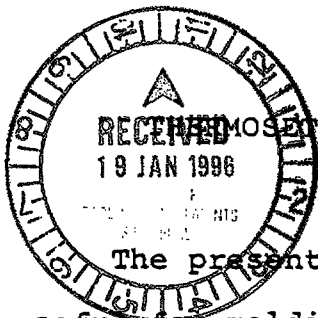


REPLACED SHEETS SG

☐ Description : paged to paged
☒ Claim(s) : paged 26 to paged 28
☐ Drawing(s) : paged to paged
☐ Abstract : paged to paged
 DATE OF RECEIPT

- 1 -



MOSETTING RESIN COMPOSITION

1 The present invention relate to a resin composition useful for molding applications. More particularly, it relates to a resin composition useful, for example, for encapsulating electric devices, such as semiconductors. The
 5 composition has a superior processability and gives a cured product having humidity resistance, thermal resistance, low inner stress and electric insulation.

Epoxy resins have been so for widely used for encapsulating electric devices, such as semiconductors.

10 The encapsulation with epoxy resins is currently widely used, because it is more economically advantageous than hermetic seal method. In recent years, however, the encapsulants have come to be required to possess a higher quality than before, particularly in thermal
 15 resistance and humidity resistance, because the conditions of using electric devices have become severer.

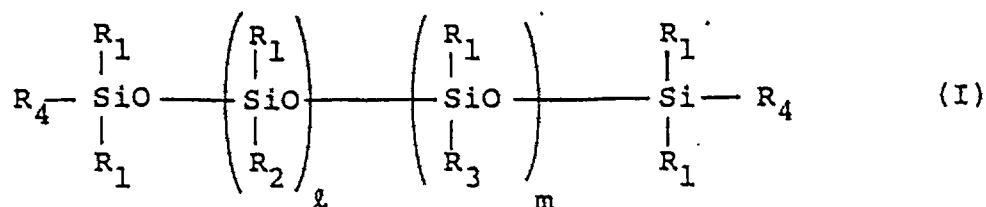
In order to meet the requirement, various types of resin compositions giving a cured product which has a superior thermal resistance and humidity resistance
 20 have been proposed. However, electric devices have a tendency to become larger and to rise in integration level today. So, using conventional epoxy resin compositions for encapsulating semiconductors causes such problems that the passivation layer or the resin encapsulating
 25 the electric device readily cracks, or a bonding wire is

1 readily cut due to the thermal stress caused by the
difference in coefficient of linear expansion between
the resin for encapsulation and the tip or leadframe.
Therefore, resin compositions giving a cured product
5 which has an excellent low inner stress as well as an
excellent thermal resistance and humidity resistance
have long been desired.

Under these circumstances, the present inventors
have undertaken extensive studies for developing resin com-
10 positions of high processability giving a cured product
which has an excellent thermal resistance, humidity resist-
ance, electric insulation and low inner stress, and as a
result, found that the object can be accomplished by resin
compositions comprising a specified novolak resin, a
15 specified polymaleimide compound and at least one
specified silicone resin.

Based on the above-mentioned findings, the
present invention was accomplished.

According to the present invention, there is
20 provided a thermosetting resin composition which comprises
(A) a phenol novolak resin having hydroxy groups and
allyl-etherified hydroxy groups, (B) a poly-
maleimide compound having two or more maleimide groups
in the molecule, and (c) at least one silicone resin
25 having the following formula (I):



1 wherein R_1 and R_2 , which may be the same or different, are
methyl or phenyl; R_3 and R_4 , which may be the same or dif-
ferent, are methyl, phenyl, hydrogen or a group having an
amino group or an epoxy group but at least one of R_3 and R_4
5 is hydrogen or a group having an amino group or an epoxy
group; and l and m are a number of 0-400, respectively.

The phenol novolak resin having hydroxy groups
and allyl-etherified hydroxy groups, used in the invention
(hereinafter referred to as partially allyl-etherified
10 novolak), can be prepared by allyl-etherifying a part
of phenolic hydroxy groups of a conventional phenol
novolak resin usually having a mean nuclei number of
2 to 15.

The conventional phenol novolak resin used for
15 preparing the partially allyl-etherified novolak can
be prepared by a conventional condensation reaction of
at least one phenol selected from the group consisting
of unsubstituted phenol and substituted phenol having
one or more alkyl, alkenyl, aryl, aralkyl groups or a
20 halogen atom as substituent (specific examples of
said substituted phenol are cresol, ethylphenol, iso-
propylphenol, butylphenol, octylphenol, nonylphenol,
vinylphenol, isopropenylphenol, phenylphenol, benzylphenol,
chlorophenol, bromophenol, xylenol, methylbutylphenol and

1 their isomers), with an aldehyde compound such as formal-
dehyde, furfural acrolein, glyoxal and the like.

The allyl-etherification can be carried out
by reacting a novolak resin with an allyl halide such
5 as allyl chloride, allyl bromide, allyl iodide and
the like, in the presence of an alkali. In the reaction,
the allyl halide is used in a molar amount less than the
molar amount of the phenolic hydroxy groups in the phenol
resin, and the alkali is used in a molar amount equal
10 to or more than the molar amount of the allyl halide.

Particularly, the allyl-etherified novolak resin
can be easily obtained by carrying out the allyl-etherifica-
tion reaction using allyl bromide or in a aprotic polar
solvent such as dimethylformamide, dimethyl sulfoxide,
15 N-methyl-pyrrolidone, acetonitrile, dimethyl acetamide,
hexamethylphosphortriamide.

