

EPOXY RESIN COMPOSITION FOR SEMICONDUCTOR SEALING

1 The present invention relates to an epoxy resin composition for semiconductor sealing, which is excellent in soldering heat resistance, thermal impact resistance and moldability.

5 Epoxy resins are excellent in heat resistance, electrical properties, mechanical strengths and adhesion, and find wide uses in coatings, adhesives, resins for sealing of electronic parts, resins for laminated plates and various other applications.

10 For example, in resin sealing of semiconductor devices (e.g., IC, LSI, transistor and diode), electronic circuits, etc., there are generally used epoxy resin compositions in view of the properties and cost of intended products.

15 In such resin sealing, however, there have been considered problems of (a) increase in package crack caused by temperature cycle and (b) increase in package crack caused by thermal impact of soldering during surface mounting, because of changes to larger IC size and smaller
20 and thinner package size. Accordingly, effective measures for solving these problems are desired seriously.

 For solving the problems, investigations are being made on (1) lower elastic modulus, (2) lower thermal expansion coefficient, (3) higher impact strength and
25 (4) lower water absorbability.

1 With respect to the lower elastic modulus (1),
it is said that the use of a silane-modified epoxy resin
compound is effective [Japanese Patent Application
Kokai (Laid-Open) No. 73725/1986 and Japanese Patent
5 Application Kokai (Laid-Open) No. 174222/1987]. However,
the adoption of a lower elastic modulus alone gives
lower strength and hence lower heat resistance for
soldering, and accordingly it was impossible to obtain
a good resin composition for semiconductor sealing.

10 With respect to the lower thermal expansion
coefficient (2), it is said that increasing the amount
of silica filler used in a resin composition is effective.
However, this approach brings about a problem of viscosity
increase of the resin composition caused by increase in
15 filler amount, and accordingly it was necessary to clear
the significant reduction in moldability.

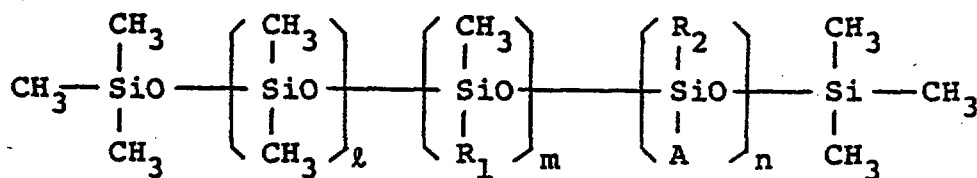
 With respect to the higher impact strength
(3), it is said that the use of a biphenyl type epoxy
resin or a trifunctional epoxy resin [Japanese Patent
20 Application Kokai (Laid-Open) No. 168620/1986] is
effective. However, the use of any of these resins gives
reduction in moldability, particularly reduction in thin
flash property and mold staining property.

 With respect to the lower water absorbability
25 (4), it is said that the use of a silicone-modified
resin or the increase in amount of filler used is
effective. However, any of these approaches has the
above-mentioned drawbacks and is not put into practical

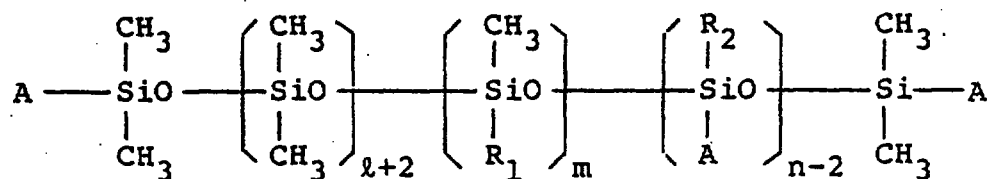
1 application.

The present invention has been made in view of the above situation and is intended to provide an epoxy resin composition for semiconductor sealing, which is
5 satisfactory in all of soldering heat resistance, thermal impact resistance and moldability.

The present inventors made extensive study in order to obtain an epoxy resin composition for semiconductor sealing, which is free from the drawbacks of
10 the prior art and has excellent balanced properties. As a result, it was found that an epoxy resin composition obtained by incorporating into (A) an epoxy resin, (B) a phenolic resin curing agent comprising 30-100% by weight, based on the total amount of the phenolic
15 resin curing agent, of a silicone-modified phenolic resin curing agent obtained by reacting a phenolic resin with at least one of silicone compounds represented by the following formulas [I] and [II] capable of imparting remarkably high toughness and low elasticity without
20 sacrificing moldability,

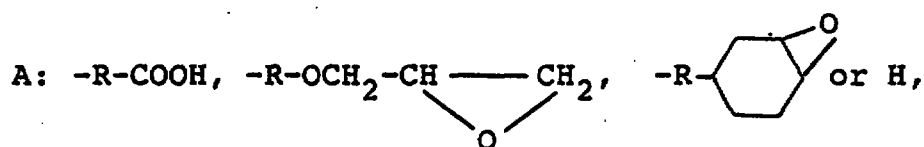
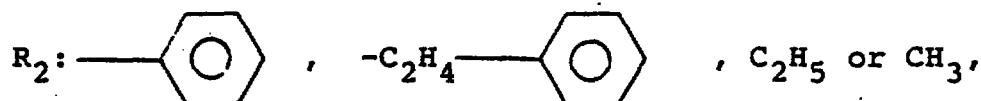
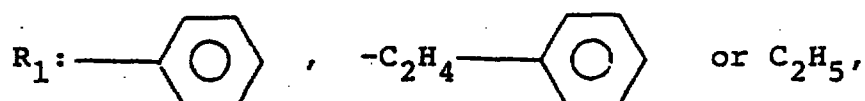


[I]



[III]

wherein



R: a lower alkylene group,

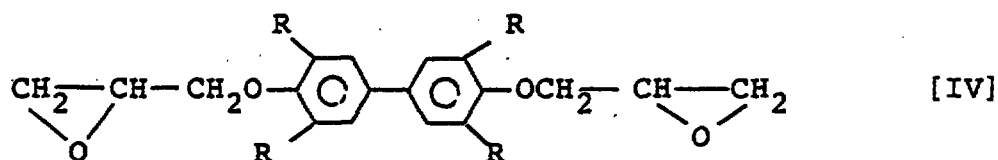
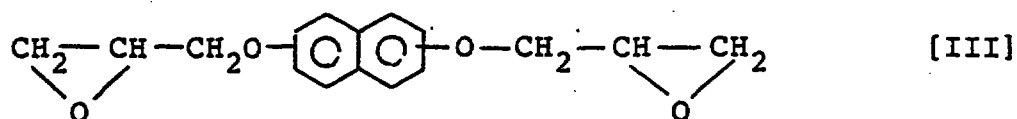
$$10 \leq N = l + m + n + 2 \leq 200,$$

$$0 \leq m/N \leq 0.1, \text{ and } 5 \leq N/n \leq 50,$$

- 1 (C) an inorganic filler and (D) a curing accelerator,
- and give significant improvements in all of moldability,
- soldering heat resistance and thermal impact resistance,
- even to thin and large chip packages. The above finding
- 5 has led to the completion of the present invention.

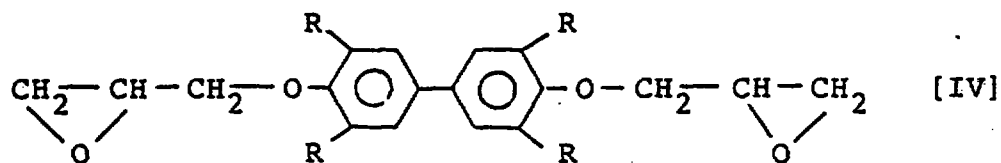
The first preferable embodiment of the present invention consists of an epoxy resin composition as mentioned above, wherein the epoxy resin comprises

- 1 30-100% by weight, based on the total amount of the epoxy resin, of at least one epoxy compound selected from the group consisting of naphthalene type epoxy compounds represented by the following formula [III]
- 5 and biphenyl type epoxy compounds represented by the following formula [IV] all effective for obtaining improved impact strength and lower viscosity

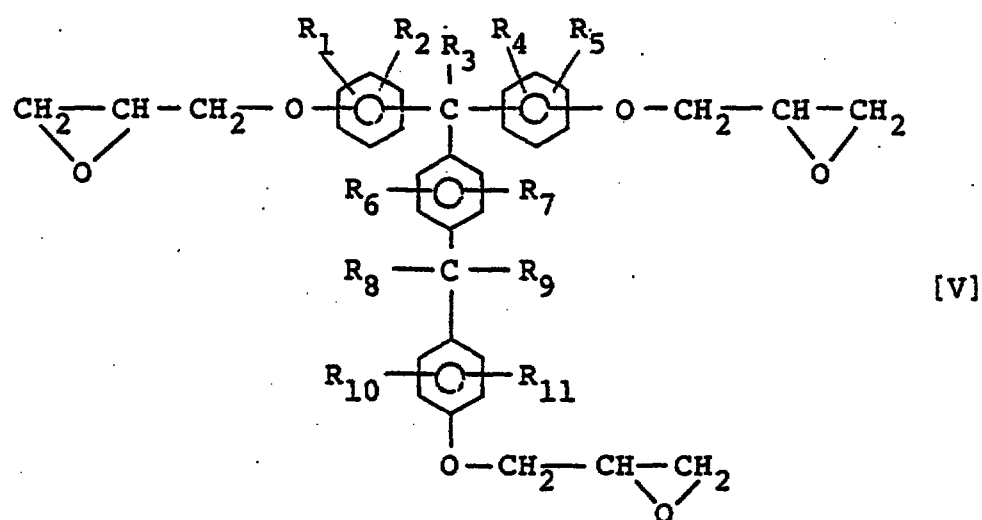


wherein R: H or CH₃, and the inorganic filler is used in an amount of 70-90% by weight based on the total amount
10 of the composition.

The second preferable embodiment of the present invention consists of an epoxy resin composition as mentioned above, wherein the epoxy resin comprises 50-100% by weight, based on the total amount of the epoxy resin,
15 of a mixture of a biphenyl type epoxy resin represented by the following formula [IV] effective for obtaining improved thermal impact resistance and lower viscosity



1 wherein R:H or CH₃, and a trifunctional epoxy resin represented by the following formula [V] effective for obtaining improved heat resistance for soldering



wherein R₁ to R₁₁ are each an atom or an atomic group
5 selected from hydrogen, halogens and alkyl groups.

The epoxy resin used in the present invention as the component (A) can be any epoxy resin as long as it has at least two epoxy groups in the molecule. As the epoxy resin, there can be cited, for example,
10 bisphenol A type epoxy resins, bisphenol F type epoxy resins, phenol novolac type epoxy resins, cresol novolac type epoxy resins, alicyclic epoxy resins and resins obtained by modifying them. These epoxy resins can be used alone or in admixture of two or more.

1 Of these epoxy resins, preferable are those
having an epoxy equivalent of 150-250 and a softening
point of 60-130°C and containing ionic impurities such
as Na^+ , Cl^- and the like in amounts as small as possible.

5 The naphthalene type epoxy resin represented
by the formula [III] and the biphenyl type epoxy resin
represented by the formula [IV] both used in the first
preferable embodiment of the present invention have a
viscosity as low as several centipoises at the molding
10 temperature (165-185°C) of the present resin composition,
and accordingly can reduce the viscosity of the composi-
tion significantly. Therefore, the use of these epoxy
resins can significantly increase the amount of filler
used in the resin composition, as compared with the
15 usual level.

 These epoxy compounds, having a planar struc-
ture and being dense in molecular packing, can allow
the resulting resin composition to have improved impact
strength and excellent thermal impact resistance,
20 soldering heat resistance and moisture resistance after
soldering.

 However, the epoxy resin comprising these epoxy
compounds in a total amount of 30% by weight or more,
is inferior in reactivity and compatibility with other
25 resins and has low viscosity; therefore, the resin has
had a problem of allowing the resulting resin composition
to have reduced moldability, particularly, reduced thin
flash property and mold staining property.

1 The problem, however, could be cleared by using
the above-mentioned silicone-modified phenolic resin in
combination.

 The naphthalene type epoxy compound represented
5 by the formula [III], or the biphenyl type epoxy compound
represented by the formula [IV], or a mixture thereof
may be mixed with other epoxy resins; however, the amount
of the compound [III] or the compound [IV] or the mixture
in the total epoxy resin amount is preferably 30% by
10 weight or more.

 When the amount is less than 30% by weight,
it is difficult to obtain sufficiently low viscosity,
low water absorbability and high impact strength, and
the resulting resin composition has relatively insuf-
15 ficient soldering heat resistance and fluidity.

 When the naphthalene type epoxy resin repre-
sented by the formula [III] and the biphenyl type epoxy
resin represented by the formula [IV] are used in
combination, it is preferable that the former and the
20 latter be used at a weight ratio of 10/90 to 90/10.

 The naphthalene type epoxy compound has high
reactivity and gives increased strength, and accordingly
can give improved soldering heat resistance. However,
the compound has no sufficient thermal impact resistance
25 and moreover is difficult to handle because it is
liquid.

 Meanwhile, the biphenyl type epoxy compound
has excellent soldering heat resistance and thermal

1 impact resistance and gives no inconvenience in handling because it is crystalline. However, the compound has somewhat low reactivity.

Hence, the combined use of the above two
5 compounds can give a resin composition wherein their drawbacks are supplemented by each other.

The biphenyl type epoxy resin represented by the formula [IV], which is used in the second preferable embodiment of the present invention, has a low viscosity
10 of few centipoises at a molding temperature (165-185°C) and accordingly can significantly reduce the viscosity of the resulting resin composition. The biphenyl type epoxy resin further has a planar structure and has sufficiently dense molecular packing and therefore, can
15 improve the strength and thermal impact resistance of the resulting resin composition. This resin, however, has poor reactivity and compatibility with other resins and possesses low viscosity and accordingly, has been inferior in moldability, particularly thin flash property
20 and mold staining property.

This problem could be cleared by the combined use with the above-mentioned silicone-modified phenolic resin.

When the amount of the trifunctional epoxy
25 resin of the formula [V] used is appropriately controlled, the resulting resin composition can have a maximum resistance to soldering stress. In the formula, R_1 , R_2 , R_4 to R_7 , R_{10} and R_{11} are each preferably hydrogen atom,

1 and R_3 , R_8 and R_9 are each preferably methyl group.

The trifunctional epoxy resin, as compared with ordinary phenol novolac type epoxy resins, has a structure wherein motion of the main chain is restricted; accordingly, has high T_g and excellent heat resistance.

The total amount of the epoxy resins of the formula [IV] and the formula [V] is preferably 50-100% by weight based on the total epoxy resin amount. When it is less than 50% by weight, the resulting resin composition tends to be insufficient in both or either of soldering heat resistance and fluidity.

The weight ratio of the epoxy resins of the formula [IV] and the formula [V] is preferably $[IV]/[V] = 10/90$ to $90/10$. When it is less than $10/90$, the resulting resin composition tends to have reduced fluidity and increased viscosity. When it is more than $90/10$, the composition tends to have reduced resistance to soldering heat.

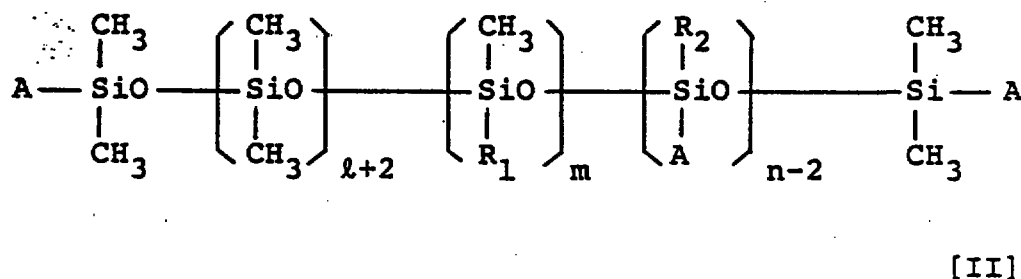
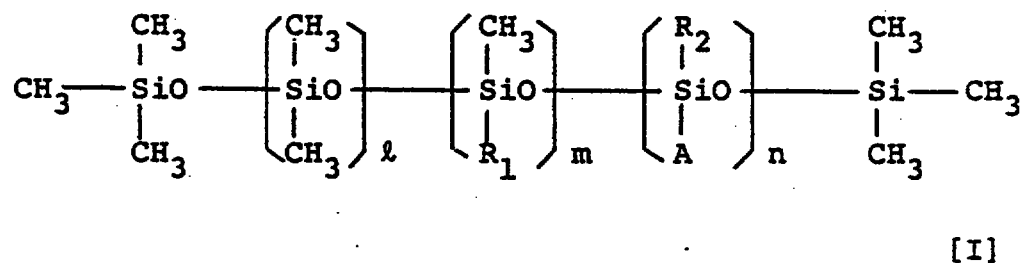
The silicone-modified phenolic resin curing agent used as the component (B) in the present invention can increase both soldering heat resistance and thermal impact resistance, and is a very important component. The phenolic resin as the one raw material for the silicone-modified phenolic resin includes, for example, phenol novolac resins, cresol novolac resins and resins obtained by modifying them, etc. These resins can be used alone or in admixture of two or more.

