

GLYCIDYL ETHERS OF PHENOLIC COMPOUNDS
AND PROCESS FOR PRODUCING THE SAME

1 The present invention relates to an epoxy resin
applied for the electric and electronic industries,
particularly for encapsulating and laminating materials
and also relates to a process for producing the epoxy
5 resin.

In recent years the transfer moldings of epoxy
resin compositions have been applied for encapsulating
semiconductors such as LSIs, ICs, and transistors because
of its high productivity and low cost. LSIs encapsulated
10 by the epoxy resin compositions have been surface-mounted
and directly submerged in the solder baths. A glycidyl
ether of o-cresol novolac, which is mainly used today,
has well-balanced properties, but the epoxy resin compo-
sitions thereof used to be cracked by the heat shock
15 of the direct soldering process.

Epoxy resins for encapsulating electronic
components are required to have a higher temperature
performance and other well-balanced properties such as a
moisture performance and a high purity, particularly a
20 low hydrolyzable chlorine content.

A glycidyl ether of a tris(hydroxyphenyl)methane
and alkyl-substituted products thereof exhibits a higher
temperature performance.

A tris(hydroxyphenyl)methane is, however,
25 liable to form a product of higher molecular weight or a

- 1 gel through intermolecular reaction during the glycidyl
etherification thereof. The higher molecular weight
product of the intermolecular reaction has a too high
epoxy equivalent weight and its cured products will
5 have undesirably low crosslinking density and tempera-
ture performance.

To control the intermolecular reaction and
obtain a resin of low epoxy equivalent weight, various
methods have been taken up to now.

- 10 For instance, Industrial and Engineering
Chemistry, Vol. 45, p. 2715 (1953) describes a process
which comprises adding sodium salt of tris(hydroxyphenyl)-
methane into 5 moles of epichlorohydrin per mole of
the phenolic hydroxyl groups.

- 15 According to this process, however, the epoxy
content of the product is as low as 0.32 equivalent
per 100 g (viz. the epoxy equivalent weight is as high
as 313) and the product yield is also as low as 54%.
Thus this process is not satisfactory.

- 20 U.S. Patent No. 4,394,496 describes a two-
step process which comprises reacting tris(hydroxyphenyl)-
methane with at least 10 moles of epihalohydrin per mole
of the phenolic hydroxyl groups in the presence of a
coupling catalyst in the first step and in the presence
25 of a basic compound in the second step, thereby producing
a glycidyl ether compound.

This process aims at raising the epoxy conver-
sion of tris(hydroxyphenyl)methane, and the epoxy equivalent

1 weight of the resultant glycidyl ether compound is 158,
which is close to the theoretical value. This product,
however, contains a very large amount of hydrolyzable
chlorine, and hence is not satisfactory for use in the
5 electric or electronic industry.

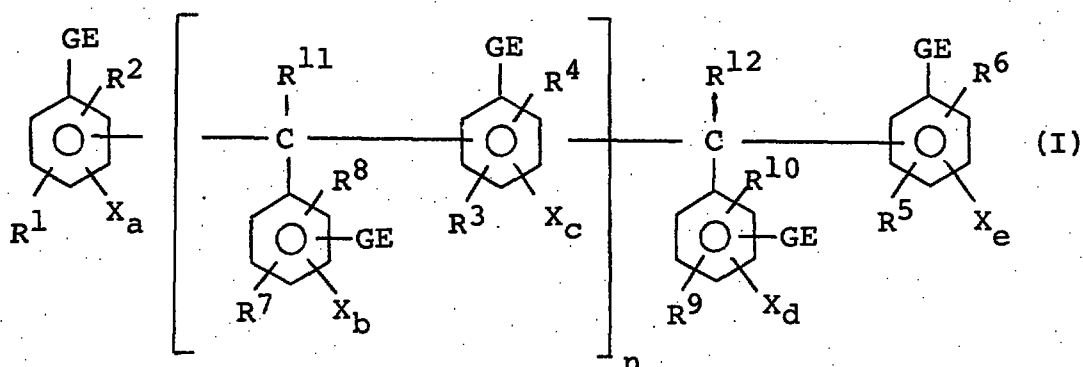
While this U.S. Patent discloses also an
oligomeric compound resulting from intermolecular
reaction and a process for producing the oligomer,
it does not disclose any glycidyl ether compounds suitable
10 for encapsulating electronic components at the present
technical level.

Of glycidyl ethers of the tris(hydroxyphenyl)-
methane and alkyl-substituted products thereof, the
compound having no alkyl substituent and compounds
15 having a small number of lower alkyl substituents are
highly hygroscopic and compounds having a large number
of higher alkyl substituents show a poor temperature
performance. Thus, it is necessary to develop a glycidyl
ether compound having better balanced properties.