The desired partially allyl-etherified novolak
resin can be obtained more easily by using a phenol
novolak resin prepared from a substituted phenol.
20 Accordingly, substituted phenols are preferred as the
phenol compound usable in the present invention. Particu-
larly, phenol novolak resins prepared from o-cresol
are more preferable, because the resin compositions prepared
from such resins give a cured product having a particu-
25 larly improved humidity resistance.

The molar ratio of the allyl-etherified hydroxy
groups to the unsubstituted hydroxy groups is preferably
0.2:1 to 9:1, and more preferably 0.3:1 to 6:1. If the

1 proportion of the allyl-etherified hydroxy groups is higher
than 9:1 or lower than 0.2:1, the curability and thermal
resistance of the product are tend to be deteriorated.

The polymaleimide compound having two or more
5 maleimide groups in the molecule, used in the invention,
has two or more maleimide groups of the formula (III)
in the molecule:

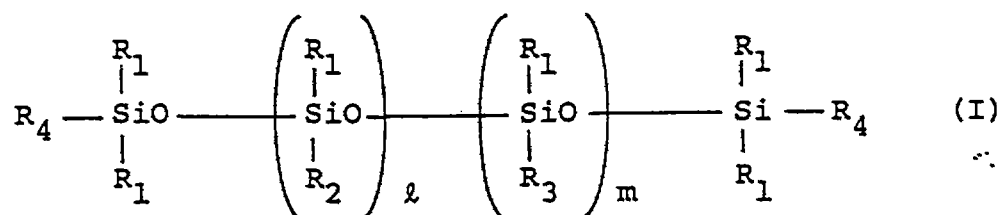


wherein R is hydrogen or a lower alkyl group having 1 to
5 carbon atoms.

10 Specific examples of the polymaleimide compounds
are N,N'-bismaleimide compounds such as N,N'-diphenyl-
methane-bismaleimide, N,N'-phenylenebismaleimide, N,N'-
diphenyl ether bismaleimide, N,N'-diphenyl sulfone
bismaleimide, N,N'-dicyclohexylmethane-bismaleimide,
15 N,N'-xylene-bismaleimide, N,N'-tolylene-bismaleimide,
N,N'-xylylene-bismaleimide, N,N'-diphenylcyclohexane-
bismaleimide, N,N'-dichlorodiphenylmethane-bismaleimide,
N,N'-diphenylmethane-bismethylmaleimide, N,N'-diphenyl
ether bismethylmaleimide, N,N'-diphenyl sulfone bismethyl-
20 maleimide (including isomers), N,N'-ethylenebismaleimide,
N,N'-hexamethylenebismaleimide and N,N'-hexamethylene-
bismethylmaleimide; prepolymers having N,N'-bismaleimide
skeletons at their molecular ends which can be obtained

1 by adding a diamine compound to the above-mentioned
N,N'-bismaleimide compounds; and maleimide and methyl
maleimide derivatives of aniline-formaldehyde polycon-
densate. Among them, N,N'-diphenylmethane-bismaleimide
5 and N,N'-diphenyl ether bismaleimide are particularly
preferable.

The silicone resins usable in the present
invention are those having the following formula (I).



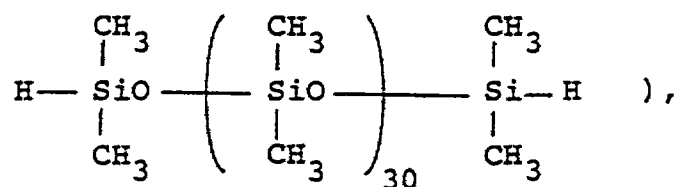
wherein R_1 and R_2 , which may be the same or different, are
10 methyl or phenyl; R_3 and R_4 , which may be the same or dif-
ferent, are methyl, phenyl, hydrogen or a group having an
amino group or an epoxy group but at least one of R_3 and R_4
is hydrogen or a group having an amino group or an epoxy
group; and l and m are a number of 0-400, respectively.

15 Among the silicone resins represented by the
formula (I), the resin having the formula wherein $m=0$,
 R_4 is hydrogen or a group having an amino group or an
epoxy group is more preferable than the others because the
others are apt to cause gelation.

20 Two or more of the above-mentioned silicone
resins can be used together. It is particularly
preferable to use a resin containing hydrogen as R_3 or R_4

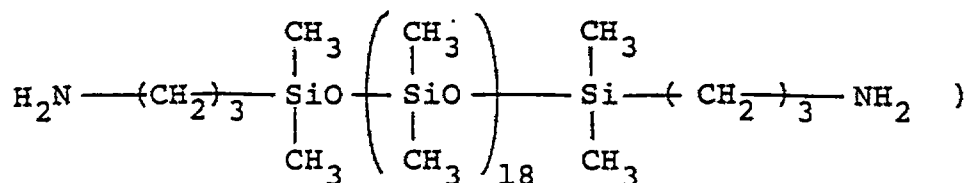
1 together with a resin containing a group having an amino
 group as R_3 or R_4 , because using these resins particularly
 improves the mechanical properties and inner stress of
 the product.

5 Specific examples of the silicone resin contain-
 ing hydrogen as R_3 or R_4 (hereinafter referred to as
 hydrogen-containing silicone resin) are X-21-7628 (a trade
 mark for a silicone resin manufactured by Shinetsu
 Silicone Co. having the formula,



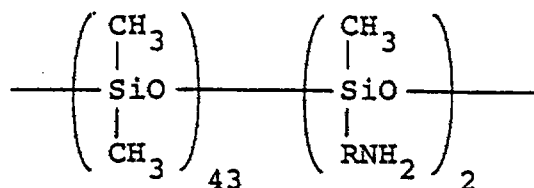
10 and the like.