Of these phenolic resins, preferable are those

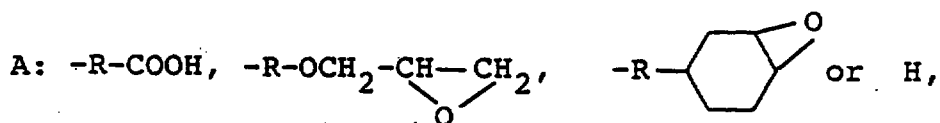
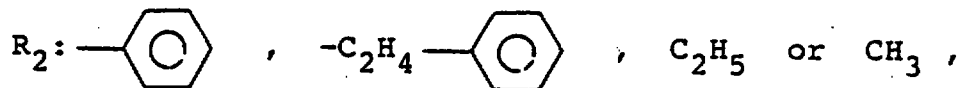
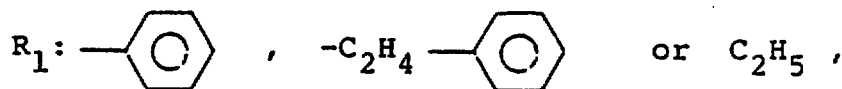
1 which have a hydroxyl group equivalent of 80-150 and a softening point of 60-120°C and which contain ionic impurities (e.g., Na⁺, Cl⁻) in an amount as small as possible.

5 The organopolysiloxane as the other raw material for the silicone-modified phenolic resin of the present invention has functional groups capable of reacting with the above phenolic resin. The functional groups include carboxyl group, cyclohexyl type
10 epoxy group, glycidyl type epoxy group and active hydrogen.

The organopolysiloxane is represented by the following formula [I] or [II]:



1 wherein



R: a lower alkylene group,

$$10 \leq N = l + m + n + 2 \leq 200,$$

$$0 \leq m/N \leq 0.1, \text{ and } 5 \leq N/n \leq 50.$$

When $N (l + m + n + 2)$ is less than 10, the resulting resin composition has increased elastic modulus and decreased strength, and it is difficult to synthesize a silicone-modified phenolic resin curing agent because an organopolysiloxane having in the molecule no group reactive with the phenolic resin (i.e., having no group A in the formula [I] or [II]) is formed as a by-product at a higher probability.

10 When N is larger than 200, the organopolysiloxane has reduced miscibility with the phenolic resin, which makes the reaction with the phenolic resin insufficient, invites bleeding of the silicone oil from the phenolic resin and resultantly reduces the moldability

1 of the resulting composition greatly.

In the organopolysiloxane of the formula [I] or [II], m/N is preferably 0-0.1. When m/N is larger than 0.1, the thermal motion of siloxane chain is suppressed and the T_g of siloxane component is shifted to a higher temperature side; as a result, a lower stress effect is obtained only in a high temperature range and the resulting resin composition has reduced thermal impact resistance.

10 Moreover, when m/N is larger than 0.1, the synthesis of organopolysiloxane costs high.

The ratio m/N can take any value as long as it is not larger than 0.1, but is preferably about 0.05. It is because there is no T_g shift of the siloxane to a higher temperature side, and furthermore because the presence of side chain functional groups increases the compatibility with the phenolic resin and the synthesis of silicone-modified phenolic resin is easy.

Further, $5 \leq N/n \leq 50$ is preferable.

20 When N/n is larger than 50, the reactivity between the organopolysiloxane and the phenolic resin is poor; therefore, there is bleeding of unreacted organopolysiloxane and the resulting resin composition has reduced moldability. When N/n is smaller than 5, 25 gelling occurs during the synthesis reaction and it is impossible to obtain a satisfactory silicone-modified phenolic resin.

The amount of the silicone component used for

1 producing a silicone-modified phenolic resin is preferably
10-50 parts by weight per 100 parts by weight of the
raw material phenolic resin.

When the amount of the silicone component
5 is less than 10 parts by weight, the resulting silicone-
modified phenolic resin is insufficient in thermal impact
resistance. When the amount is more than 50 parts by
weight, the reaction degree of the silicone component
is reduced, there occurs bleeding of unreacted organo-
10 polysiloxane, and the resulting resin composition has
reduced moldability.

As the organopolysiloxane, there is preferred
an organopolysiloxane having an epoxy group-containing
organic group. Such an organopolysiloxane having an
15 epoxy group-containing organic group can be obtained
by subjecting an organohydrogenpolysiloxane and an
unsaturated double bond group-containing epoxy (e.g.,
allyl glycidyl ether) to an addition reaction in the
presence of chloroplatinic acid as a catalyst in an
20 organic solvent.

The silicone-modified phenolic resin can be
obtained, for example, by subjecting an organopolysiloxane
and a phenolic resin to a ring-opening addition reaction
in an organic solvent in the presence of at least one
25 catalyst selected from imidazoles, organic phosphines and
tertiary amines.

In the present invention, the silicone-
modified phenolic resin curing agent can be used alone,

1 but may be used in admixture with conventional phenolic
resin curing agent(s). When the silicone-modified
phenolic resin curing agent is used as a mixed system,
it is necessary that the system comprises at least 30%
5 by weight, based on the total system amount, of the
silicone-modified phenolic resin curing agent. When the
content of the silicone-modified phenolic resin curing
agent is less than 30% by weight, the resulting resin
composition has reduced thermal impact resistance. It
10 is preferable that the silicone-modified phenolic resin
curing agent be used in an amount of at least 50% by
weight. In this case, any epoxy resin can be used as
the component (A) without impairing the object and effect
of the present invention.

15 The compounding ratio of the total epoxy
component and the total phenolic resin component is
preferably 70/100 to 100/70 in terms of the ratio of
epoxy group/phenolic hydroxyl group. When the ratio is
less than 70/100 or more than 100/70, there occurs
20 reduction in Tg, reduction in hardness when hot, reduction
in moisture resistance, etc., and the resulting resin
composition is insufficient for use in semiconductor
sealing.

 When in an ordinary epoxy resin-phenolic resin
25 system there is incorporated a naphthalene type epoxy
compound or a biphenyl type epoxy compound or a mixture
thereof, the resulting composition has reduced thin flash
property. However, when in an epoxy resin/silicone-

1 modified phenolic resin system there is incorporated a
naphthalene type epoxy compound or a biphenyl type
epoxy compound or a mixture thereof as in the present
invention, the low-molecular epoxy compound reacts also
5 with the phenolic resin having a high polymerization
degree owing to the silicone modification; consequently,
bleeding is unlikely to occur and there arises no
reduction in thin flash property.

The inorganic filler used as the component (C)
10 in the present invention includes crystalline silica,
fused silica, alumina, calcium carbonate, talc, mica,
glass fiber, etc. These fillers can be used alone or
in admixture of two or more. Of them, crystalline
silica or fused silica is particularly preferable.

15 In the embodiment of the present invention
wherein the naphthalene type epoxy compound or the
biphenyl type epoxy compound or the mixture thereof is
used, the amount of the inorganic filler used is prefer-
ably 70-90% by weight based on the total resin composition
20 amount. When the amount is less than 70% by weight,
the resulting resin composition tends to have increased
thermal expansion coefficient, no sufficiently low stress
and accordingly reduced thermal impact resistance; tends
to have higher water absorbability and accordingly
25 reduced resistance to soldering heat; and tends to have
too low a viscosity and accordingly thin flash and
decreased moldability.

When the amount of the inorganic filler used

1 is more than 90% by weight, the resulting resin composition has too high a viscosity, making the molding difficult.

The curing accelerator used as the component
5 (D) in the present invention can be any one as long as it can accelerate the reaction between epoxy group and phenolic hydroxyl group. There can be widely used curing accelerators which are generally used in sealing materials. For example, the following compounds can be
10 used alone or in admixture of two or more; tertiary amines such as BDMA and the like, imidazoles, 1,8-diazabicyclo[5,4,0]undecene-7, and organic phosphorus compounds such as triphenylphosphine and the like.

Into the epoxy resin composition of the present
15 invention there can further be incorporated, as necessary, release agents (e.g., wax), flame retardants (e.g., hexabromobenzene, decabromobiphenyl ether, and antimony trioxide), coloring agents (e.g., carbon black, and red iron oxide), silane coupling agents, thermoplastic
20 resins, etc.

The epoxy resin composition for semiconductor sealing according to the present invention can be easily produced by a general process. That is, raw materials of given proportions are thoroughly mixed by a mixer
25 or the like; the mixture is melt-kneaded by rolls, a kneader or the like; the kneaded product is cooled and solidified; and the solid is ground to an appropriate size.

1 The present invention can provide an epoxy
resin composition having high heat resistance, high
thermal impact resistance and good moldability, which
has been unobtainable with the prior art. This epoxy
5 resin composition is excellent in cracking resistance
and thermal impact resistance when subjected to heat
stress by rapid temperature change at a soldering step.
Accordingly, the epoxy resin composition of the present
invention can be suitably used for sealing, coating,
10 insulation, etc. of electronic and electric parts,
particularly high integration large thin chip ICs mounted
on surface mounting packages and requiring a high degree
of reliability.

The present invention is described in more
15 detail referring to Synthesis Examples, Examples and
Comparative Examples.

Synthesis Example I

As shown in Table I-1, 20 parts by weight of
an organopolysiloxane (one of *I-1 to *I-8 shown later)
20 was reacted with 100 parts by weight of a phenol novolac
resin in 200 parts by weight of a butanol solvent in the
presence of a catalyst to obtain silicone-modified
phenolic resins I(a) to I(h).

Example I-1

Cresol novolac type epoxy resin 90 parts by weight
(epoxy equivalent = 200, soften-
ing point = 65°C)

Brominated phenol novolac type epoxy resin (epoxy equivalent = 272, softening point = 75°C, bromine content = 32%)	10 parts by weight
Silicone-modified phenol novolac resin curing agent I(a)	60 parts by weight
Fused silica	450 parts by weight
Antimony trioxide	25 parts by weight
Silane coupling agent	2 parts by weight
Triphenylphosphine	2 parts by weight
Carbon black	3 parts by weight
Carnauba wax	3 parts by weight

1 The above materials were mixed thoroughly at
room temperature. The mixture was kneaded by a twin roll
at 95-100°C. The kneaded product was cooled, crushed
and made into tablets to obtain an epoxy resin composi-
5 tion for semiconductor sealing.

 This material was made into a molding using a
transfer molding machine (mold temperature = 175°C,
curing time = 2 minutes), whereby the material was
examined for mold staining and resin flash. The molding
10 was after-cured at 175°C for 8 hours and examined for
markability, thermal impact resistance, soldering moisture
resistance and soldering heat resistance. The results
are shown in Table I-2.

Examples I-2 and I-3

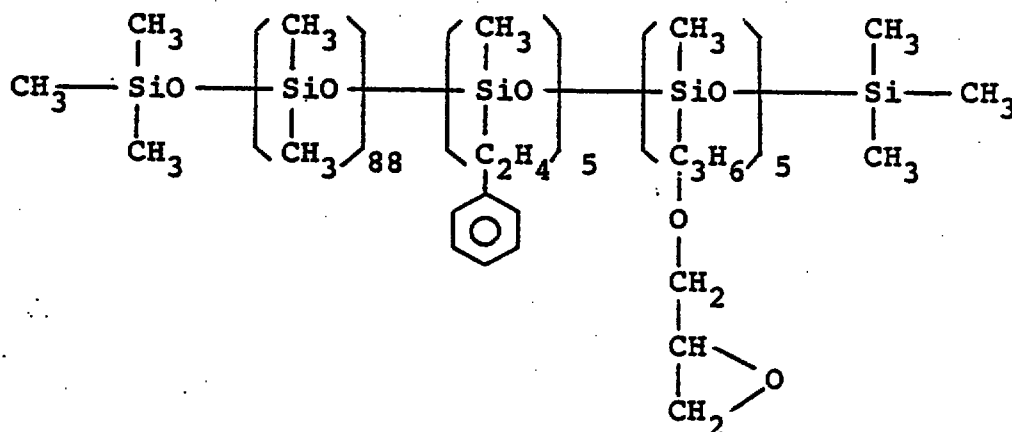
15 Components were compounded in accordance with
the recipes shown in Table I-2 and treated in the same

1 manner as in Example I-1 to obtain epoxy resin compositions for semiconductor sealing. These resin compositions were examined for properties, and the results are shown in Table I-2.

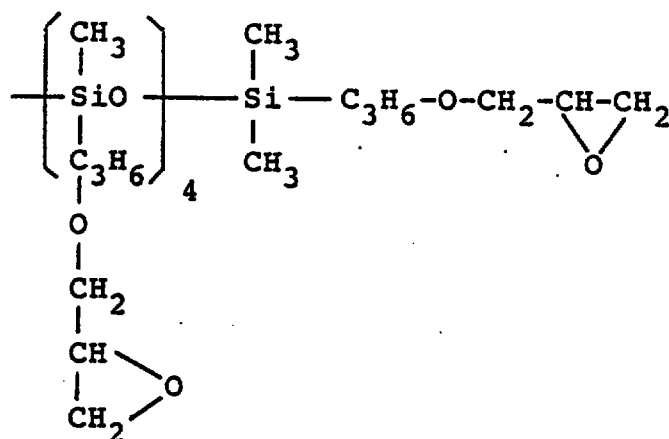
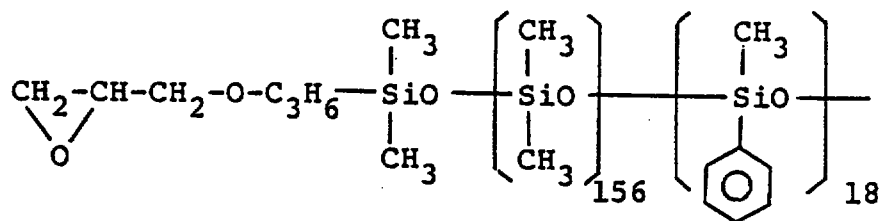
5 Comparative Examples I-1 to I-6

Components were compounded in accordance with the recipes shown in Table I-2 and treated in the same manner as in Example I-1 to obtain epoxy resin compositions for semiconductor sealing. These resin compositions were examined for properties, and the results are shown in Table I-2.

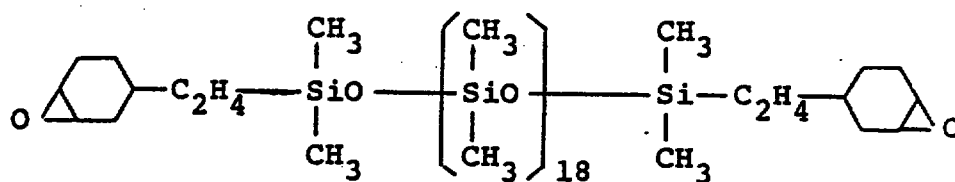
Organopolysiloxane *I-1



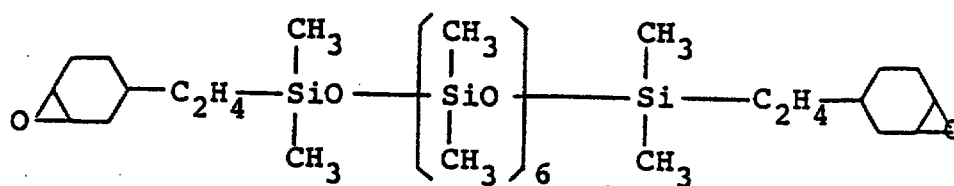
Organopolysiloxane *I-2



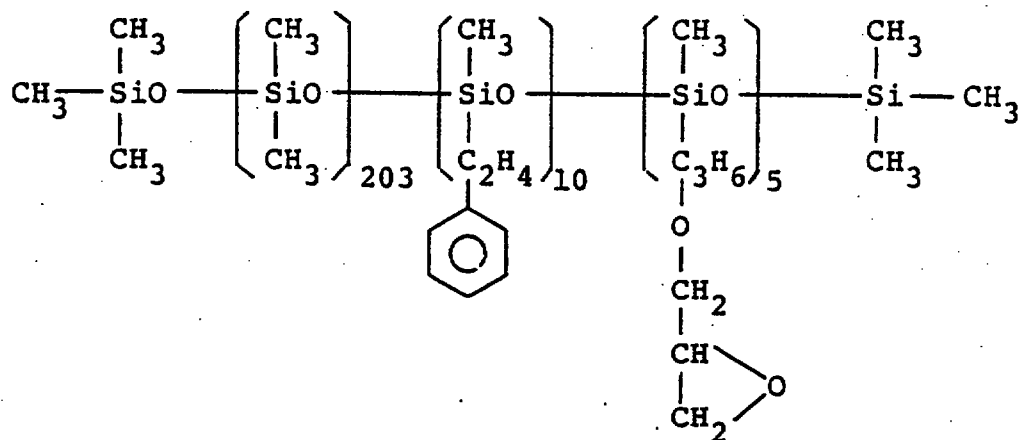
Organopolysiloxane *I-3



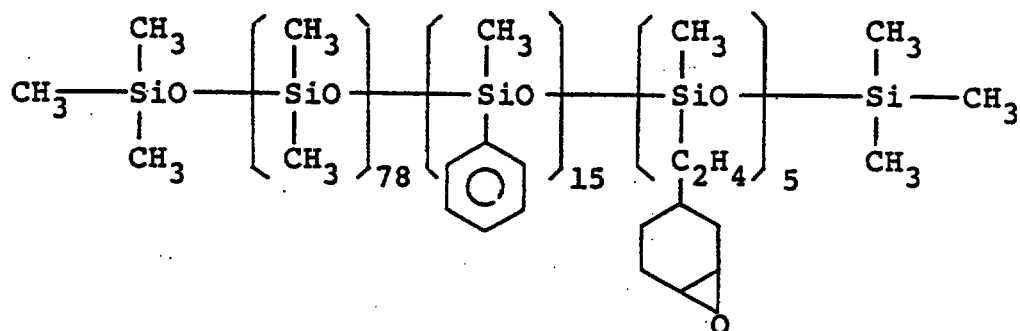
Organopolysiloxane *I-4



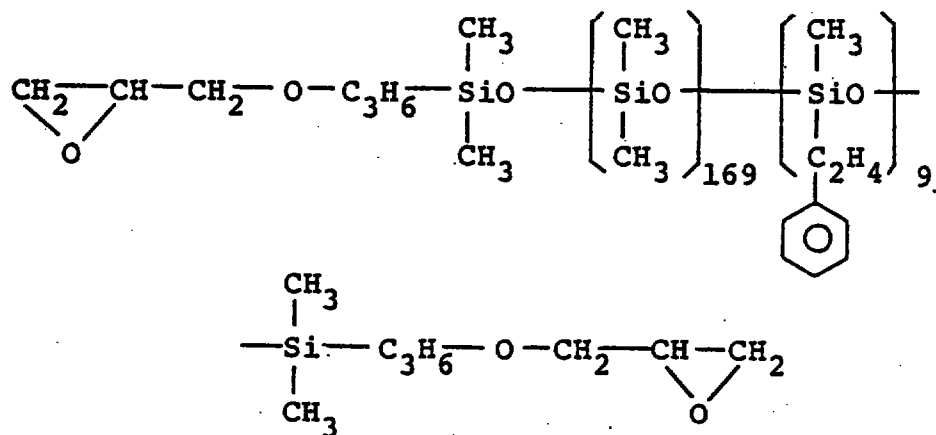
Organopolysiloxane *I-5



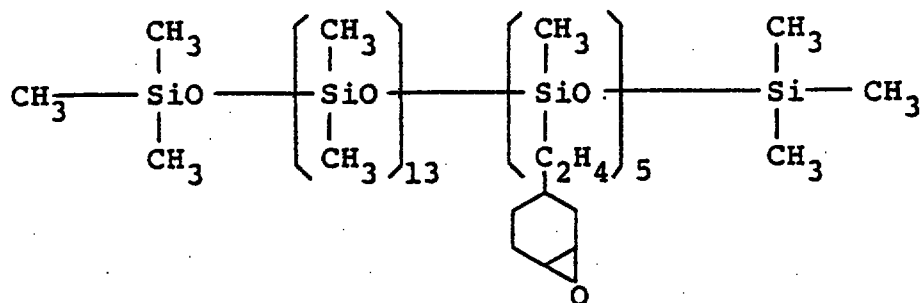
Organopolysiloxane *I-6



Organopolysiloxane *I-7



1 Organopolysiloxane *I-8



*I-9 Epoxy resin ESX-221 produced by Sumitomo Chemical Co., Ltd. (epoxy equivalent = 210 g/eq; softening point = 84°C).