20 U.S. Patent No. 4,390,664 discloses glycidyl
ethers of phenolic compounds produced by the condensation
of aromatic aldehydes with phenols such as phenol, alkyl-
monosubstituted phenols, and halogen-substituted phenols.
While the invention of this U.S. Patent aims at providing
25 a glycidyl ether compound improved in high temperature
performance over glycidyl ethers of tris(hydroxyphenyl)-
methane, the product compound is not low in hygroscopicity
and moreover the glycidyl etherifying reaction is carried

1 out according to the conventional method and therefore the product glycidyl ether compound has low purity and contains a large amount of hydrolyzable chlorine in particular.

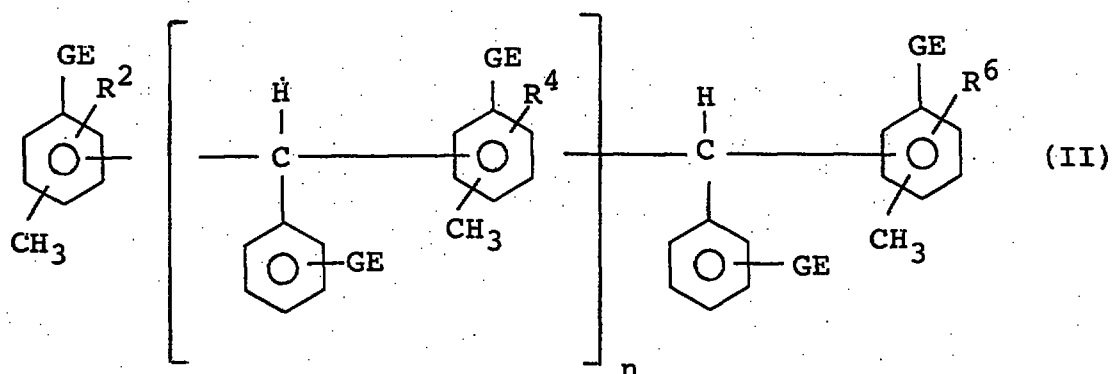
5 The present invention involves a glycidyl ether of a phenolic compound of the formula (I):



, wherein each of R^1 through R^6 represents an alkyl group of from 1 to 6 carbon atoms; each of R^7 through R^{12} represents a hydrogen atom, an alkyl group of from 1 to 4 carbon atoms, or an alkoxy group of from 1 to 4 carbon atoms; X represents a chlorine or bromine atom; GE represents a glycidyl ether group; a, b, c, d, and e are 0 or 1; and n is an average number of from 0.5 to 5.

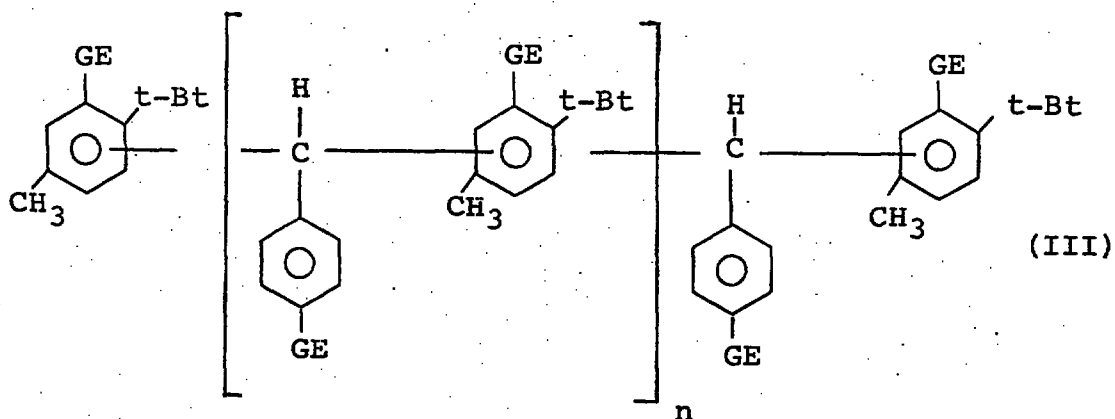
Of the glycidyl ether compounds represented by formula (I), preferred in performance are compounds in which each of R^1 , R^3 , and R^5 is methyl, each of R^2 , R^4 , and R^6 is an alkyl group of from 3 to 6 carbon atoms, each of R^7 , R^8 , R^9 , R^{10} , R^{11} , and R^{12} is a hydrogen atom, and each of a, b, c, d, and e is 0, that is, compounds represented

1 by the formula (II):



, wherein each of R^2 , R^4 , and R^6 represents an alkyl group of from 3 to 6 carbon atoms, n is an average number of 0.5 to 5, and GE represents a glycidyl ether group.