Specific examples of the silicone resin
 containing a group having an amino group as R_3 or R_4
 (hereinafter referred to as amino-containing silicone
 resin) are X-22-161A (manufactured by Shinetsu Silicone
 15 Co. having the formula,



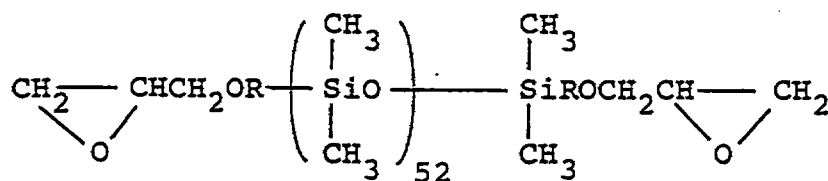
and SF-8417 (manufactured by Toray Silicone Co. having

1 the formula,



wherein R is a lower alkylene group), etc.

Specific examples of the silicone resin containing an epoxy group as R₃ or R₄ (hereinafter referred to as epoxy-containing silicone resin) are
 5 BX16-855B (manufactured by Toray Silicone Co. having the formula,



wherein R is a lower alkylene group), etc.

Although the number average molecular weight of the silicone resin is not critical, it is preferably
 10 about 500 to about 30,000, more preferably about 500 to 5,000.

The silicone resin may be simply mixed with the partially allyl-etherified phenol novolak and the polymaleimide compound to prepare the resin composition
 15 of the present invention. However, when the hydrogen-containing silicone resin or the epoxy-containing silicone

1 resin is used, it is preferable to react the silicone
resin with the partially allyl-etherified novolak resin
prior to the mixing of the other constituents of the
resin composition. And when the amino-containing silicone
5 resin is used, it is preferable to react the silicone
resin with the polymaleimide compound prior to the mixing
of the other constituents of preparation of the resin
composition. Particularly it is preferable that the
hydrogen-containing silicone resin reacted in advance
10 with the allyl-etherified novolak resin is used together
with amino-containing silicone resin reacted in advance
with the polymaleimide compound. In other words, it is
particularly preferable that the resin composition
comprises the reaction product of the hydrogen-containing
15 silicone resin with the allyl-etherified novolak resin
and a reaction product of the amino-containing silicone
resin with the polymaleimide compound.

The reaction between the hydrogen-containing
silicone resin and the allyl groups of the allyl-etherified
20 novolak resin, a hydro silylation, can be easily carried
out in a conventional manner using a platinum catalyst.

The epoxy-containing silicone resin can be
easily reacted with the hydroxy groups of the allyl-
etherified novolak resin using a basic catalyst such as
25 imidazole.

And the amino-containing silicone resin can
be easily reacted with the maleimide groups of the

1 polymaleimide compound.

Carrying out the above-mentioned reactions prevents the bleeding of the silicone resin from the cured product obtained from the resin composition and
5 morphologically uniformly disperses the silicone resin in the cured product.

The quantitative ratios between the ingredients in the resin composition of the present invention may be appropriately determined in accordance with the use and
10 intended thermal resistance of the cured product. Generally saying, the ratio of the number of maleimide group in the polymaleimide compound to the number of allyl group in the partially allyl-etherified novolak resin in the thermosetting resin composition is preferably 0.4:1 to 3:1, particularly
15 preferably 0.5:1 to 2:1. If the ratio is larger or smaller than the range defined above, the curability and thermal resistance of the cured product is tend to be deteriorated. The ratio can be calculated from the data of the ^1H -NMR spectroscopy on the protons of allyl group ($-\text{CH}_2\text{CH}=\text{CH}_2$)
20 and methyl group attached to benzene ring (- CH_3).

And the proportion of the silicone resin is preferably controlled so that the amount of the silicone resin is from 3 to 30% by weight per the total weight of partially allyl-etherified novolak resin, polymaleimide
25 compound and silicone resin in the composition. If the amount of the silicone resin is smaller than the lower limit mentioned above, the inner stress of the cured

1 product increases, and if the amount is larger than the
upper limit, the curability and thermal resistance
of the cured product are tend to be deteriorated.

In preparing the resin composition of the
5 present invention, the reaction product of the partially
allyl-etherified phenol novolak resin with the silicone
resin or the reaction product of the polymaleimide
compound with the silicone resin may be reacted with
other ingredients to give a prepolymer. Carrying out
10 any of these reactions improves the moldability of the
composition and gives morphologically uniform cured
product. Thus, the advantages of the present invention
can be advanced.

The resin composition of the present invention
15 can easily be cured without a catalyst. However, it
can be cured more easily, if a catalyst for accelerating
the curing is used. The types of the catalyst is not
critical. Specific examples of the catalyst include
organic phosphine compounds such as triphenylphosphine,
20 tri-4-methylphenylphosphine, tri-4-methoxyphenylphosphine,
tributylphosphine, trioctylphosphine, tri-2-cyanoethyl-
phosphine; free-radical polymerization initiators such as
benzoylperoxide, di-tert-butylperoxide, dicumylperoxide,
lauroylperoxide, acetylperoxide, methylethylketoneperoxide,
25 cyclohexanoneperoxide, t-butylhydroperoxide, azobisiso-
butylnitrile; amines such as trimethylamine, triamyl-
amine; tetraammonium salts such as tertiary amines such
as trimethylamine, triamylamine; quaternary ammonium salt

1 such as benzyl-triethylammonium chloride, benzyl-
triethylammonium hydroxide; imidazole compounds, boron
trifluoridamine complex, transition metal acetylacetonate,
and the like.