5 *I-10 Epoxy resin ESX-222 produced by Sumitomo Chemical Co., Ltd. (epoxy equivalent = 210 g/eq; softening point = 85°C).

Table I-1

Raw materials		Silicone			Silicone- modified phenolic resin I (a)	Silicone- modified phenolic resin. I (b)	Silicone- modified phenolic resin I (c)
Phenolic resin	Phenol novolac resin (OH equivalent: 105, softening point: 95°C) (parts by weight)		100	100	100		
Silicone	Organopolysiloxane *I-1 (parts by weight)		20				
	Organopolysilxoane *I-2 (parts by weight)			20			
	Organopolysiloxane *I-3 (parts by weight)				20		
	Organopolysiloxane *I-4 (parts by weight)						
	Organopolysiloxane *I-5 (parts by weight)						
	Organopolysiloxane *I-6 (parts by weight)						
	Organopolysiloxane *I-7 (parts by weight)						
	Organopolysiloxane *I-8 (parts by weight)						
	N (polymerization degree of siloxane)		100	180	20		
	m/N (molar fraction of phenol group or phenylethyl group)		0.05	0.10	0		
N/n (siloxane polymerization degree/number of functional groups)			20	30	10		

- to be cont'd

Table I-1 (cont'd.)

Silicone- modified phenolic resin I (d)	Silicone- modified phenolic resin I (e)	Silicone- modified phenolic resin I (f)	Silicone- modified phenolic resin I (g)	Silicone- modified phenolic resin I (h)
100	100	100	100	100
20				
	20			
		20		
			20	
				20
8	220	100	180	20
0	0.05	0.15	0.05	0
4	44	20	90	4

Table I-1 (cont'd.)

Reaction conditions	Kind of solvent			
	Amount of solvent (parts by weight)	Butanol	Butanol	Butanol
Reaction conditions	Kind of catalyst	200	200	200
	Amount of catalyst (parts by weight)	DBU	Triphenyl-phosphine	DBU
	Reaction temperature (°C)	2	2	2
	Reaction time (hr)	150	150	150
Properties	Hydroxyl group equivalent (g/eq)	10	20	10
	Softening point (°C)	134	128	128
		107	109	105

- to be cont'd. -

Table I-1 (cont'd.)

Butanol	Butanol	Butanol	Butanol	Butanol
200	200	200	200	200
Triphenyl- phosphine	Triphenyl- phosphine	DBU	DBU	Triphenyl- phosphine
2	2	2	2	2
150	150	150	150	150
20	20	10	10	20
131	131	128	132	132
105	111	112	106	108

Table I-2

	Example		
	I-1	I-2	I-3
Epoxy resin	Cresol novolac type epoxy resin (epoxy equivalent: 200, softening point: 65°C) (parts by weight)		
	90		
	Epoxy resin *I-9 (parts by weight)		
		90	
Epoxy resin	Epoxy resin *I-10 (parts by weight)		
			90
	Brominated phenol novolac type epoxy resin (epoxy equivalent: 272, softening point: 75°C, bromine content: 32%) (parts by weight)		
	10	10	10
Phenolic resin curing agent	Silicone-modified phenolic resin I(a) (parts by weight)		
	"	I(b)	(")
	"	I(c)	(")
	"	I(d)	(")
	"	I(e)	(")
	"	I(f)	(")
	"	I(g)	(")
	"	I(h)	(")
	60	30	50
Phenol novolac resin (OH equivalent: 105, softening point: 95°C) (parts by weight)			
		25	10

- to be cont'd. -

Table I-2 (cont'd.)

Comparative Example					
I-1	I-2	I-3	I-4	I-5	I-6
				90	
	90		90		90
90		90			
10	10	10	10	10	10
10	60	50	40	60	30
40		10	15		25

- to be cont'd. -

Table I-2 (cont'd.)

Inorganic filler and others	Properties		450			
			95	80	86	
Fused silica	Moldability	Spiral flow (cm) *I-11	☐	☐	☐	86
Antimony trioxide		Length of resin flash (mm) *I-12	☐	☐	☐	< 0.5
Silane coupling agent		Mold staining (number of shots) *I-13	☐	☐	☐	2300
Triphenylphosphine		Markability (number of marks removed) *I-14	☐	☐	☐	1
Carnauba wax	Reliability	Thermal impact resistance (number of cracked moldings) *I-15	☐	☐	☐	1
Carbon black		Average life in soldering moisture resistance test (hr) *I-16	☐	☐	☐	> 300
		Soldering heat resistance (number of cracked moldings) *I-17	☐	☐	☐	1
Overall evaluation			☐	☐	☐	

- to be cont'd. -

Table I-2 (cont'd.)

450									
25									
2									
2									
3									
3									
○ 87	○ 99	X 48	○ 98	X 42	X 23				
○ < 0.5	X > 5	Δ 1.9	○ < 0.5	X 4.3	○ < 0.5				
○ 2400	Δ 800	X 70	○ 2600	X 90	○ 2500				
○ 1	X 36	X 50	○ 0	X 43	○ 0				
X 17	Δ 9	Δ 10	X 18	Δ 8	X 15				
X 100	Δ 220	Δ 200	X 80	Δ 200	X 60				
Δ 11	Δ 9	Δ 10	X 14	Δ 7	X 18				
X	X	X	X	X	X				

1 Evaluation methods

*I-11 Spiral flow

This is a length of a molding obtained when 20 g of a sample was molded at a molding temperature of 175°C at a molding pressure of 7.0 Mpa for 2 minutes, using a mold for spiral flow measurement.

*I-12 Length of resin flash

There was measured the length of resin flash of the bent portion of the molding obtained.

10 *I-13 Mold staining

Mold staining was examined by the number of molding shots when the mold first showed clouding.

*I-14 Markability

50 marks were given to 50 moldings of 10th shot; then, a cellophane tape was applied to each of the moldings; the tape was removed by peeling; and the number of marks removed was examined.

In Table I-2, there is shown the number of peeled marks among the total 50 marks applied.

20 *I-15 Thermal impact resistance

20 same moldings (chip size = 36 mm^2 , package thickness = 2.0 mm, after-curing = 175°C x 8 hours) were subjected to a temperature cycle test (150°C to -196°C) consisting of 500 cycles, to examine the thermal impact resistance by the number of moldings which gave crack(s). In Table I-2, there is shown the number of moldings which gave crack(s).

*I-16 Average life in soldering moisture resistance test

A sealed test sample was treated in steam of

- 1 85°C and 85% R.H. for 72 hours; the treated test sample was immersed in a solder bath of 240°C for 10 seconds; the resulting test sample was subjected to a pressure cooker test (125°C, 100% R.H.) to examine the poor opening of circuit.

*I-17 Soldering heat resistance

- 20 same moldings (chip size = 36 mm^2 , package thickness = 2.05 mm) were treated in steam of 85°C and 85% R.H. for 72 hours; the treated moldings were immersed in a solder bath of 240°C for 10 seconds to examine the soldering heat resistance by the number of moldings which gave crack(s). In Table I-2, there is shown the number of moldings which gave crack(s).

Synthesis Example II

- 15 As shown in Table II-1, an organopolysiloxane (one or two of *II-1 to *II-8 shown later) was reacted with a phenol novolac resin (softening point = 105°C, OH equivalent = 105) in a solvent in the presence of a catalyst to obtain silicone-modified phenolic resins II(a) to II(h).

Example II-1

1,6-Dihydroxynaphthalene diglycidyl ether	90 parts by weight
Brominated bisphenol A type epoxy resin (epoxy equivalent = 370, softening point = 65°C, bromine content = 37%)	10 parts by weight

Silicone-modified phenol novolac resin II(a)	70 parts by weight
Crushed fused silica	800 parts by weight
Antimony trioxide	10 parts by weight
Silane coupling agent	2 parts by weight
Triphenylphosphine	2 parts by weight
Carbon black	3 parts by weight
Carnauba wax	3 parts by weight

1 The above materials were mixed thoroughly at room temperature. The mixture was kneaded by a twin roll at 95-100°C. The kneaded product was cooled, crushed and made into tablets to obtain an epoxy resin
5 composition for semiconductor sealing.

 This material was made into a molding using a transfer molding machine (mold temperature = 175°C, curing time = 2 minutes). The molding was after-cured at 175°C for 8 hours and examined for properties.

10 The results are shown in Table II-2.

Examples II-2 to II-4

 The epoxy resin compositions for semiconductor sealing whose compounding recipes are shown in Table II-2 were obtained in the same manner as in Example II-1.

25 These resin compositions were examined for properties, and the results are shown in Table II-2.

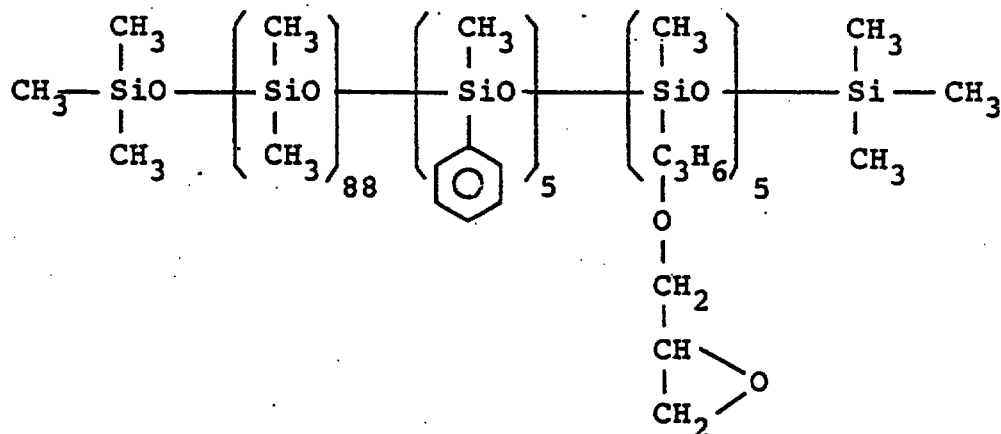
Comparative Examples II-1 to II-6

 The epoxy resin compositions for semiconductor

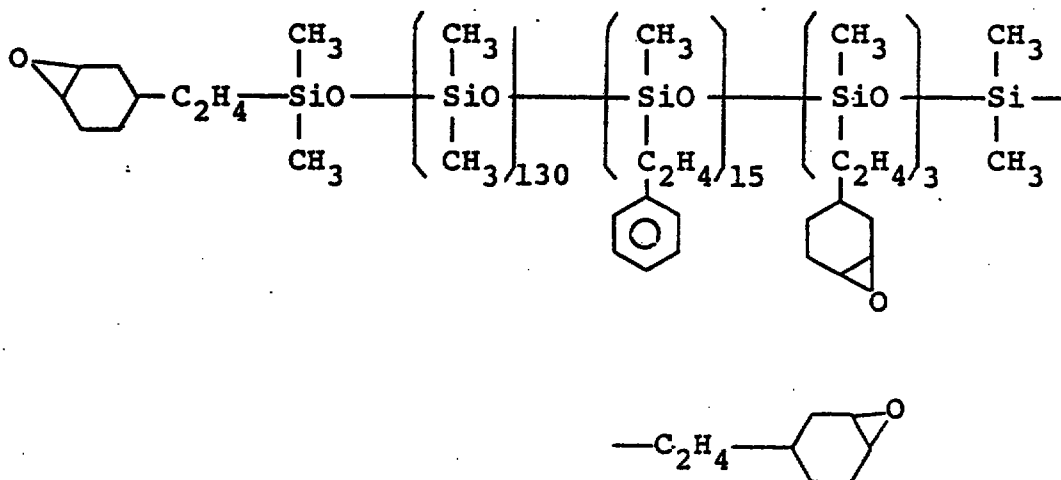
1 sealing whose compounding recipes are shown in Table II-2 were obtained in the same manner as in Example II-1.

These resin compositions were examined for 5 properties, and the results are shown in Table II-2.

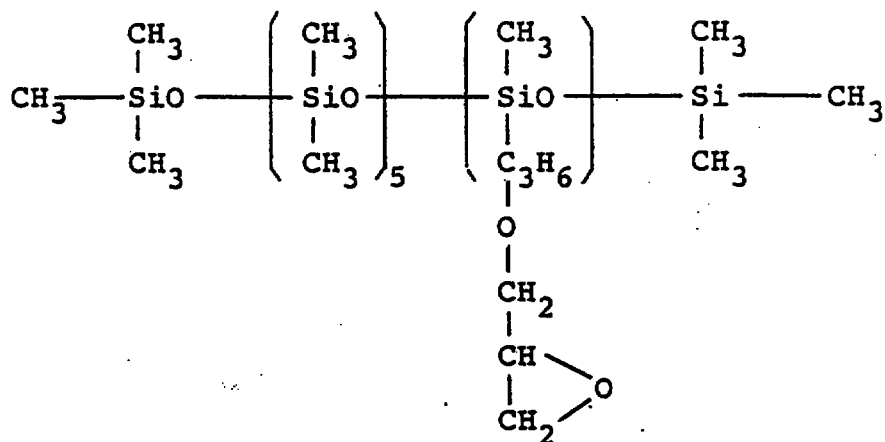
Organopolysiloxane *II-1



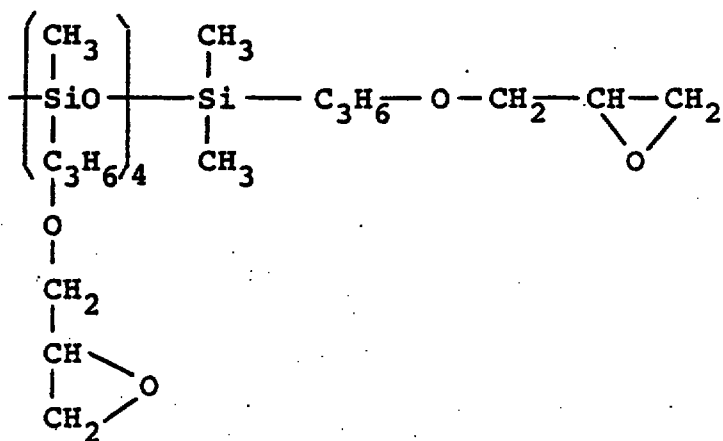
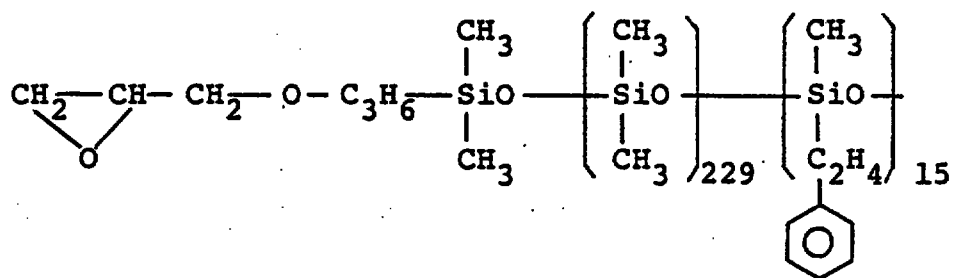
Organopolysiloxane *II-2

