a maximum particle size not more than 10 μm and (b) a spherical silica of an average particle size of 4 μm to 10 μm and a maximum particle size of not more than 50 μm, with the compounding ratio in weight being (a)/[(a)+(b)] = 0.05 - 0.50.

4. A liquid epoxy resin potting material, as set forth in claim 2, wherein the (D) inorganic filler comprises (a) a spherical silica having an average particle size of 0.1 μm to 3.0 μm and a maximum particle size not more than 10 μm and (b) a spherical silica of an average particle size of 4 μm to 10 μm and a maximum



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particle size of not more than 50 μm , with the compound-
ing ratio in weight being $(a)/[(a)+(b)] = 0.05 - 0.50$.