5 Among the catalysts mentioned above, an
organic phosphine compound or imidazole compound is
particularly preferable.

Known polymerization inhibitors may be used
to regulate the curing rate. Examples of the polymeriza-
10 tion inhibitors include phenol compounds such as 2,6-di-
tert-butyl-4-methylphenol, 2,2-methylenebis(4-ethyl-6-
tert-butylphenol), 4,4'-methylenebis(2,6-di-tert-
butylphenol), 4,4'-thiobis(3-methyl-6-tert-butylphenol),
hydroquinonemonomethylether; polyhydric phenol such as
15 hydroquinone, catechol, p-tert-butylcatechol, 2,5-di-
tert-butylhydroquinone, methylhydroquinone, pyrogallol;
phenothiazine compounds such as phenothiazine, benzo-
phenothiazine, acetamidophenothiazine; N-nitrosoamine
compounds such as N-nitrosodiphenylamine, N-nitroso-
20 dimethylamine, and the like.

The resin composition of the present invention
may contain a known epoxy resin and a known curing
agent for epoxy resin. Examples of the epoxy resin
include one or more members selected from novolak type
25 epoxy resins derived from novolak resins which are
prepared by the reaction of formaldehyde and a phenol
such as phenol, o-cresol, and the like; glycidyl ether
compounds derived from dihydric, trihydric or higher-hydric

1 phenols such as Bisphenol A, Bisphenol F, hydroquinone,
resorcine, phloroglucin, tris(4-hydroxyphenyl)-methane,
1,1,2,2-tetrakis-(4-hydroxyphenyl)-ethane and the like
or halogenated bisphenols such as tetrabromo-Bisphenol
5 A and the like; amine type epoxy resins derived from
aniline, p-aminophenol, m-aminophenol, 4-aminometacresol,
6-aminometacresol, 4,4'-diaminodiphenylmethane, 3,3'-
diaminodiphenylmethane, 4,4'-diaminodiphenyl ether, 3,4'-
diaminodiphenyl ether, 1,4-bis(4-aminophenoxy)-benzene,
10 1,4-bis(3-aminophenoxy)-benzene, 1,3-bis(4-aminophenoxy)-
benzene, 1,3-bis(3-aminophenoxy)-benzene, 2,2-bis(4-
aminophenoxyphenyl)-propane, p-phenylenediamine, m-
phenylenediamine, 2,4-toluenediamine, 2,6-toluenediamine,
p-xylylenediamine, m-xylylenediamine, 1,4-cyclohexane-
15 bis(methylamine), 1,3-cyclohexane-bis(methylamine),
5-amino-1-(4'-aminophenyl)-1,3,3-trimethylindane, 6-
amino-1-(4'-aminophenyl)-1,3,3-trimethylindane and the
like; glycidyl ester compounds derived from aromatic
carboxylic acids such as p-oxybenzoic acid, m-oxybenzoic
20 acid, terephthalic acid, isophthalic acid and the like;
hydantoin type epoxy resins derived from 5,5-dimethyl-
hydantoin and the like; alicyclic epoxy resins such as
2,2'-bis(3,4-epoxycyclohexyl)-propane, 2,2-bis-(4-(2,3-
epoxypropyl)cyclohexyl)-propane, vinylcyclohexene
25 dioxide, 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane-
carboxylate and the like; N,N-diglycidylaniline and the
like.

The curing agents for epoxy resins include

1 novolak resins such as phenolnovolak, cresol novolak and
the like; aromatic polyamines such as diaminodiphenyl
methane, diaminodiphenylsulfone; acid anhydrides such
as pyromellitic acid anhydrides, benzophenonetetracarboxylic
5 acid anhydrides, and the like.

The resin composition of the present invention
may further contain an inorganic filler.

The filler is usually indispensable when the
resin composition is used for encapsulating semiconductor.
10 Examples of the inorganic fillers are silica powder,
alumina, talc, calcium carbonate, titanium white, clay,
asbestos, mica, iron oxide red, glass fiber, and the
like. Among the examples, silica powder or alumina
is particularly preferable. For using the composition
15 for encapsulating semiconductors, the amount of the
inorganic fillers may be 25 to 90% by weight, preferably
60 to 80% by weight per the total weight of the resin
composition.

The resin composition of the present invention
20 may further contain a natural wax; a synthetic wax; a
higher fatty acid; a metal salt thereof; mold releasing
agent such as paraffin and the like; a coloring agent
such as carbon black; a coupling agent; a flame retarder
such as antimony trioxide, phosphorus compounds, brominated
25 epoxy resin and the like. Brominated epoxy resin is
particularly preferable to prepare a cured product of
high flame retardancy.

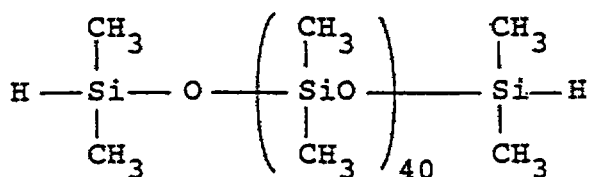
The resin composition of the present invention

1 is used for encapsulating electric devices such as semi-
conductors. And it shows a superior processability,
and gives a cured product having an excellent thermal
resistance, humidity resistance, and in particular,
5 lower inner stress than before. In summary, it is an
excellent resin composition for encapsulant.