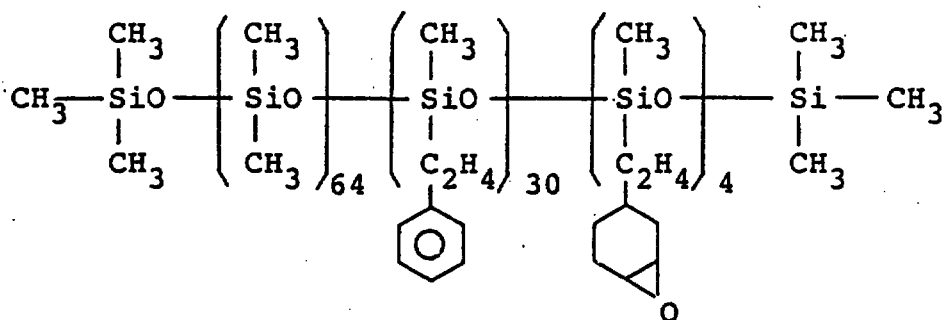


Organopolysiloxane *II-3

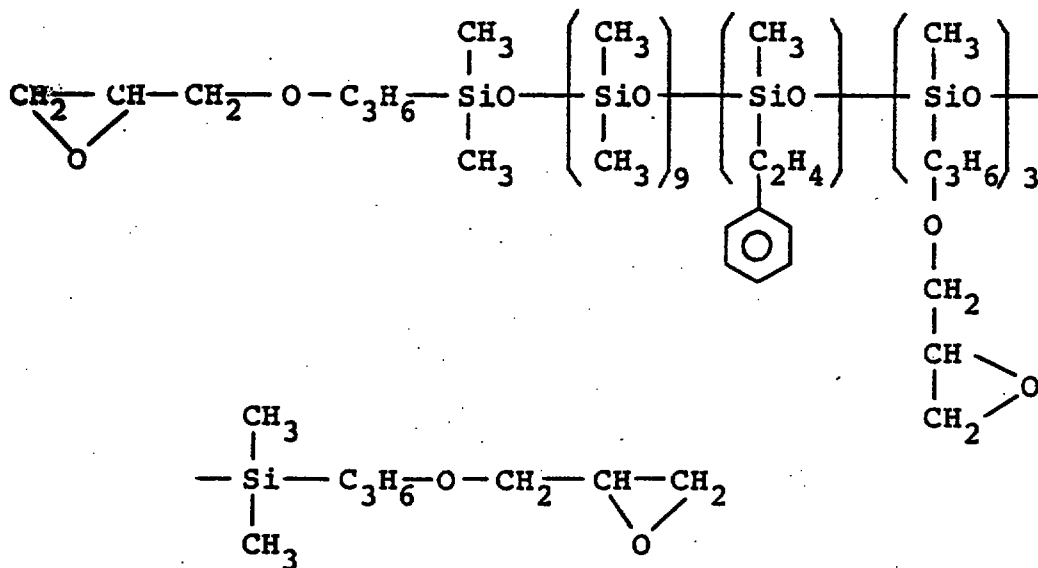


Organopolysiloxane *II-4

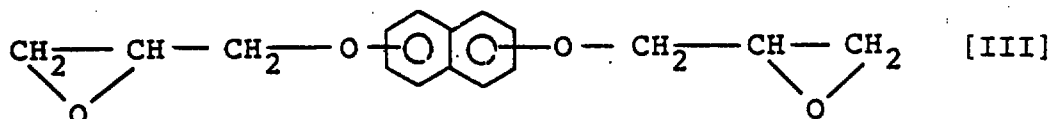


[illegible]

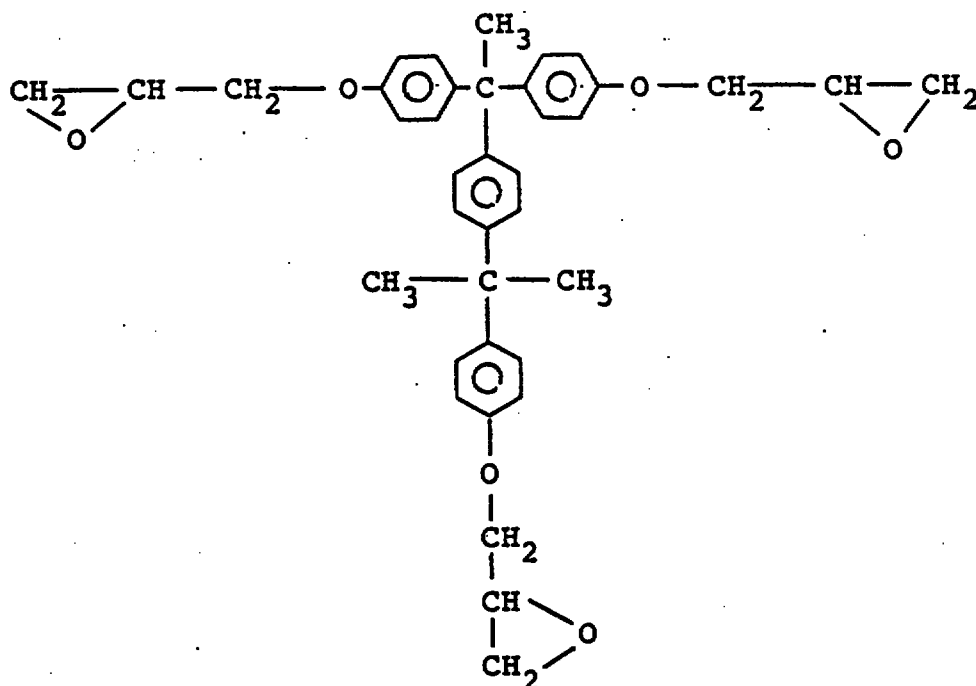
Organopolysiloxane *II-7



- 1 *II-8 Naphthalene type epoxy compound represented by the following formula [III]

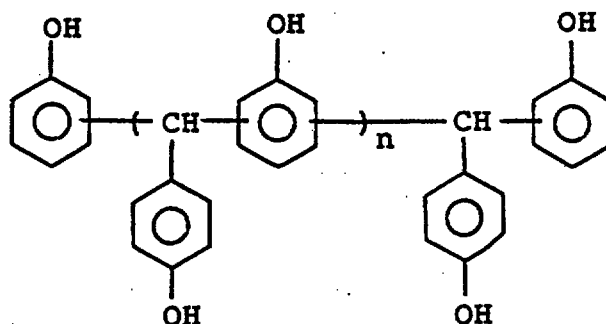


- *II-9 Epoxy resin represented by the following formula



- *II-10 Phenolic resin represented by the following

5 formula



$$n = 6 \sim 9$$

Table II-1

Raw materials	Phenolic resin	Phenol novolac resin (OH equivalent: 105, softening point: 105°C) (parts by weight)	Silicone-	Silicone-	Silicone-
			modified phenolic resin II (a)	modified phenolic resin II (b)	modified phenolic resin II (c)
Silicone	Organopolysiloxane	*II-1 (parts by weight)	100	100	100
		*II-2 (parts by weight)	30	30	20
		*II-3 (parts by weight)			
		*II-4 (parts by weight)			
		*II-5 (parts by weight)			
		*II-6 (parts by weight)			
		*II-7 (parts by weight)			
	N (polymerization degree of siloxane)		100	150	-
	m/N (molar fraction of phenyl group or phenylethyl group)		0.05	0.10	-
	N/n (siloxane polymerization degree/number of functional groups)		20	30	-

- to be cont'd. -

Table II-1 (cont'd.)

Silicone- modified phenolic resin II(d)	Silicone- modified phenolic resin II(e)	Silicone- modified phenolic resin II(f)	Silicone- modified phenolic resin II(g)	Silicone- modified phenolic resin II(h)
100	100	100	100	100
30				
	30			
		30		
			30	
				30
8	250	100	180	15
0	0.06	0.30	0	0.07
8	41.6	25	60	3

- to be cont'd. -

Table II-1 (cont'd.)

Reaction conditions	Kind of solvent			
	Amount of solvent (parts by weight)	Kind of catalyst	Amount of catalyst (parts by weight)	Reaction temperature (°C)
Proper- ties	200	Triphenyl-phosphine	2	100
	200	Triphenyl-phosphine	2	100
	200	Triphenyl-phosphine	2	100
	200	Triphenyl-phosphine	2	100
	200	Triphenyl-phosphine	2	100
Proper- ties	137	138	137	140
	105	107	105	110
	Hydroxyl group equivalent (g/eq)	Softening point (°C)	Hydroxyl group equivalent (g/eq)	Softening point (°C)
	137	138	137	140
	105	107	105	110

- to be cont'd. -

Table II-1 (cont'd.)

Toluene	Toluene	Toluene	Toluene	Toluene
200	250	200	200	200
Triphenyl-phosphine	Triphenyl-phosphine	Triphenyl-phosphine	Triphenyl-phosphine	Triphenyl-phosphine
2	2	3	3	2
100	100	100	100	100
5	7	5	5	5
135	136	140	142	137
106	106	108	110	105

Table II-2

		Example			
		II-1	II-2	II-3	II-4
Epoxy resin	Naphthalene type epoxy resin *II-8	(parts by weight)	90	90	50
	Epoxy resin *II-9	(parts by weight)			40
	Brominated bisphenol A type epoxy resin (epoxy equivalent: 370, softening point: 65°C)	(parts by weight)	10	10	10
Phenolic resin curing agent	Silicone-modified phenol novolac resin II(a)	(parts by weight)	70		
	II(b)	(")	70		30
	II(c)	(")		70	10
	II(d)	(")			
	II(e)	(")			
	II(f)	(")			
	II(g)	(")			
	II(h)	(")			
Phenolic resin *II-10	Phenol novolac resin (OH equivalent: 105, softening point: 105°C)	(parts by weight)			
	Phenolic resin *II-10	(parts by weight)			30
	Crushed filler	(parts by weight)	800	800	
Filler	Spherical filler	(")			1000

- to be cont'd. -

Table II-2 (cont'd.)

Comparative Example					
II-1	II-2	II-3	II-4	II-5	II-6
90	90	90	90	90	80
					5
10	10	10	10	10	10
70	70	70	70	70	10
					50
800	800	800	800	800	800

- to be cont'd. -

Table II-2 (cont'd.)

Spiral flow (cm) *II-11	95	96	101	92
Length of resin flash (mm) *II-12	0.5	0.4	0.6	0.4
Flexural strength (kg/mm ²)/elastic modulus (kg/mm ²) *II-13	1450/ 16.0	1450/ 16.2	1430/ 15.9	1450/ 16.0
Flexural expansion coefficient (x 10 ⁻⁵ /°C) *II-14	1.40	1.41	1.38	1.35
Tg (°C) *II-15	155	160	152	155
Thermal impact resistance (number of cracked moldings) *II-16	0	0	0	0
Soldering heat resistance (number of cracked moldings) *II-17	0	0	1	0
Overall evaluation	○	○	○	○

Table II-2 (cont'd.)

45	85	91	89	62	85
0.6	5.3	0.6	4.2	0.5	> 10
1450/ 16.0	1510/ 15.0	1450/ 16.1	1520/ 15.3	1450/ 15.5	1700/ 16.5
1.50	1.40	1.41	1.42	1.40	1.50
145	149	155	152	159	158
2	2	5	2	3	10
3	2	0	1	2	2
Δ	X	Δ	X	Δ	X

1 Evaluation methods

*II-11 Spiral flow

Measured by the same method as for *I-11.

*II-12 Length of resin flash

5 Measured by the same method as for *I-12.

*II-13 Flexural strength and elastic modulus

Measured at a span of 100 mm at a speed of 10 mm/min at room temperature, using a TENSILON flexural strength tester.

10 *II-14 Thermal expansion coefficient

Measured at 25°C for a sample of 15 x 3 x 4 mm, using a thermal expansion coefficient tester.

*II-15 T_g (glass transition temperature)

Measured for a sample of 15 x 3 x 4 mm, using
15 a thermal expansion coefficient tester.

*II-16 Thermal impact resistance

Measured by the same method as for *I-15.

*II-17 Soldering heat resistance

20 Moldings (chip size = 36 mm², package thickness = 2.0 mm) were treated in steam of 85°C and 85% R.H. for 72 hours, and the treated moldings were subjected to VPS (vapor phase soldering) treatment at 215°C for 90 seconds to examine the soldering heat resistance by the number of moldings which gave crack(s).

25 Synthesis Example III

As shown in Table III-1, an organopolysiloxane (one or two of *III-1 to *III-7 shown later) was reacted

- 1 with a phenol novolac resin (softening point = 105°C, OH equivalent = 105) in a solvent in the presence of a catalyst to obtain silicone-modified phenolic resins III(a) to III(h).

5 Example III-1

3,5,3',5'-Tetramethyl-4,4'-dihydroxybiphenyl diglycidyl ether	90 parts by weight
Brominated bisphenol A type epoxy resin (epoxy equivalent = 370, softening point = 65°C, bromine content = 37%)	10 parts by weight
Silicone-modified phenol novolac resin III(a)	70 parts by weight
Crushed fused silica	800 parts by weight
Antimony trioxide	10 parts by weight
Silane coupling agent	2 parts by weight
Triphenylphosphine	2 parts by weight
Carbon black	3 parts by weight
Carnauba wax	3 parts by weight

The above materials were mixed thoroughly at room temperature. The mixture was kneaded by a twin roll at 95-100°C. The kneaded product was cooled, crushed and made into tablets to obtain an epoxy resin composition for semiconductor sealing.

10

This material was made into a molding using a transfer molding machine (mold temperature = 175°C, curing time = 2 minutes). The molding was after-cured at 175°C for 8 hours and examined for properties. The

1 results are shown in Table III-2.

Example III-2

An epoxy resin composition for semiconductor sealing was obtained in the same manner as in Example
5 III-1 except that the amount of 3,5,3',5'-tetramethyl-4,4'-dihydroxybiphenyl diglycidyl ether was changed from 90 parts by weight to 50 parts by weight and there was newly added 35 parts by weight of 4,4'-dihydroxybiphenyl diglycidyl ether.

10 The resin composition was examined for properties, and the results are shown in Table III-2.

Examples III-3 to III-4

Epoxy resin compositions for semiconductor sealing whose compounding recipes are shown in Table
15 III-2 were obtained in the same manner as for Example III-1.

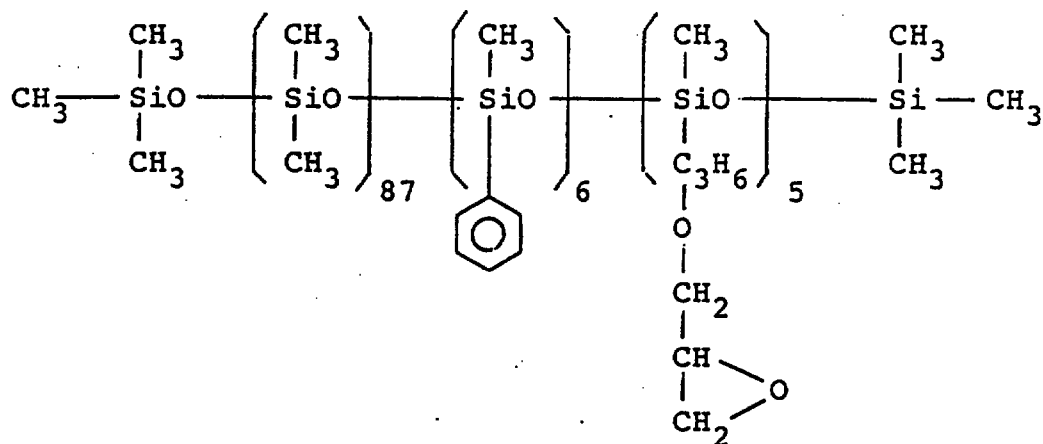
The resin compositions were examined for properties, and the results are shown in Table III-2.

Comparative Examples III-1 to III-6

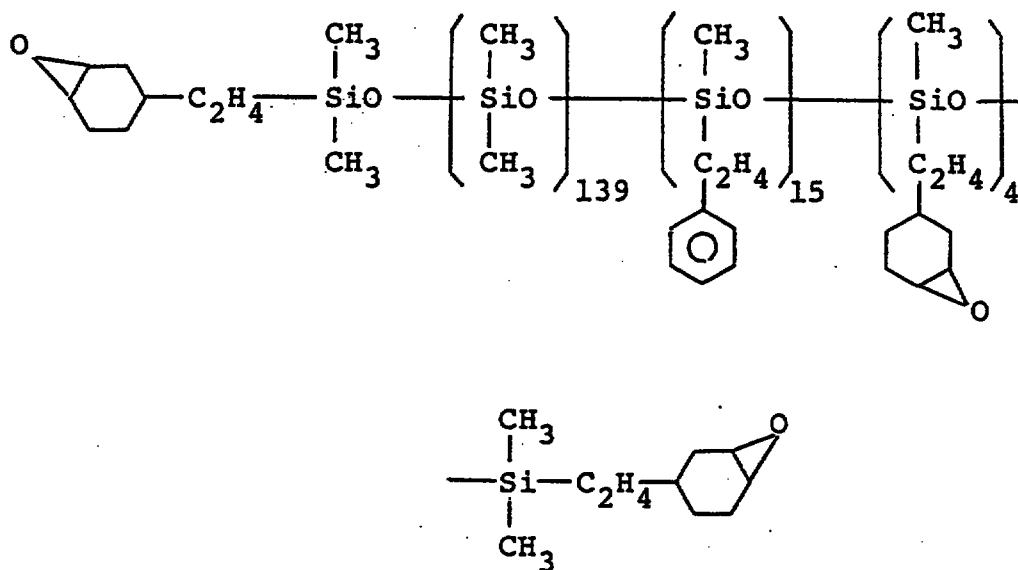
20 Epoxy resin compositions for semiconductor sealing whose compounding recipes are shown in Table III-2 were obtained in the same manner as for Example III-1.