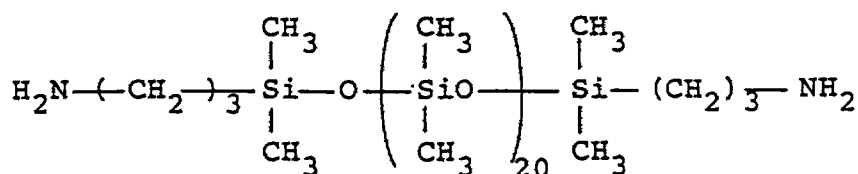
The following examples serve to give specific
illustrations of the practice of the present invention
but they are not intended in any way to limit the scope
10 of the present invention.

Silicone resins used in the following Reference
Examples, Examples and Comparative Examples are shown
below.

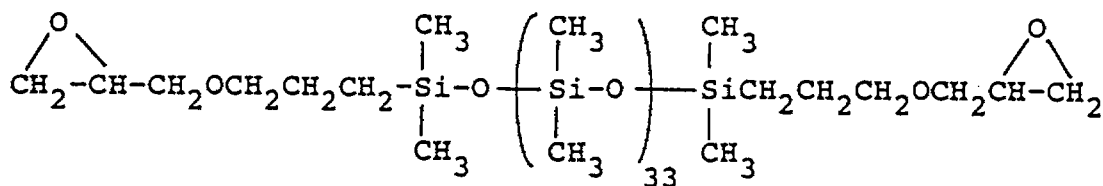
Silicone resin (a)



Silicone resin (b)



1 Silicone resin (c)



Reference Example 1

Into a reactor equipped with a thermometer,
a stirrer, a dropping funnel and a reflux condenser
5 were charged 236 parts (2 equivalents) of o-cresol novolak
resin having a softening point of 90°C and 840 parts of
dimethylsulfoxide as a reaction solvent. After the resin
had been completely dissolved, 41 parts (1.0 equivalent)
of 97% sodium hydroxide was added thereto and thoroughly
10 stirred. Then 80 parts (1.05 equivalents) of allyl
chloride was added by drops over a period of one hour
while keeping the temperature of the system at 40°C.
Then, the reaction system was heated to 50°C and kept
at this temperature for 5 hours. After dimethylsulfoxide
15 had been distilled off, 300 parts of methylisobutylketone
was added to dissolve the resulting resin. The
resulting solution was washed with water and
filtered to remove the inorganic salt contained therein.
Concentrating the filtrate gave 262 parts of a red-
20 orange colored semisolid resin having a degree of allyl-
etherification of 50%, and an OH equivalent of 276 g/eq.
Hereinafter, this resin is referred to as ALN.

1 Reference Example 2

[Silicone Modification]

Into a reactor were charged 100 parts of ALN obtained in Reference Example 1, 2 parts of platinum
5 black catalyst (containing 1% by weight of platinum relative to the total weight of the catalyst) and 331 parts of xylene as a reaction solvent. Then, the reaction system (the mixture) was heated and water in the system was completely, azeotropically distilled off
10 from the reaction system. Thereafter 42 parts of silicone resin (a) was added thereto by drops over a period of about 1 hour at the distillation temperature, and the reaction system was kept at the reflux temperature of xylene for about 5 hours. Then, the reaction system
15 was filtered to completely remove the platinum black and the filtrate was concentrated to obtain a silicone-modified resin (hereinafter referred to as modified resin (a)).

Reference Example 3

20 [Silicone Modification]

Into a reactor were charged 100 parts of N,N'-diphenylmethanebismaleimide (hereinafter referred to as BMI) and 369 parts of 1,4-dioxane as a reaction solvent. And the reaction system was heated up to 100°C and
25 BMI was dissolved completely. Then, 58 parts of silicone resin (b) was added thereto by drops over a period of about one hour and the reaction system was kept

1 at this temperature for one hour. Removing dioxane
from the reaction system by distillation gave a silicone
modified resin (hereinafter referred to as modified
resin (b)).

5 Reference Example 4

[Silicone Modification]

Into a reactor were charged 100 parts of ALN
obtained in Reference Example 1, 0.08 part of 4-methyl-
imidazole and 331 parts of xylene. The reaction system
10 was heated up to 140°C and the resin was dissolved com-
pletely. And 42 parts of silicone resin (c) was added
thereto by drops over a period of about one hour and the
reaction system was kept at 140°C for about 2 hours.
Then, xylene in the system was removed by distillation
15 to obtain a silicone modified resin (hereinafter
referred to as modified resin (c)).

Reference Example 5

[Silicone Modification]

Into a reactor were charged 38 parts of ALN
20 obtained in Reference Example 1, 142 parts of modified
resin (a), 358 parts of BMI and 770 parts of 1,4-
dioxane as a solvent. The reaction system was heated
up to 80°C and the resins were dissolved completely.
And then, a solution obtained by dissolving 30 parts
25 of silicone resin (b) into 30 parts of 1,4-dioxane was
added thereto by drops over a period of about one hour and

1 the reaction system was kept at 80°C for one hour.
Then 1,4-dioxane in the system was removed by distillation to obtain a silicone modified resin (hereinafter referred to as modified resin (d)).