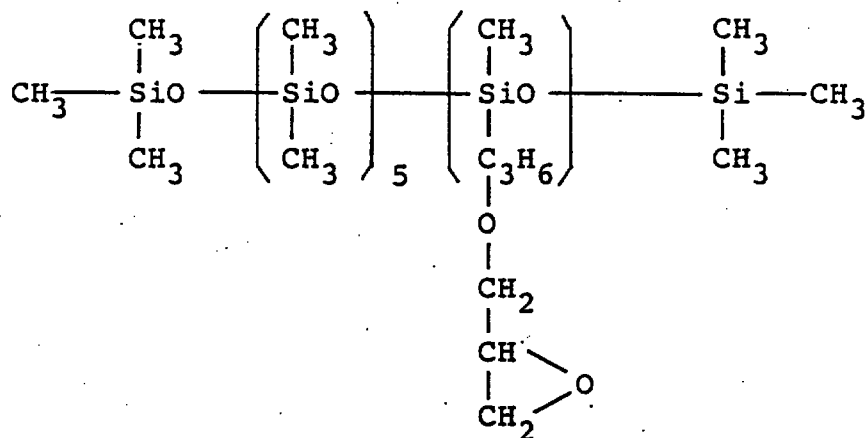
The resin compositions were examined for
25 properties, and the results are shown in Table III-2.

Organopolysiloxane *III-1

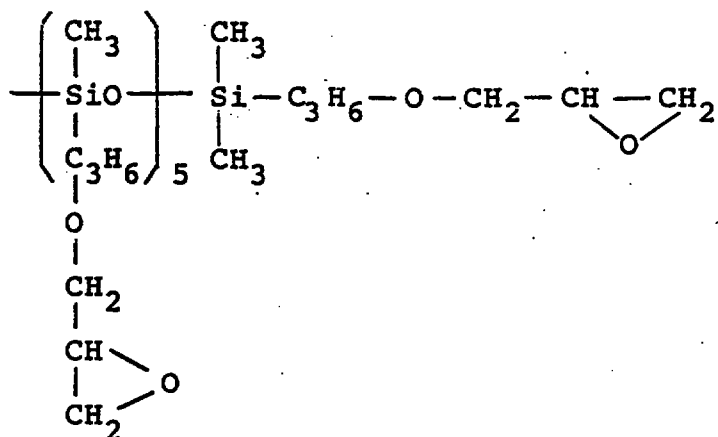
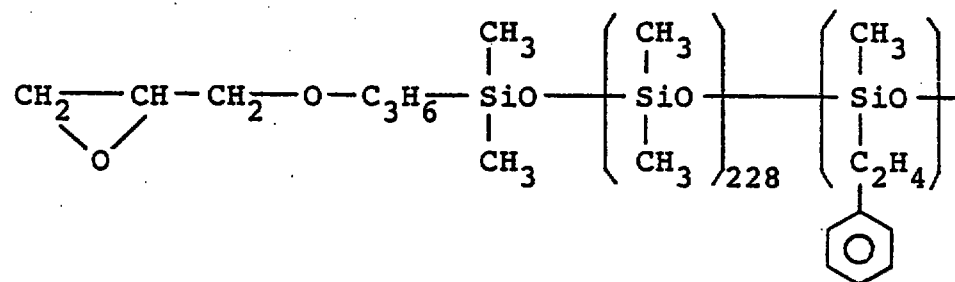


Organopolysiloxane *III-2

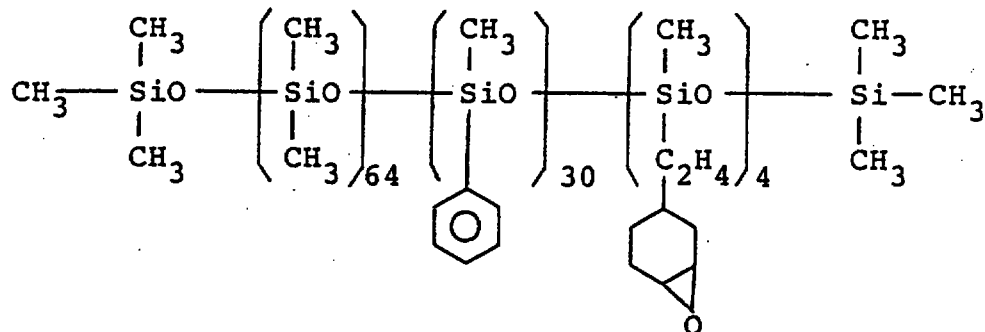




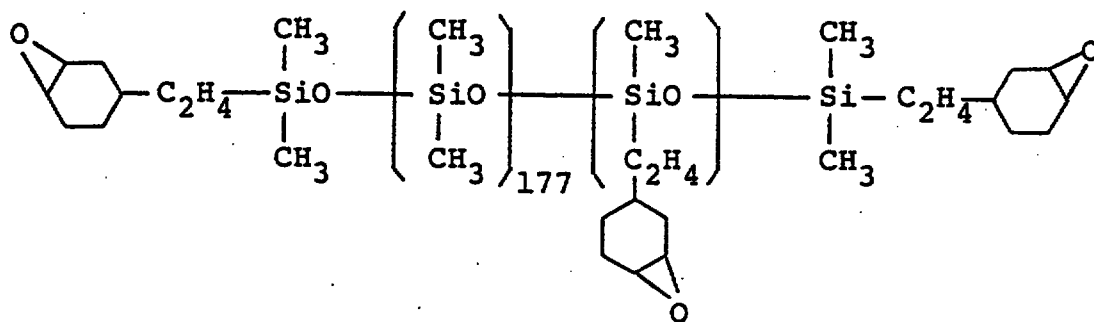
Organopolysiloxane *III-4



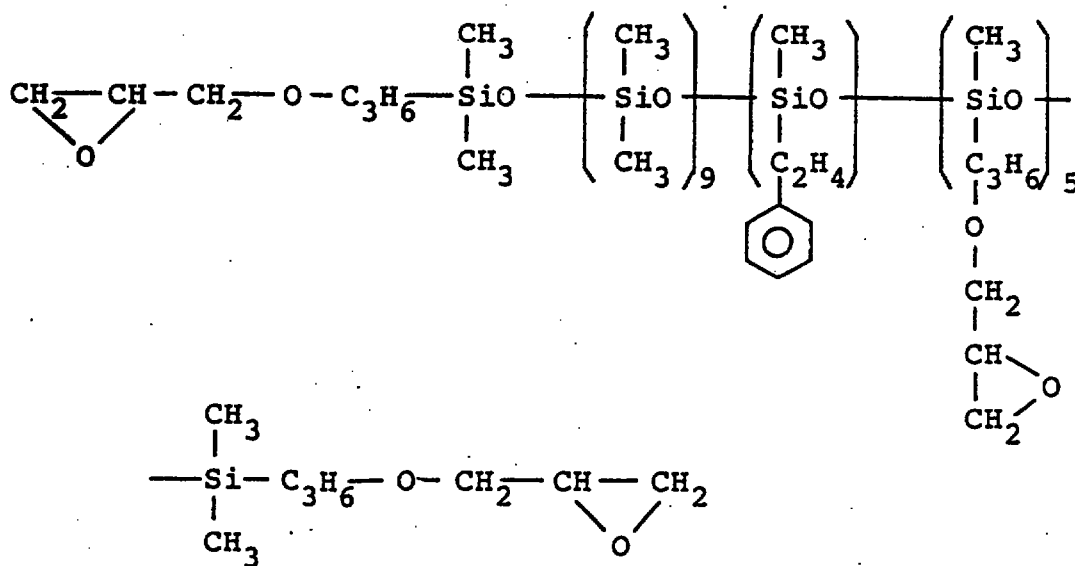
Organopolysiloxane *III-5



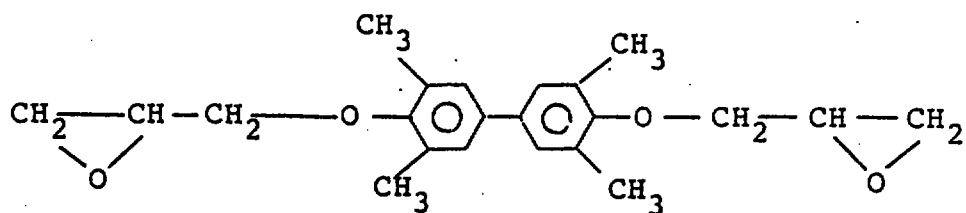
Organopolysiloxane *III-6



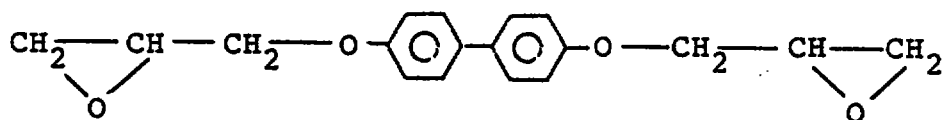
Organopolysiloxane *III-7



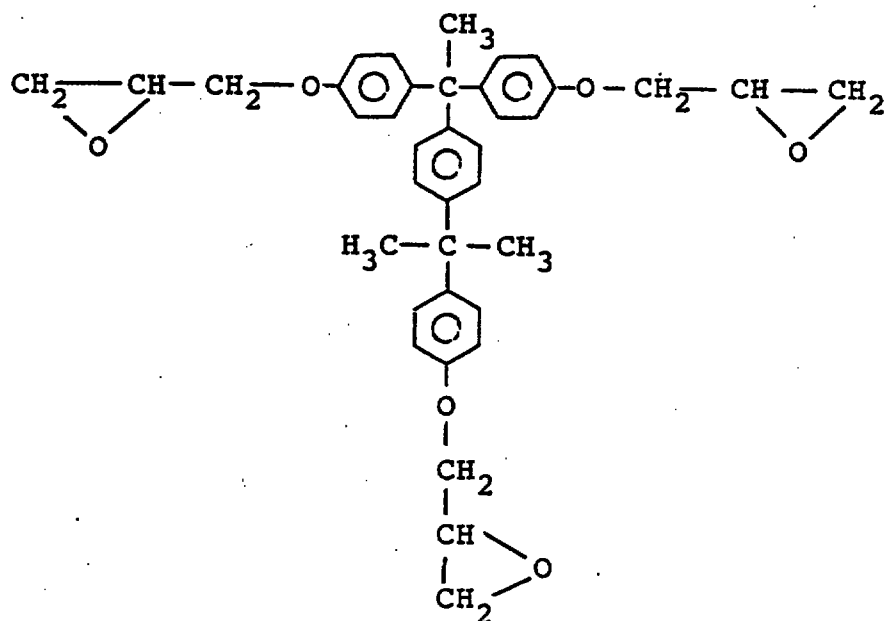
*III-8 Biphenyl type epoxy compound represented by the following formula (epoxy equivalent = 185)



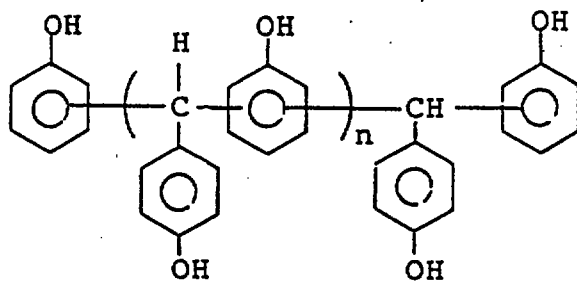
*III-9 Biphenyl type epoxy compound represented by the following formula



*III-10 Epoxy resin represented by the following formula



*III-11 Phenolic resin represented by the following formula



$n = 0 \sim 9$

Table III-1

		Silicone-modified phenolic resin III(a)	Silicone-modified phenolic resin III(b)	Silicone-modified phenolic resin III(c)
Raw Materials	Phenolic resin	100	100	100
	Phenol novolac resin (OH equivalent: 105, softening point: 105°C) (parts by weight)			
	Organopolysiloxane *III-1 (parts by weight)	30		10
	Organopolysiloxane *III-2 (parts by weight)		30	20
	Organopolysiloxane *III-3 (parts by weight)			
	Organopolysiloxane *III-4 (parts by weight)			
	Organopolysiloxane *III-5 (parts by weight)			
	Organopolysiloxane *III-6 (parts by weight)			
	Organopolysiloxane *III-7 (parts by weight)			
	N (polymerization degree of siloxane)	100	160	-
Silicone				
	m/N (molar fraction of phenyl group or phenylethyl group)	0.06	0.094	-
	N/n (siloxane polymerization degree/number of functional groups)	20	26.7	-

- to be cont'd. -

Table III-1 (cont'd.)

Silicone- modified phenolic resin III(d)	Silicone- modified phenolic resin III(e)	Silicone- modified phenolic resin III(f)	Silicone- modified phenolic resin III(g)	Silicone- modified phenolic resin III(h)
100	100	100	100	100
30				
	30			
		30		
			30	
				30
8	236	100	180	17
0	0.004	0.30	0	0.06
8	33.7	25	60	2.4

- to be cont'd. -

Table III-1 (cont'd.)

Properties	Reaction conditions			
	Kind of solvent	Toluene	Toluene	Toluene
	Amount of solvent (parts by weight)	200	200	200
	Kind of catalyst	Triphenyl-phosphine	Triphenyl-phosphine	Triphenyl-phosphine
	Amount of catalyst (parts by weight)	2	2	3
	Reaction temperature (°C)	100	100	100
	Reaction time (hr)	5	5	7
	Hydroxyl group equivalent (g/eq)	137	138	140
	Softening point (°C)	105	107	110

- to be cont'd. -

Table III-1 (cont'd.)

Toluene	Toluene	Toluene	Toluene	Toluene
230	250	200	200	200
Triphenyl-phosphine	Triphenyl-phosphine	Triphenyl-phosphine	Triphenyl-phosphine	Triphenyl-phosphine
2	2	3	3	2
100	100	100	100	100
5	7	5	5	5
135	136	140	136	138
106	106	108	111	106

Table III-2

	Example			
	III-1	III-2	III-3	III-4
Epoxy resin	90	50	20	30
	3,5,3',5'-Tetramethyl-4,4'-dihydroxybiphenyl diglycidyl ether *III-8 (parts by weight)			
	4,4'-Dihydroxybiphenyl diglycidyl ether *III-9 (parts by weight)	35	60	30
	Epoxy resin *III-10 (parts by weight)			40
Phenolic resin curing agent	10	10	10	10
	Brominated bisphenol A type epoxy resin (epoxy equivalent: 370, softening point: 65°C) (parts by weight)			
	Silicone-modified phenol novolac resin III(a) (parts by weight)	70	70	
	" III(b) (") " III(c) (") " III(d) (") " III(e) (") " III(f) (") " III(g) (") " III(h) (")		70	50
Phenolic resin	Phenolic novolac resin (OH equivalent: 105, softening point: 105°C) (parts by weight)			
	Phenolic resin *III-11 (parts by weight)			20

- to be cont'd. -

Table III-2 (cont'd.)

Comparative Example						
III-1	III-2	III-3	III-4	III-5	III-6	
90	90	90	90	90	80	
						5
10	10	10	10	10	10	
70	70	70	70	70		10
					50	

- to be cont'd. -

Table III-2 (cont'd.)

Filler	Crushed filler	(parts by weight)		(parts by weight)	
	Spherical filler	800	800	800	1000
- 61 -					
Spiral flow (cm) *III-12		97	96	102	92
Length of resin flash (mm) *III-13		0.5	0.4	0.6	0.5
Flexural strength (kg/mm^2)/elastic modulus (kg/mm^2) *III-14		1450/ 15.5	1420/ 16.0	1420/ 15.9	1450/ 16.0
Thermal expansion coefficient ($\times 10^{-5}/^{\circ}\text{C}$) *III-15		1.42	1.41	1.40	1.35
Tg ($^{\circ}\text{C}$) *III-16		155	159	152	195
Thermal impact resistance (number of cracked moldings) *III-17		0	0	0	0
Soldering heat resistance (number of cracked moldings) *III-18		1	1	1	0
Overall evaluation		○	○	○	○

- to be cont'd. -

Table III-2 (cont'd.)

800	800	800	800	800	800	800
45	85	91	91	62	85	
0.6	5.3	0.6	4.2	0.5	> 10	
1440/ 16.0	1510/ 15.0	1450/ 16.1	1520/ 15.3	1490/ 15.5	1690/ 16.5	
1.50	1.45	1.41	1.42	1.40	1.50	
145	149	154	152	159	158	
2	2	5	2	4	10	
3	2	0	1	2	2	
Δ	X	Δ	X	Δ	X	

1 Evaluation methods

*III-12 Spiral flow

Measured by the same method as for *I-11.

*III-13 Length of resin flash

5 Measured by the same method as for *I-12.

*III-14 Flexural strength and elastic modulus

Measured by the same method as for *II-13.

*III-15 Thermal expansion coefficient

Measured by the same method as for *II-14.

10 *III-16 Tg (glass transition temperature)

Measured by the same method as for *II-15.

*III-17 Thermal impact resistance

Measured by the same method as for *I-15.

*III-18 Soldering heat resistance

15 Measured by the same method as for *II-17.

Synthesis Example IV

As shown in Table IV-1, an organopolysiloxane (one or two of *IV-1 to *IV-7 shown later) was reacted with a phenol novolac resin (softening point = 105°C, OH equivalent = 105) in a solvent in the presence of a catalyst to obtain silicone-modified phenolic resins IV(a) to IV(h).

20

Example IV-1

Naphthalene type epoxy compound 50 parts by weight

25 Biphenyl type epoxy compound A 50 parts by weight

Brominated bisphenol A type epoxy resin (epoxy equivalent = 370, softening point = 65°C, bromine content = 37%)	10 parts by weight
Silicone-modified phenol novolac resin IV(a)	70 parts by weight
Crushed fused silica	800 parts by weight
Antimony trioxide	10 parts by weight
Silane coupling agent	2 parts by weight
Triphenylphosphine	2 parts by weight
Carbon black	3 parts by weight
Carnauba wax	3 parts by weight

1 The above materials were mixed thoroughly at
room temperature. The mixture was kneaded by a twin
roll at 95-100°C. The kneaded product was cooled,
crushed and made into tablets to obtain an epoxy resin
5 composition for semiconductor sealing.