5 Reference Example 6
[Silicon Modification]

Into a reactor were charged 196 parts of modified resin (a) obtained in Reference Example 2, 358 parts of BMI and 800 parts of 1,4-dioxane as a solvent.
10 The reaction system was heated up to 80°C and the resins were dissolved completely. And then, a solution obtained by dissolving 29 parts of silicone resin (b) into 29 parts of 1,4-dioxane was added thereto by drops over a period of about one hour and the reaction system was kept at
15 80°C for one hour. Then 1,4-dioxane in the system was removed by distillation to obtain a silicone modified resin (hereinafter referred to as modified resin (e)).

Reference Example 7
[Prepolymerization]

20 Into a 1-liter, four-necked flask were charged 100 parts of modified resin (a) and 183 parts of BMI. And the reaction system was heated up to 130°C to fuse and mix the system. Then, the mixed reaction system was kept at this temperature for about one hour while
25 stirring to obtain a prepolymer. Hereinafter, the prepolymer is referred to as prepolymer A.

1 Reference Example 8

[Prepolymerization]

Into a 1-liter, four-necked flask were charged
100 parts of ALN obtained in Reference Example 1 and 301
5 parts of Modified Resin (b) obtained in Reference
Example 3. And the reaction system was heated up to
130°C to fuse and mix the system. Then, the mixed
reaction system was kept at this temperature for about
one hour while stirring to obtain a prepolymer.

10 Hereinafter, the prepolymer is referred to as
prepolymer B.

Reference Example 9

[Prepolymerization]

Into a 1-liter, four-necked flask were charged
15 100 parts of the modified resin (c) obtained in Reference
Example 4 and 183 parts of BMI. And the reaction system
was heated up to 130°C to fuse and mix the system. Then,
the mixed reaction system was kept at this temperature
for about one hour while stirring to obtain a prepolymer.

20 Hereinafter, the prepolymer is referred to as prepolymer
C.

Examples 1 - 5

A resin composition for molding was prepared
by mixing modified resin (e) or (d), prepolymer A, B or
25 C, an o-cresol novolak type epoxy resin (trade name:
ESCN-195XL; manufactured by Sumitomo Chemical Company,

1 Limited), curing accelerating catalysts, a filler, a
coupling agent and a mold releasing agent as
shown in Table 1. The resin composition was
fused and kneaded at a temperature shown in Table 1 for
5 five minutes, then cooled, and crushed. Then, the
crushed composition was transfer molded at 70 Kg/cm²
and 175°C for 3 minutes and post-cured at 200°C for
additional 5 hours to obtain each cured resin product.
The physical properties of each cured resin product
10 were evaluated. Table 2 shows the results.

Comparative Example 1

A resin composition for molding was prepared
by mixing an o-cresol novolak type epoxy resin (ESCN-
195XL), phenol novolak resin (OH equivalent: 110 g/eq,
15 softening point: 90°C) curing accelerating catalysts,
a filler, a coupling agent and a mold releasing agent
as shown in Table 1. And the resin composition
was fused and kneaded at a temperature shown in
Table 1 for five minutes, and cooled and crushed. The
20 crushed composition was transfer molded at 70 Kg/cm²
and 175°C for 5 minutes and post-cured at 180°C for
additional 5 hours to obtain a cured resin product. The
physical properties of each cured product were evaluated.
Table 2 shows the results.

Table 1

(Numbers in Table 1 represent parts by weight)

Example No.	Example								Comparative example
	1	2	3	4	5	6	7	8	1
Prepolymer A	100	100	100	-	-	-	-	-	-
Prepolymer B	-	-	-	100	100	-	-	-	-
Prepolymer C	-	-	-	-	-	100	-	-	-
Modified resin (e)	-	-	-	-	-	-	100	-	-
Modified resin (d)	-	-	-	-	-	-	-	100	-
ESCN-195XL ^{*1}	-	-	-	-	-	-	-	-	100
Phenol novolak resin ^{*5}	-	-	-	-	-	-	-	-	56
Triphenyl phosphine	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	-
4-Methyl imidazole	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	-
1,8-Diaza(5,4,0)bicyclo-undecen-7	-	-	-	-	-	-	-	-	2
Carnava wax	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	1
Silane coupling agent 1 ^{*2}	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	-

- to be cont'd. -

Table 1 (Cont'd.)

Silane coupling agent 2 ^{*3}	-	-	-	-	-	-	-	-	2
Fused silica ^{*4}	233	246	333	233	246	233	333	333	364

*1 ESCN-195XL: o-Cresol novolak resin manufactured by Sumitomo Chemical Co., Ltd. having an epoxy equivalent of 195 g/eq.

*2 Silane coupling agent 1: KBM-573 (manufactured by Shinetsu Silicone Co.)

*3 Silane coupling agent 2: SH-6040 (manufactured by Toray Silicone Co.)

*4 Fused silica: FS-891 (manufactured by Denki Kagaku Kogyo Co.)

*5 Phenol novolak resin: (OH equivalent: 110 g/eq, softening point: 90°C)