 This material was made into a molding using a
transfer molding machine (mold temperature = 175°C, curing
time = 2 minutes). The molding was after-cured at 175°C
for 8 hours and examined for properties. The results
10 are shown in Table IV-2.

Examples IV-2 to IV-4

 Epoxy resin compositions whose compounding
recipes are shown in Table IV-2 were obtained in the same
manner as in Example IV-1.

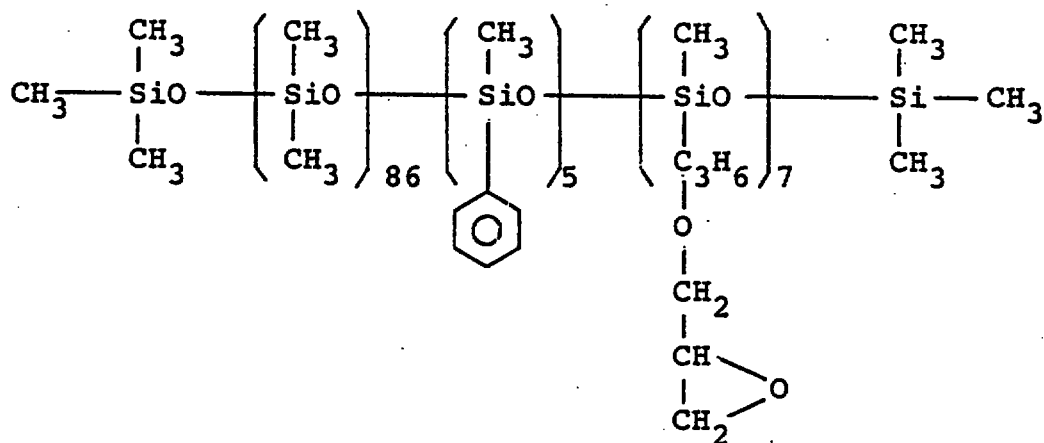
15 These resin compositions were measured for
properties, and the results are shown in Table IV-2.

1 Comparative Examples IV-1 to IV-6

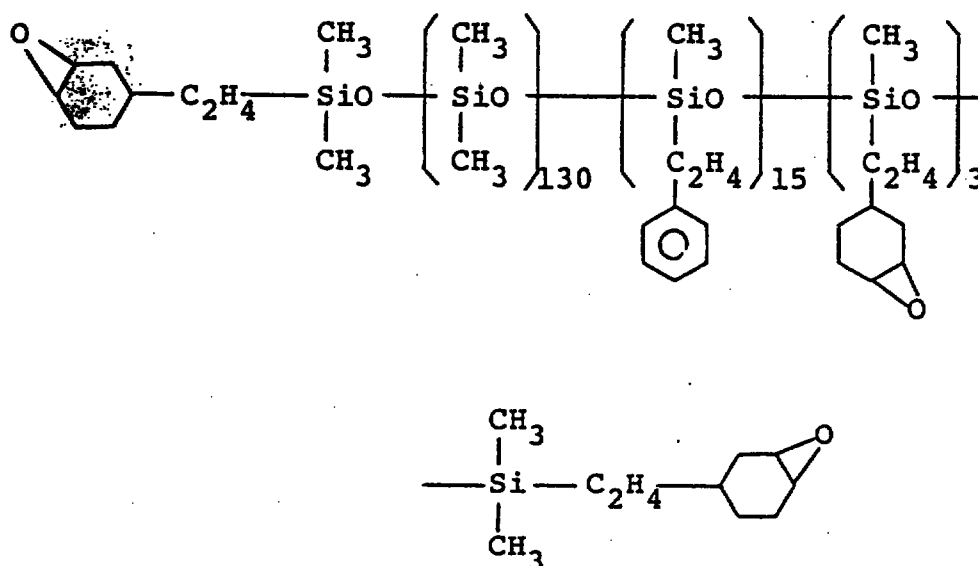
Epoxy resin compositions whose compounding recipes are shown in Table IV-2 were obtained in the same manner as in Example IV-1.

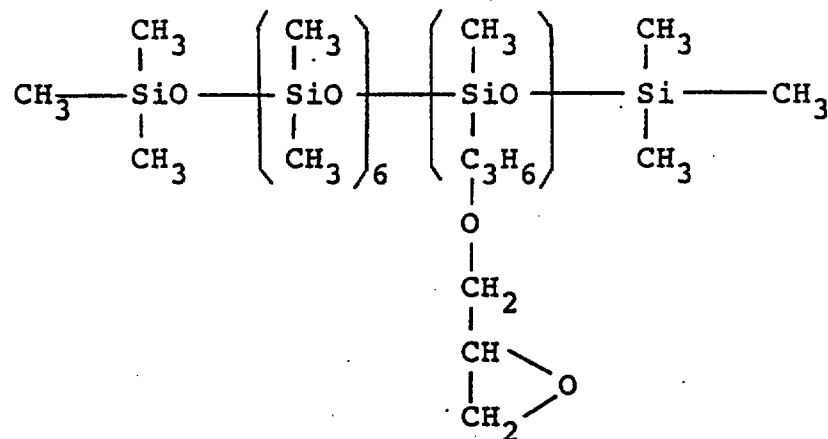
5 These resin compositions were measured for properties, and the results are shown in Table IV-2.

Organopolysiloxane *IV-1

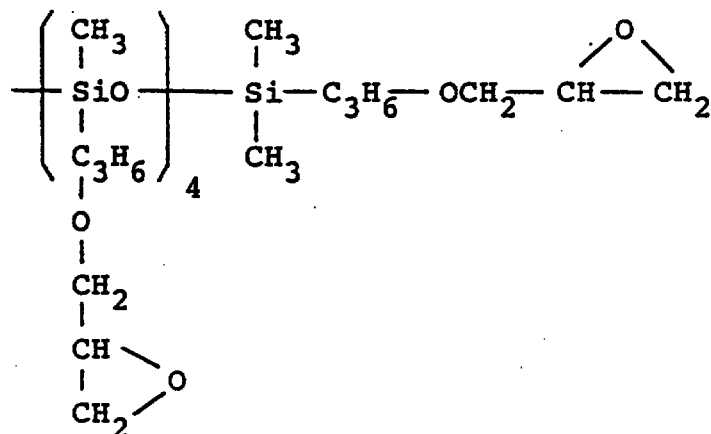
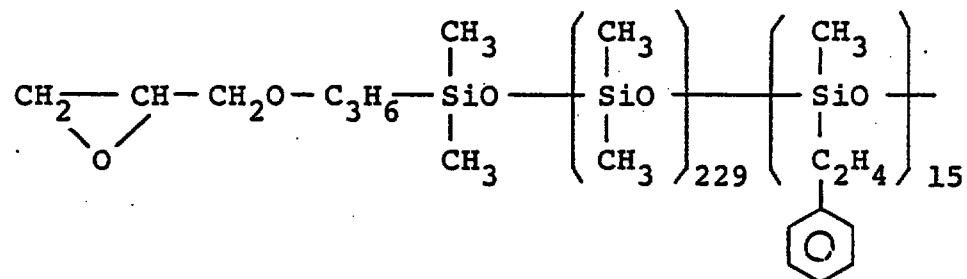


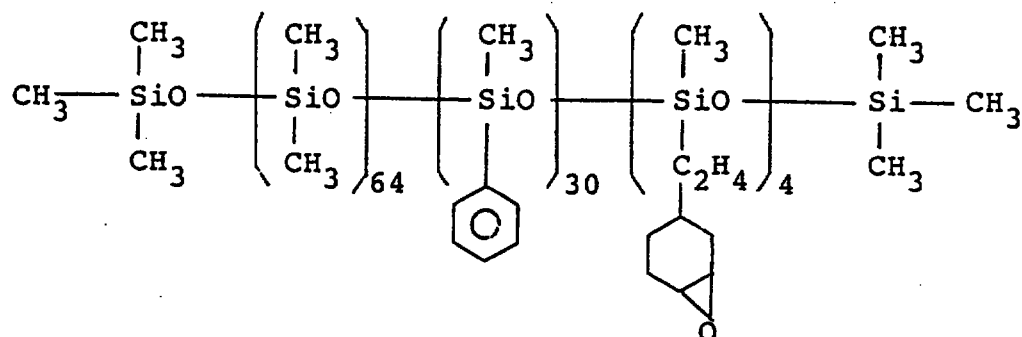
Organopolysiloxane *IV-2



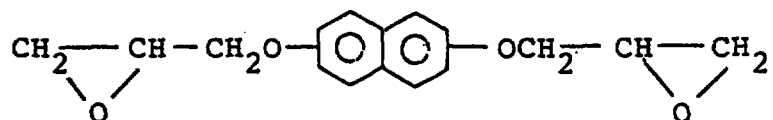


Organopolysiloxane *IV-4

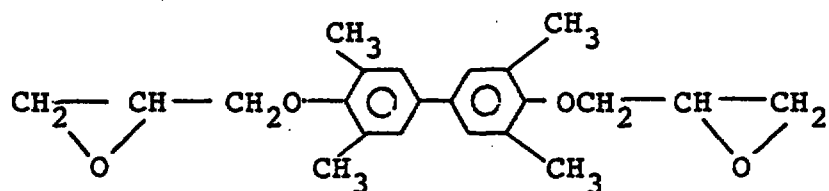


[illegible][illegible]

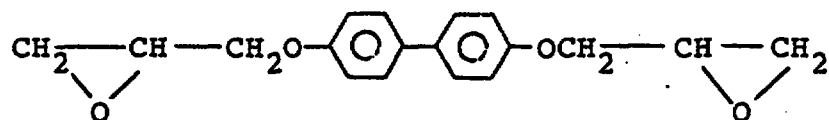
*IV-8 Naphthalene type epoxy compound represented by the following formula (epoxy equivalent = 151)



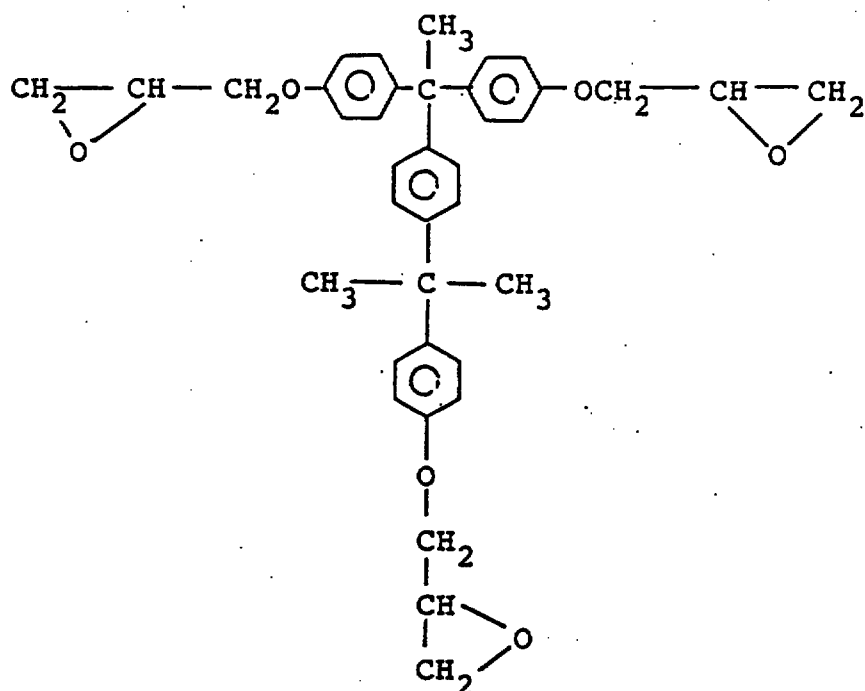
*IV-9 Biphenyl type epoxy compound A represented by the following formula (epoxy equivalent = 185)



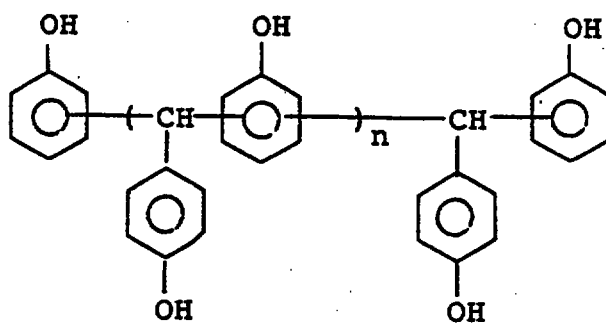
*IV-10 Biphenyl type epoxy compound B represented by the following formula (epoxy equivalent = 155)



*IV-11 Epoxy resin represented by the following formula



*IV-12 Phenolic resin represented by the following formula



$$n = 0 \sim 9$$

Table IV-1

Raw materials		Silicone- modified phenolic resin IV (a)	Silicone- modified phenolic resin IV (b)	Silicone- modified phenolic resin IV (c)
Phenolic resin	Phenol novolac resin (OH equivalent: 105, softening point: 105°C) (parts by weight)	100	100	100
	Organopolysiloxane *IV-1 (parts by weight)	30		10
	Organopolysiloxane *IV-2 (parts by weight)		30	20
	Organopolysiloxane *IV-3 (parts by weight)			
	Organopolysiloxane *IV-4 (parts by weight)			
	Organopolysiloxane *IV-5 (parts by weight)			
	Organopolysiloxane *IV-6 (parts by weight)			
	Organopolysiloxane *IV-7 (parts by weight)			
	N (polymerization degree of siloxane)	100	150	-
	m/N (molar fraction of phenyl group or phenylethyl group)	0.05	0.1	-
Silicone				
N/n (siloxane polymerization degree/number of functional groups)		14.3	30	-

- to be cont'd. -

Table IV-1 (cont'd.)

Silicone- modified phenolic resin IV(d)	Silicone- modified phenolic resin IV(e)	Silicone- modified phenolic resin IV(f)	Silicone- modified phenolic resin IV(g)	Silicone- modified phenolic resin IV(h)
100	100	100	100	100
30				
	30			
		30		
			30	
				30
9	250	100	180	16
0	0.05	0.30	0	0.06
9	41.6	25	60	2.7

- to be cont'd. -

Table IV-1 (cont'd.)

Reaction conditions	Kind of solvent	Toluene		
		Triphenyl-phosphine		
Properties	Amount of solvent (parts by weight)	200	200	200
	Kind of catalyst	Triphenyl-phosphine	Triphenyl-phosphine	Triphenyl-phosphine
	Amount of catalyst (parts by weight)	2	2	3
	Reaction temperature (°C)	100	100	100
	Reaction time (hr)	5	5	7
	Hydroxyl group equivalent (g/eq)	136	138	138
	Softening point (°C)	104	107	110

- to be cont'd. -

Table IV-1 (cont'd.)

Toluene	Toluene	Toluene	Toluene	Toluene
200	250	200	200	200
Triphenyl- phosphine	Triphenyl- phosphine	Triphenyl- phosphine	Triphenyl- phosphine	Triphenyl- phosphine
2	2	3.5	3	2.5
100	100	100	100	100
7	7	5	5	5
135	136	140	140	137
106	105	108	110	106

Table IV-2

		Example			
		IV-1	IV-2	IV-3	IV-4
Epoxy resin	Naphthalene type epoxy compound *IV-8 (parts by weight)	50	50	30	25
	Biphenyl type epoxy compound A *IV-9 (parts by weight)	50		50	10
	Biphenyl type epoxy compound B *IV-10 (parts by weight)		40	20	20
	Epoxy resin *IV-11 (parts by weight)				40
	Brominated bisphenol A type epoxy resin (epoxy equivalent: 370, softening point: 65°C) (parts by weight)	10	10	10	10
Phenolic resin curing agent	Silicone-modified phenol novolac resin IV(a) (parts by weight)	70	70		30
	" IV(b) (")			70	10
	" IV(c) (")				
	" IV(d) (")				
	" IV(e) (")				
	" IV(f) (")				
	" IV(g) (")				
	" IV(h) (")				
Phenolic resin	Phenol novolac resin (OH equivalent: 105, softening point: 105°C) (parts by weight)				
	Phenolic resin *IV-12 (parts by weight)				30

- to be cont'd. -

Table IV-2 (cont'd.)

Comparative Example					
IV-1	IV-2	IV-3	IV-4	IV-5	IV-6
50	50	50	50	50	40
20	20	20	20	20	
30	30	30	30	30	40
					5
10	10	10	10	10	10
70	70	70	70	70	10
					50

-- to be cont'd. --

Table IV-2 (cont'd.)

Property	Crushed filler Spherical filler	(parts by weight) (")	800			
			800	800	800	1000
Spiral flow (cm) *IV-13			95	96	101	99
Length of resin flash (mm) *IV-14			0.5	0.4	0.4	0.4
Flexural strength (kg/mm^2)/elastic modulus (kg/mm^2) *IV-15			1400/ 16.0	1420/ 16.2	1430/ 15.9	1450/ 16.0
Thermal expansion coefficient ($10^{-5}/^{\circ}\text{C}$) *IV-16			1.40	1.41	1.38	1.35
Tg ($^{\circ}\text{C}$) *IV-17			155	160	152	155
Thermal impact resistance (number of cracked moldings) *IV-18			0	0	0	0
Soldering heat resistance (number of cracked moldings) *IV-19			0	0	1	0
Overall evaluation			○	○	○	○

- to be cont'd. -

Table IV-2 (cont'd.)

800	800	800	800	800	800	800
45	85	90	89	60	85	
0.6	5.3	0.6	5.0	0.5	> 10	
1450/ 15.5	1510/ 15.8	1450/ 16.1	1520/ 15.3	1490/ 15.5	1700/ 16.5	
1.50	1.38	1.41	1.42	1.40	1.45	
145	149	156	152	159	158	
3	4	5	2	4	20	
4	4	0	1	2	2	
Δ	X	Δ	X	Δ	X	X

1 Evaluation methods

*IV-13 Spiral flow

Measured by the same method as for *I-11.

*IV-14 Length of resin flash

5 Measured by the same method as for *I-12.

*IV-15 Flexural strength and elastic modulus

Measured by the same method as for *II-13.

*IV-16 Thermal expansion coefficient

Measured by the same method as for *II-14.

10 *IV-17 Tg (glass transition temperature)

Measured by the same method as for *II-15.

*IV-18 Thermal impact resistance

Measured by the same method as for *I-15 except that the number of cycles was increased to 1,000.

15 *IV-19 Soldering heat resistance

20 Moldings (chip size = 36 mm^2 , package thickness = 2.0 mm) were treated in steam of 85°C and 85% R.H. for 72 hours, and the resulting moldings were subjected to an infrared reflow treatment at 240°C to
20 examine the soldering heat resistance by the number of moldings which gave crack(s).

Synthesis Example V

As shown in Table V-1, an organopolysiloxane (one or two of *V-1 to *V-7 shown later) was reacted
25 with a phenol novolac resin (softening point = 105°C, OH equivalent = 105) in a solvent in the presence of a catalyst to obtain silicone-modified phenolic resins

1 V(a) to V(h).

Example V-1

Biphenyl type epoxy resin A *V-8	40 parts by weight
Trifunctional epoxy resin *V-10	50 parts by weight
Brominated bisphenol A type epoxy resin (epoxy equivalent = 370, softening point = 65°C, bromine content = 37%)	10 parts by weight
Silicone-modified phenol novolac resin V(a)	70 parts by weight
Crushed fused silica	500 parts by weight
Antimony trioxide	10 parts by weight
Silane coupling agent	2 parts by weight
Triphenylphosphine	2 parts by weight
Carbon black	3 parts by weight
Carnauba wax	3 parts by weight

The above materials were mixed thoroughly at room temperature. The mixture was kneaded by a twin
5 roll at 95-100°C. The kneaded product was cooled, crushed and made into tablets to obtain an epoxy resin composition for semiconductor sealing.

This material was made into a molding using a transfer molding machine (mold temperature = 175°C, curing
10 time = 2 minutes). The molding was after-cured at 175°C for 8 hours and examined for properties. The results are shown in Table V-2.

1 Example V-2

An epoxy resin composition for semiconductor sealing was obtained in the same manner as in Example V-1 except that the biphenyl type epoxy resin A was
5 changed to a biphenyl type epoxy resin B (*V-9) and the silicone-modified phenol novolac resin V(a) was changed to a silicone-modified phenol novolac resin V(b).

The resin composition was examined for proper-
10 ties, and the results are shown in Table V-2.

Example V-3

An epoxy resin composition for semiconductor sealing whose compounding recipe is shown in Table V-2, was obtained in the same manner as in Example V-1.

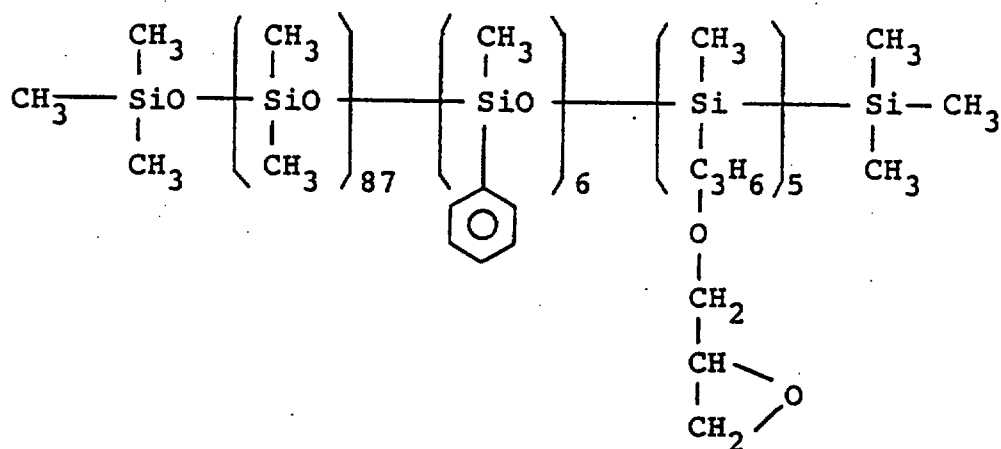
15 The resin composition was examined for properties, and the results are shown in Table V-2.

Comparative Examples V-1 to V-6

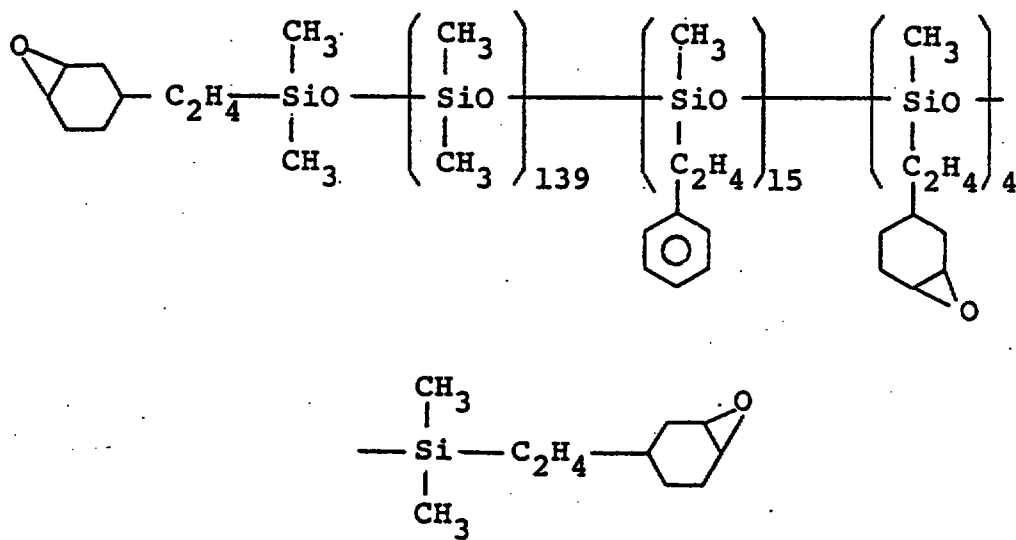
Epoxy resin compositions for semiconductor sealing whose compounding recipes are shown in Table
20 V-2, were obtained in the same manner as in Example V-1.

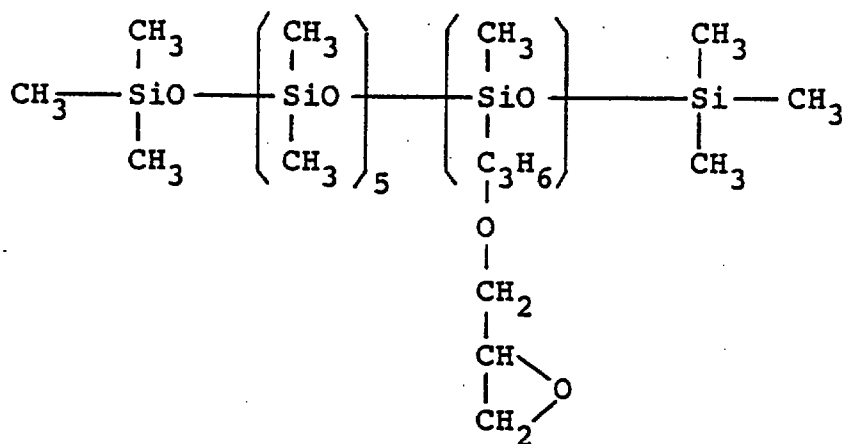
The resin compositions were examined for properties, and the results are shown in Table V-2.

Organopolysiloxane *V-1

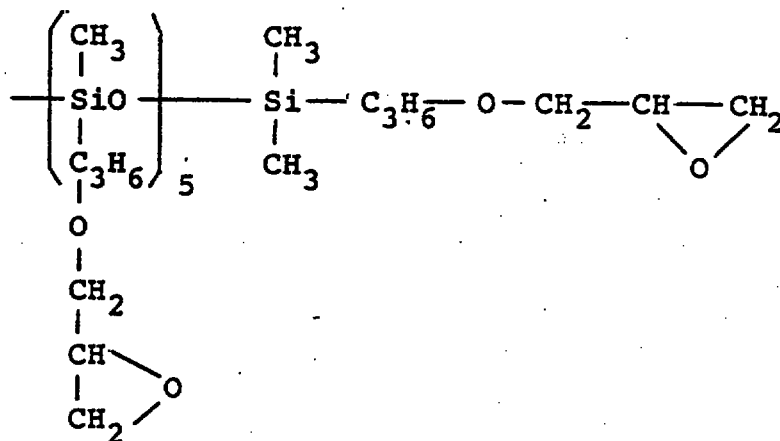
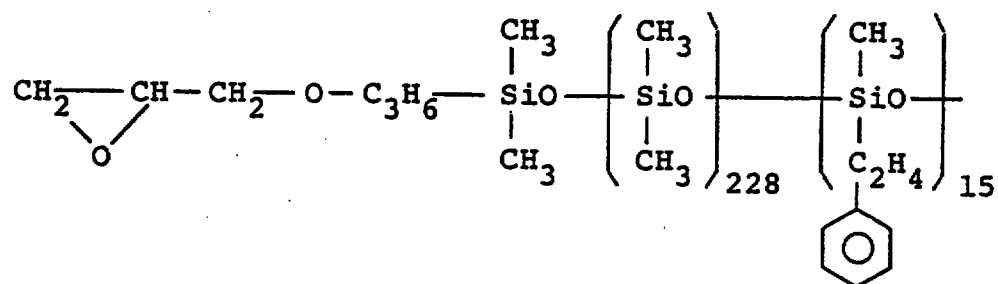


Organopolysiloxane *V-2

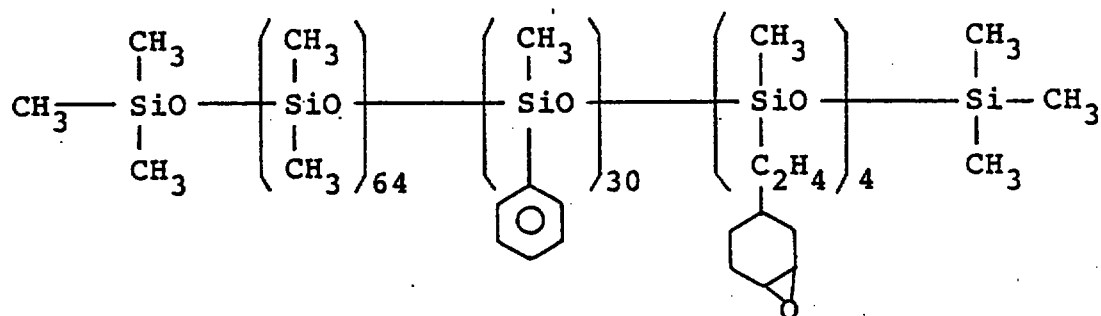




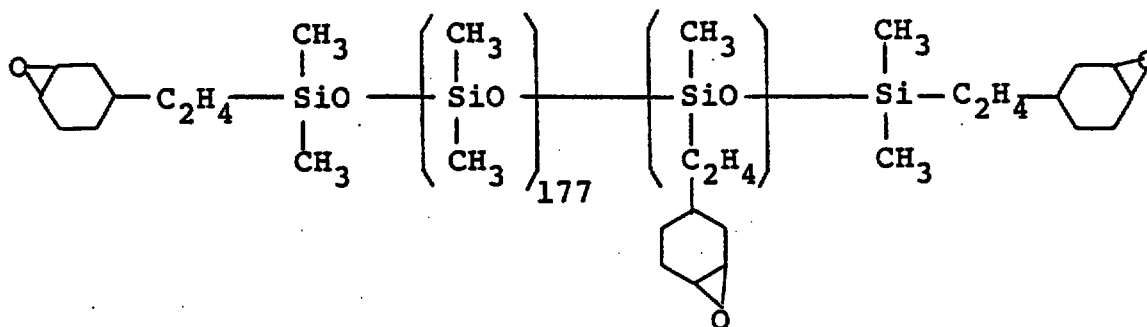
Organopolysiloxane *V-4



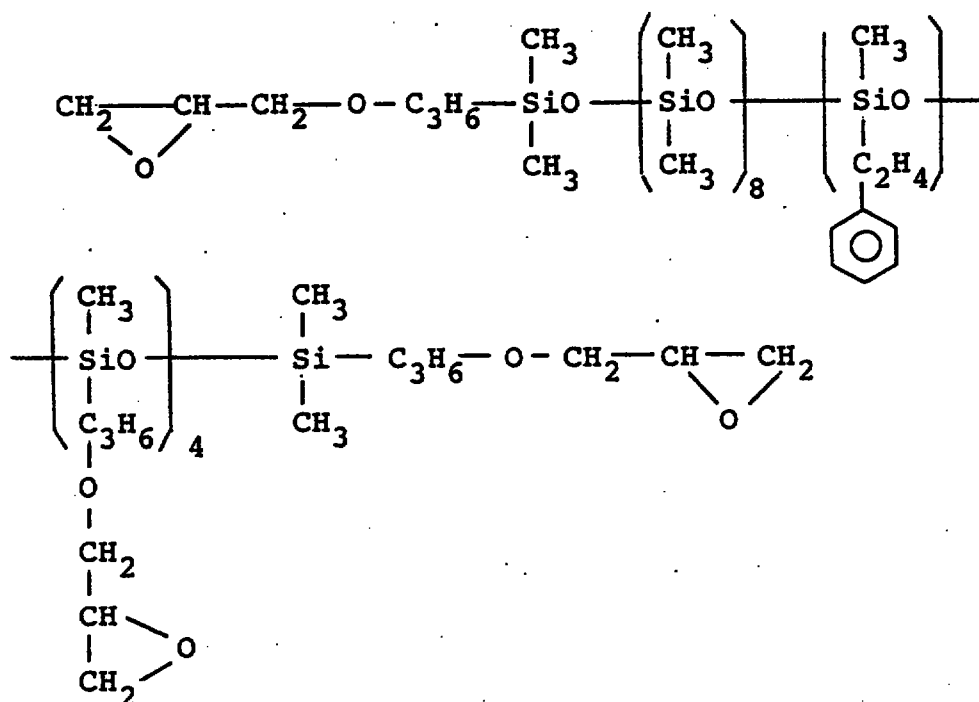
Organopolysiloxane *V-5



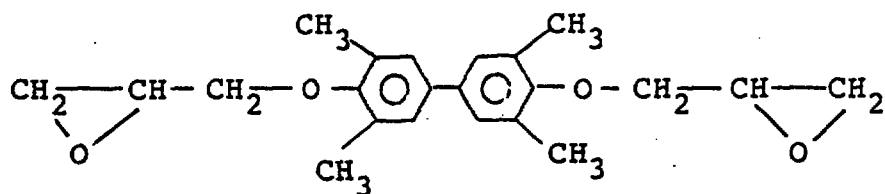
Organopolysiloxane *V-6



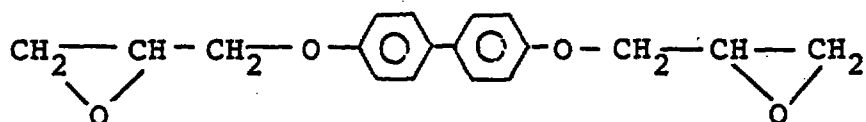
Organopolysiloxane *V-7



*V-8 Biphenyl type epoxy resin A represented by the following formula (epoxy equivalent = 185)



*V-9 Biphenyl type epoxy resin B represented by the following formula



*V-10 Epoxy resin represented by the following formula

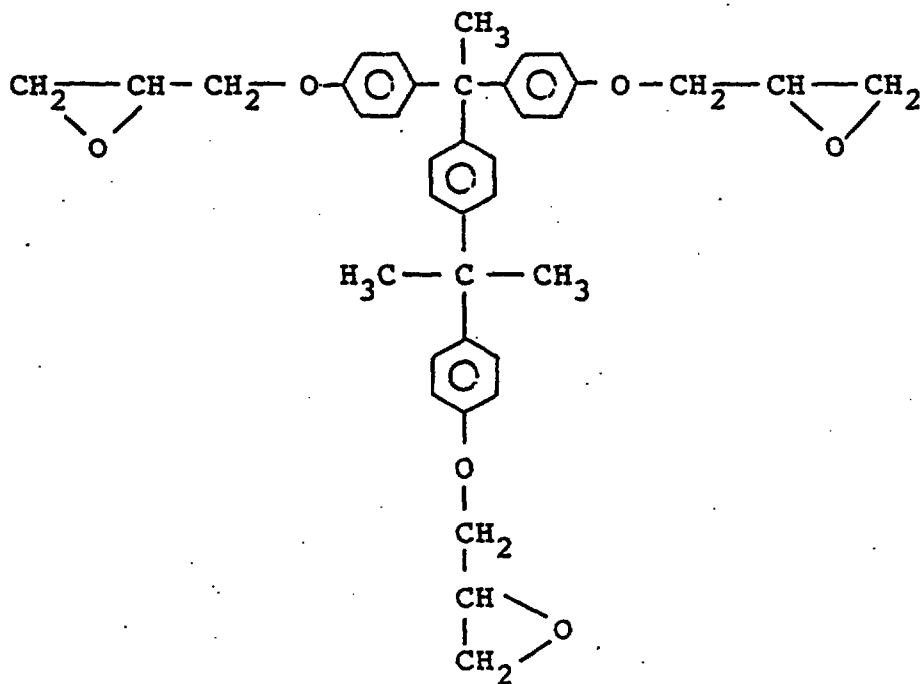


Table V-1

Raw materials		Silicone- modified phenolic resin V(a)	Silicone- modified phenolic resin V(b)	Silicone- modified phenolic resin V(c)
Phenolic resin	Phenol novolac resin (OH equivalent: 105, softening point: 105°C) (parts by weight)	100	100	100
	Organopolysiloxane *V-1 (parts by weight)	30		10
	Organopolysiloxane *V-2 (parts by weight)		30	20
	Organopolysiloxane *V-3 (parts by weight)			
	Organopolysiloxane *V-4 (parts by weight)			
	Organopolysiloxane *V-5 (parts by weight)			
	Organopolysiloxane *V-6 (parts by weight)			
	Organopolysiloxane *V-7 (parts by weight)			
	N (polymerization degree of siloxane)	100	160	-
	m/N (molar fraction of phenyl group or phenylethyl group)	0.06	0.094	-
Silicone				
N/n (siloxane polymerization degree/number of functional groups)		20	26.7	-

- to be cont'd. -

Table V-1 (cont'd.)