Table 2

Example No. Properties			Example			
			1	2	3	4
Spiral Flow (inch) 175°C x 70 Kg/cm ²			45	43	30	45
Barcol hardness 175°C/90 sec. (935) 175°C/180 sec.			67 73	68 73	75 78	67 74
Glass transition temperature Tg (°C)			267	263	263	260
Linear coefficient of expansion*1 x 10 ⁵ °C ⁻¹ (< Tg)			1.1	1.1	0.9	1.4
Bending strength (Kg/mm ²)			12.5	13.8	14.5	14.0
Bending modulus (Kg/mm ²)			1180	1200	1400	1190
Volume resistivity (Ω-cm)	Normal state		4.5 x 10 ¹⁶	5.0 x 10 ¹⁶	4.6 x 10 ¹⁶	5.5 x 10 ¹⁶
	PCT*2	100 hr	1.0 x 10 ¹⁵	1.5 x 10 ¹⁵	1.6 x 10 ¹⁵	1.0 x 10 ¹⁵
	PCT*2	300 hr	4.2 x 10 ¹⁴	7.6 x 10 ¹⁴	8.2 x 10 ¹⁴	4.5 x 10 ¹⁴
	PCT*2	500 hr	3.3 x 10 ¹⁴	6.0 x 10 ¹⁴	7.4 x 10 ¹⁴	3.3 x 10 ¹⁴
Water absorption	PCT*2	100 hr	1.01	0.98	0.93	0.99
	PCT*2	300 hr	1.15	1.10	1.06	1.10
	PCT*2	500 hr	1.20	1.16	1.11	1.20

- to be cont'd. -

*1 Measured by TMA method (with a thermomechanical analyzer manufactured by Shimadzu Corporation)

*2 PCT: Pressure cooker test (121°C x 100%RH)

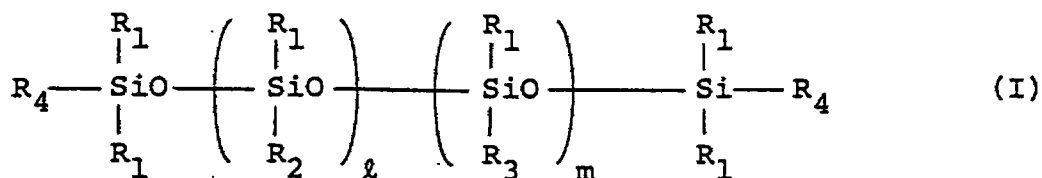
Table 2 (Cont'd.)

				Comparative Example
5	6	7	8	1
49	39	30	28	43
68	64	65	64	80
77	71	72	72	84
261	258	258	264	158
1.5	1.2	0.9	0.8	2.4
14.2	13.6	14.6	13.5	15.6
1210	1230	1200	1100	1400
6.3×10^{16}	5.0×10^{16}	4.8×10^{16}	6.5×10^{16}	8.4×10^{16}
1.6×10^{15}	1.1×10^{15}	1.5×10^{15}	1.7×10^{15}	1.6×10^{15}
8.5×10^{14}	3.5×10^{14}	7.9×10^{14}	8.0×10^{14}	4.3×10^{14}
7.0×10^{14}	2.1×10^{14}	7.2×10^{14}	7.1×10^{14}	4.2×10^{14}
0.95	1.05	0.92	0.93	0.86
1.07	1.20	1.05	1.07	1.00
1.14	1.31	1.09	1.12	1.08



WE CLAIM:

1. A thermosetting resin composition which comprises
 - (A) a phenol novolak resin having hydroxy groups and allyl-etherified hydroxy groups,
 - (B) a polymaleimide compound having two or more maleimide groups in the molecule, and
 - (C) at least one silicone resin having the following formula (I);



wherein R_1 and R_2 , which may be the same or different, are methyl or phenyl; R_3 and R_4 , which may be the same or different, are methyl, phenyl, hydrogen or a group having an amino group or an epoxy group but at least one of R_3 and R_4 is hydrogen or a group having an amino group or an epoxy group; and l and m , which may be the same or different, are a number of 0-400.

2. A composition according to Claim 1, wherein the constituent (C) is at least one silicone resin having the formula (I), wherein m is zero and R_4 is hydrogen or a group having an amino group or an epoxy group.
3. A composition according to Claim 2, wherein R_1 is methyl.
4. A composition according to Claim 2, wherein R_1 and R_3 are methyl.

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5. A composition according to Claim 2, wherein the number average molecular weight of the silicone resin ranges from about 500 to 30,000.
6. A composition according to Claim 2, wherein R_4 is one member selected from the group consisting of hydrogen, 3-aminopropyl and 3-glycidyloxypropyl.
7. A composition according to Claim 1, wherein the constituent (C) contains two silicone resins, one of which containing hydrogen as R_3 or R_4 and another of which containing a group having an amino group as R_3 or R_4 .
8. A composition according to Claim 1, wherein the constituent (C) is a silicone resin containing hydrogen or a group having an epoxy group as R_3 or R_4 .
9. A process for preparing a composition according to Claim 8, which comprises reacting the silicone resin (C) with the phenol novolak resin (A) prior to the mixing of the other constituents of the resin composition.
10. A process for preparing a composition according to Claim 8, which comprises reacting the silicone resin (C) with the phenol novolak resin (A) and then reacting the reaction product of (C) and (A) with the polymaleimide compound (B).
11. A composition according to Claim 1, wherein the constituent (C) is a silicone resin containing a group having an amino group as R_3 or R_4 .
12. A process for preparing a composition according to Claim 11, which comprises reacting the silicone resin (C) with the polymaleimide compound (B) prior to the mixing





of the other constituents of the resin composition.

13. A process for preparing a composition according to Claim 11, which comprises reacting the silicone resin (C) with the polymaleimide compound (B) and then reacting the reaction product of (C) and (B) with the phenol novolak resin (A).

14. A composition according to Claim 1, wherein the constituent (C) contains two silicone resins, one of which containing hydrogen or a group having an epoxy group as R_3 or R_4 and another of which containing a group having an amino group as R_3 or R_4 .