Silicone- modified phenolic resin V(d)	Silicone- modified phenolic resin V(e)	Silicone- modified phenolic resin V(f)	Silicone- modified phenolic resin V(g)	Silicone- modified phenolic resin V(h)
100	100	100	100	100
30				
	30			
		30		
			30	
				30
8	250	100	180	15
0	0.06	0.30	0	0.07
8	35.7	25	60	2.5

- to be cont'd. -

Table V-1 (cont'd.)

Reaction conditions	Kind of solvent		
	Amount of solvent (parts by weight)	Toluene	Toluene
Kind of catalyst		200	200
		Triphenyl-phosphine	Triphenyl-phosphine
Amount of catalyst (parts by weight)		3	3
Reaction temperature (°C)		100	100
Reaction time (hr)		5	7
Hydroxyl group equivalent (g/eq)		137	138
			139
Softening point (°C)		106	107
			110

- to be cont'd. -

Table V-1 (cont'd.)

Toluene	Toluene	Toluene	Toluene	Toluene
230	250	200	200	200
Triphenyl-phosphine	Triphenyl-phosphine	Triphenyl-phosphine	Triphenyl-phosphine	Triphenyl-phosphine
3	3	3	3	3
100	100	100	100	100
5	7	5	5	5
138	136	140	136	138
107	106	108	111	106

Table V-2

Comparative Example						
V-1	V-2	V-3	V-4	V-5	V-6	
40	40	40	40	40	40	
50	50	50	50	50	50	
10	10	10	10	10	10	
					15	
70	70	70	70	70		
						40

- to be cont'd. -

Table V-2 (cont'd.)

Properties	90	95	98
Spiral flow (cm) *V-11			
Length of resin flash (mm) *V-12	0.5	0.4	0.3
Mold staining *V-13	○	○	○
Koka type flow viscosity (poises) *V-14	231	230	245
Thermal impact resistance (number of cracked moldings) *V-15	0	0	0
Soldering heat resistance (number of cracked moldings) *V-16	0	1	0
Overall evaluation	○	○	○

-- to be cont'd. --

Table V-2 (cont'd.)

60	95	90	94	54	95
0.6	5.0	0.5	5.2	0.4	5.2
○	X	○	X	○	X
410	221	220	230	415	220
3	4	5	2	4	15
4	4	0	1	2	2
Δ	X	Δ	X	Δ	X

1 Evaluation methods

*V-11 Spiral flow

Measured by the same method as for *I-11.

*V-12 Length of resin flash

5 Measured by the same method as for *I-12.

*V-13 Mold staining

Mold staining after 1,000 shots of molding
was examined visually.

*V-14 Koka type flow viscosity

10 A Koka type flow viscosity (poises) at 175°C.

*V-15 Thermal impact resistance

Measured by the same method as for *I-15.

*V-16 Soldering heat resistance

Measured by the same method as for *II-17.

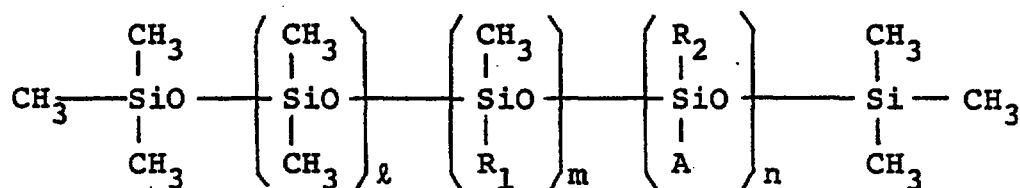


CLAIMS

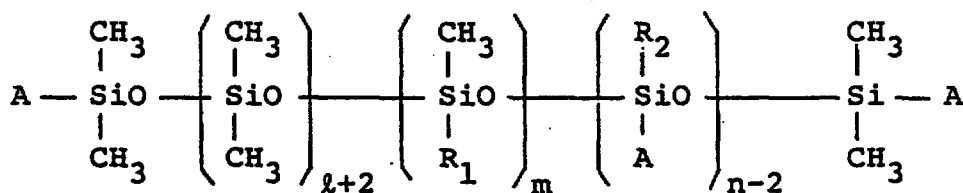
1. An epoxy resin composition for semiconductor sealing, comprising as essential components:

(A) an epoxy resin,

(B) a phenolic resin curing agent comprising 30-100% by weight, based on the total amount of the phenolic resin curing agent, of a silicone-modified phenolic resin curing agent obtained by reacting a phenolic resin with at least one of silicone compounds represented by the following formulas [I] and [II]

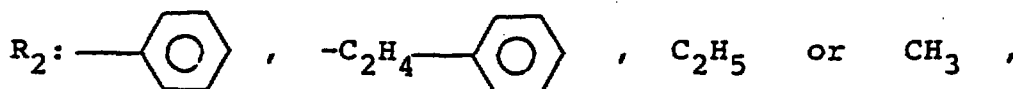
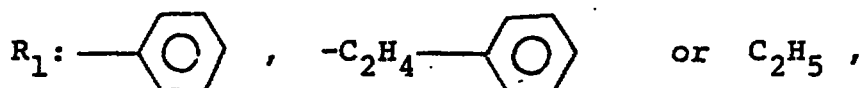


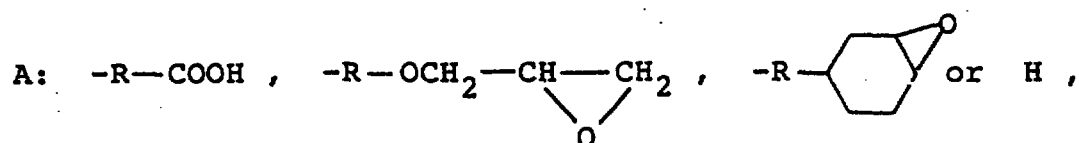
[I]



[II]

wherein





R: a lower alkylene group,

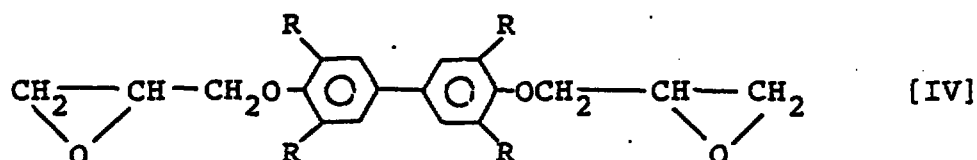
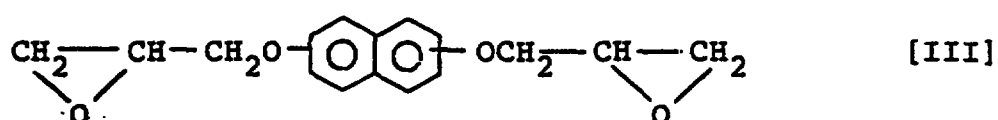
$$10 \leq N = l + m + n + 2 \leq 200 ,$$

$$0 \leq m/N \leq 0.1 , \text{ and } 5 \leq N/n \leq 50 ,$$

(C) an inorganic filler, and

(D) a curing accelerator.

2. An epoxy resin composition according to Claim 1, wherein the epoxy resin (A) comprises 30-100% by weight, based on the total amount of the epoxy resin, of at least one epoxy compound selected from the group consisting of naphthalene type epoxy compounds represented by the following formula [III] and biphenyl type epoxy compounds represented by the following formula [IV]



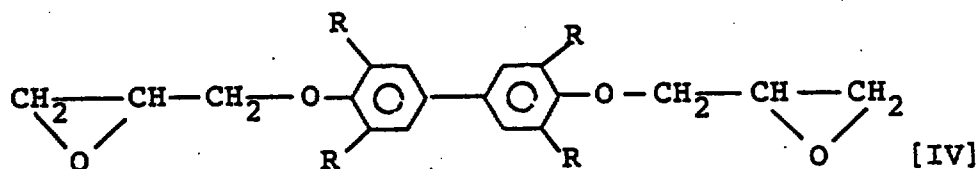
wherein R: H or CH_3 ,

and the amount of the inorganic filler (C) is 70-90% by weight based on the total amount of the composition.



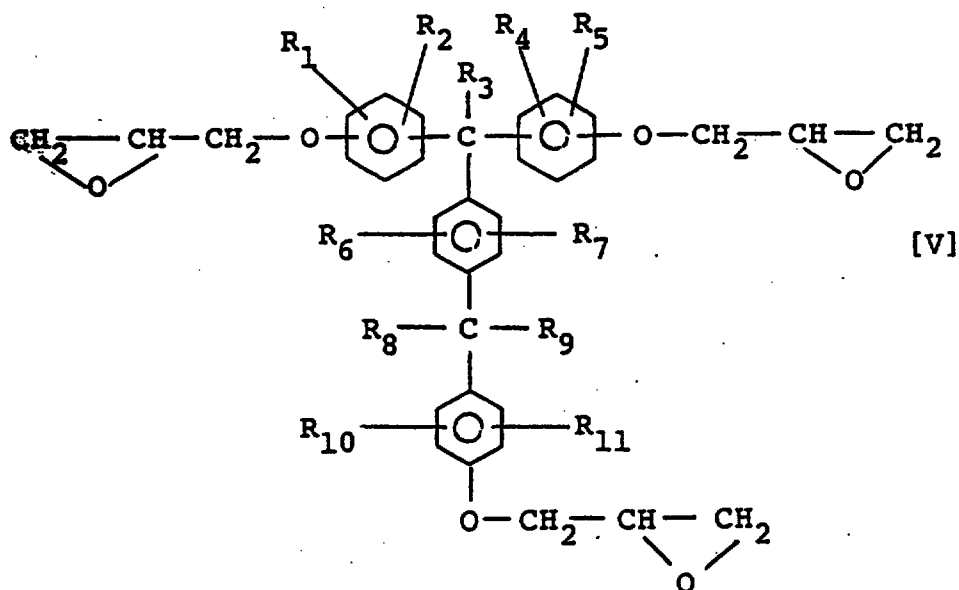
3. An epoxy resin composition according to Claim 2, wherein the epoxy resin (A) comprises the naphthalene type epoxy compound and the biphenyl type epoxy compound at a weight ratio of 10/90 to 90/10.

4. An epoxy resin composition according to Claim 1, wherein the epoxy resin (A) comprises 50-100% by weight, based on the total amount of the epoxy resin, of a mixture of a biphenyl type epoxy resin represented by the following formula [IV]



wherein R:H or CH₃,

and a trifunctional epoxy resin represented by the following formula [V]

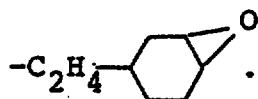




wherein R_1 to R_{11} are each an atom or atomic group selected from hydrogen, halogens and alkyl groups.

5. An epoxy resin composition according to Claim 4, wherein the epoxy resin (A) comprises the biphenyl type epoxy compound and the trifunctional epoxy compound at a weight ratio of 10/90 to 90/10.

6. An epoxy resin composition according to Claim 1, wherein in the formulas [I] and [II] representing the silicone compounds, A is $-C_3H_6-OCH_2-\underset{\text{O}}{\underset{|}{CH}}-CH_2$ or



7. An epoxy resin composition according to Claim 1, wherein the phenolic resin curing agent comprises the silicone-modified phenolic resin curing agent in an amount of 50-100% by weight based on the total amount of the phenolic resin curing agent.

8. An epoxy resin composition according to Claim 1, wherein the epoxy resin (A) has an epoxy equivalent of 150-250 and a softening point of 60-130°C and is selected from the group consisting of bisphenol A type epoxy resins, bisphenol F type epoxy resins, phenol novolac type epoxy resins, cresol novolac type epoxy resins, alicyclic epoxy resins and resins obtained by modifying them.

9. An epoxy resin composition according to Claim 4, wherein in the formula [V] representing the trifunctional epoxy resin, R_1 , R_2 , R_4 to R_7 , R_{10} and R_{11} are each hydrogen atom, and R_3 , R_8 and R_9 are each



methyl group.

10. An epoxy resin composition according to Claim 1, wherein the phenolic resin has a hydroxyl group equivalent of 80-150 and a softening point of 60-120°C and is selected from the group consisting of phenol novolac resins, cresol novolac resins and resins obtained by modifying them.

11. An epoxy resin composition according to Claim 1, wherein the silicone-modified phenolic resin curing agent is obtained by reacting 100 parts by weight of the phenolic resin with 10-50 parts by weight of at least one of the silicone compounds.

12. An epoxy resin composition according to Claim 1, wherein the epoxy resin (A) and the phenolic resin curing agent (B) are compounded at a ratio of 70/100 to 100/70 in terms of epoxy group/phenolic hydroxyl group.

13. An epoxy resin composition according to Claim 1, wherein the inorganic filler (C) is selected from the group consisting of crystalline silica, fused silica, alumina, calcium carbonate, talc, mica and glass fiber.

14. An epoxy resin composition according to Claim 1, wherein the curing accelerator (D) is selected from the group consisting of tertiary amines, imidazoles, 1,8-diazabicyclo[5.4.0]undecene-7 and organophosphorus compounds.

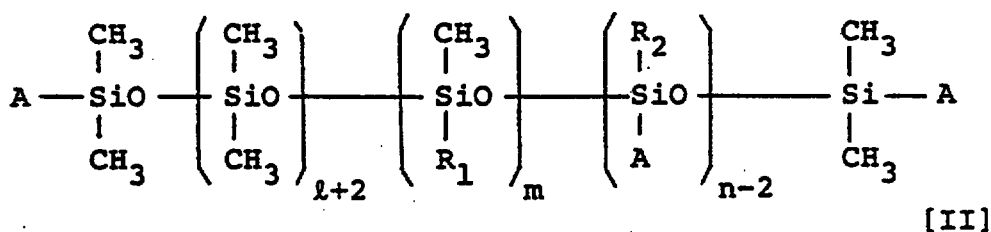
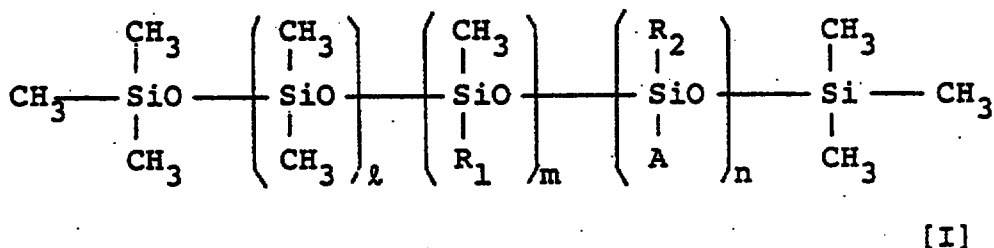
ABSTRACT

EPOXY RESIN COMPOSITION FOR SEMICONDUCTOR SEALING

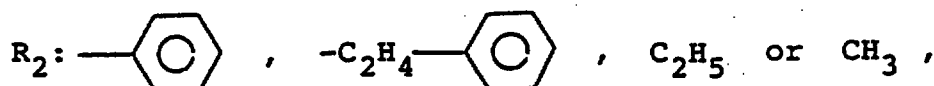
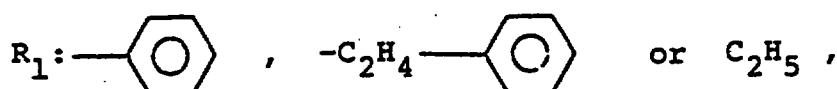
An epoxy resin composition for semiconductor sealing, comprising as essential components:

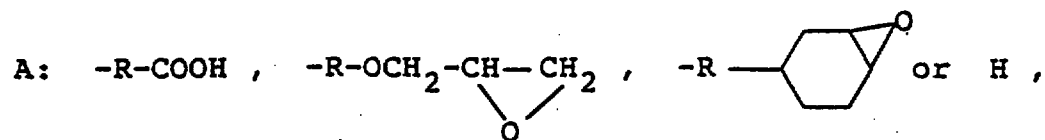
(A) an epoxy resin,

(B) a phenolic resin curing agent comprising 30-100% by weight, based on the total amount of the phenolic resin curing agent, of a silicone-modified phenolic resin curing agent obtained by reacting a phenolic resin with at least one of silicone compounds represented by the following formulas [I] and [II]



wherein





R: a lower alkylene group,

$$10 \leq N = l + m + n + 2 \leq 200 ,$$

$$0 \leq m/N \leq 0.1 , \text{ and } 5 \leq N/n \leq 50 ,$$

(C) an inorganic filler, and

(D) a curing accelerator.