15. A process for preparing a composition according to Claim 14, which comprises reacting the silicone resin (C) containing hydrogen or a group having an epoxy group as R_3 or R_4 with the phenol novolak resin (A); reacting the silicone resin (C) containing a group having an amino group as R_3 or R_4 with the polymaleimide compound (B); and then reacting both reaction products.

16. A composition according to Claim 1, wherein the ratio of the number of maleimide group in the polymaleimide compound (B) to the number of allyl group in the phenol novolak resin (A) in the composition falls in the range of from 0.4:1 to 3:1.

17. A composition according to Claim 1, wherein the amount of the constituent (C) is 3 to 30% by weight per the total weight of the phenol novolak resin (A) and polymaleimide compound (B).

18. A cured resin obtained by curing a composition according to Claim 1.

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ABSTRACT OF THE DISCLOSURE

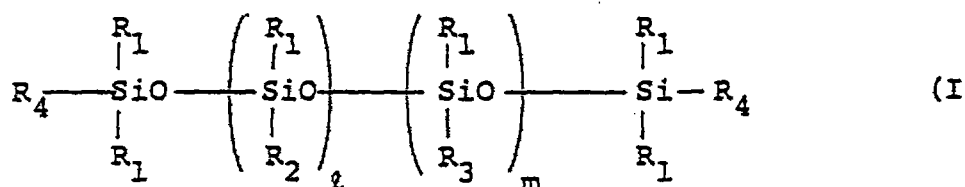
THERMOSETTING RESIN COMPOSITION

A thermosetting resin composition is prepared by mixing

(A) a phenol novolak resin having hydroxy groups and allyl-etherified hydroxy groups,

(B) a polymaleimide compound having two or more maleimide groups in the molecule, and

(C) at least one silicone resin having the following formula (I);



wherein R_1 and R_2 , which may be the same or different, are methyl or phenyl; R_3 and R_4 , which may be the same or different, are methyl, phenyl, hydrogen or a group having an amino group or an epoxy group but at least one of R_3 and R_4 is hydrogen or a group having an amino group or an epoxy group; and l and m , which may be the same or different, are a number of 0-400. The thermosetting resin composition of the present invention can be suitably used for encapsulating electric devices, for example, and gives, by curing, a cured resin product of high quality.

REPLACEMENT SHEETS SG

- ☐ Description : paged to paged
☒ Claim(s) : paged 24. to paged 24..
☐ Drawing(s) : paged to paged
☐ Abstract : paged to paged

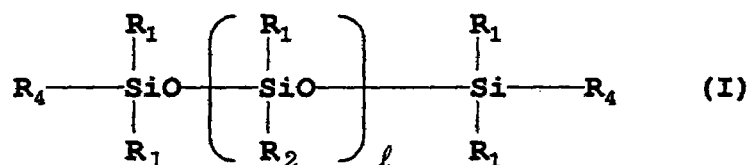
- 26 - Substitute sheet - 21 January 1999

DATE OF RECEIPT 22/1/99



WE CLAIM:

1. A thermosetting resin composition which comprises
 - (A) a phenol novolak resin having hydroxy groups and allyl-etherified hydroxy groups,
 - (B) a polymaleimide compound having two or more maleimide groups in the molecule, and
 - (C) at least one silicone resin having the following formula (I),



wherein R_1 and R_2 , which may be the same or different, are methyl or phenyl; R_4 is hydrogen, 3-aminopropyl or 3-glycidyloxypropyl; and ℓ is a number of 0-400.

2. A composition according to Claim 1, wherein R_1 is methyl.
3. A composition according to Claim 1, wherein the number average molecular weight of the silicone resin ranges from 500 to 30,000.
4. A composition according to Claim 1, wherein the constituent (C) contains two silicone resins, one of which having the formula (I), wherein R_4 is hydrogen or 3-glycidyloxypropyl and another of which having the formula (I), wherein R_4 is 3-aminopropyl.

REPLACEMENT SHEET

22 JAN 1999



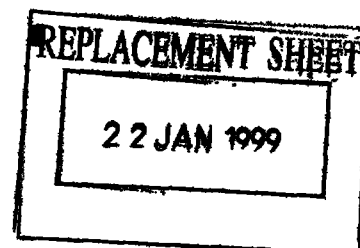
5. A composition according to Claim 1, wherein the constituent (C) contains two silicone resins, one of which having the formula (I), wherein R_4 is hydrogen and another of which having the formula (I), wherein R_4 is 3-aminopropyl.

6. A process for preparing a composition according to Claim 1, which comprises reacting the silicone resin (C) wherein R_4 is hydrogen or 3-glycidyloxypropyl with the phenol novolak resin (A) prior to the mixing of the other constituents of the resin composition.

7. A process for preparing a composition according to Claim 1, which comprises reacting the silicone resin (C) wherein R_4 is 3-aminopropyl with the polymaleimide compound (B) prior to the mixing of the other constituents of the resin composition.

8. A process for preparing a composition according to Claim 5, which comprises reacting the silicone resin (C) wherein R_4 is hydrogen with the phenol novolak resin (A); reacting the other silicone resin (C) wherein R_4 is 3-aminopropyl with the polymaleimide compound (B); and then reacting both reaction products.

9. A composition according to Claim 1, wherein the ratio of the number of maleimide group in the





polymaleimide compound (B) to the number of allyl group in the phenol novolak resin (A) in the composition falls in the range of from 0.4:1 to 3:1.

10. A composition according to Claim 1, wherein the amount of the constituent (C) is 3 to 30% by weight per the total weight of the phenol novolak resin (A) and polymaleimide compound (B).

11. A cured resin obtained by curing a composition according to Claim 1.