5 Above all, a glycidyl ether compound represented by the formula (III):

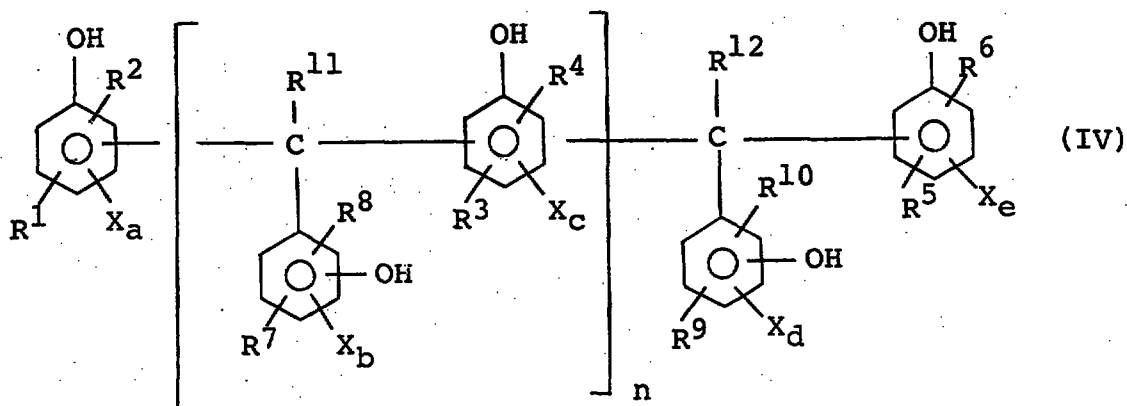


, wherein t-Bt represents tertiary butyl group, n is an average number of 0.5 to 5, and GE represents a glycidyl ether group, is particularly preferred in view of the performance
10 of the glycidyl ether compound itself, ease of the reaction

1 to form itself, and ease of obtaining the raw materials industrially.

When the number of alkyl substituents attached to aromatic rings and the number of carbon atoms in
5 each alkyl substituent are relatively small, such glycidyl ether compounds are highly hygroscopic. On the contrary, when the number of said alkyl substituents and the number of said carbon atoms are relatively large, such compounds have poor temperature performance. Chlorine
10 or bromine atom represented by X imparts flame retardance. As an increase in the average number n of repeating units, the temperature performance is improved but the viscosity increases and this causes poor moldability and processability. On the contrary, as a decrease in the average number n
15 of repeating units, the temperature performance is not enough improved. Hence, the value of n is desired to be in the range of from 0.5 to 5.

The glycidyl ether of a phenolic compound can be produced by reacting the corresponding phenolic com-
20 pound with an epichlorohydrin. The phenolic compound corresponding to the glycidyl ether compound of the formula (I) is represented by the formula (IV):



1 , wherein the symbols are the same as those in the
formula (I).

The phenolic compound of the formula (IV) can
be produced by the condensation of phenols with hydroxy
5 aromatic carbonyl compounds by applying the well known
novolak synthesizing reaction. This reaction is carried
out at a temperature of 0 to 180°C in the presence of
a well known acid catalyst for novolak synthesis. Such
catalysts include mineral acids, e.g., hydrochloric acid,
10 sulfuric acid, and phosphoric acid; organic acids, e.g.,
oxalic acid and toluenesulfonic acid; and salts, e.g.,
zinc acetate. For this reaction may be used an aromatic
solvent such as toluene or chlorobenzene.

The molar ratio of the hydroxy aromatic carbonyl
15 compounds to the phenols is approximately from 0.3:1.0
to 1.0:1.0.

In order to achieve a larger average number n
of repeating units, it is necessary to carry out the
reaction by using a higher proportion of the hydroxy
20 aromatic carbonyl compound at a somewhat higher temperature
in the presence of a larger amount of catalyst.

Suitable alkyl-substituted phenols include
phenols substituted by two alkyl groups of from 1 to 6
carbon atoms and chlorine- or bromine-substituted products
25 of these dialkyl phenols. Preferably, one of the two
alkyl substituents is methyl and the other is an alkyl
group of from 3 to 6 carbon atoms. Examples of the
preferable dialkylphenols are methylpropylphenol,

1 methylpentylphenol, methylbutylphenol, and methylhexyl-
phenol. Above all, methyl-tert-butylphenol is most
desirable in view of the glycidyl etherifying reaction
as well as the performance of the product glycidyl ether
5 compound.

These dialkylphenols may be used alone or in
combination. Small amounts of other phenols, e.g.,
phenol, cresol, resorcinol, catechol, and bisphenol A,
can be used additionally for the purpose of further
10 imparting various desirable properties.

Suitable hydroxy aromatic carbonyl compounds
include hydroxy aromatic ketones and hydroxy aromatic
aldehydes, for example, hydroxyacetophenone, methyl-
hydroxyacetophenone, methoxyhydroxy acetophenone, hydroxy-
15 benzaldehyde, methylhydroxybenzaldehyde, methoxy
hydroxy benzaldehyde, dimethylhydroxybenzaldehyde,
chlorohydroxybenzaldehyde, and bromohydroxybenzaldehyde.
Of these compounds, preferred is hydroxybenzaldehyde
and particularly preferred is p-hydroxybenzaldehyde in
20 view of the performance of the product. Two or more of
these hydroxy aromatic carbonyl compounds may be used
in combination and further with small amounts of other
aldehydes such as formaldehyde, acetoaldehyde, acrolein,
croton aldehyde, benzaldehyde, and glyoxal.

25 Phenolic compounds of the present invention
can be also given the substituents by the alkylation,
chlorination, or bromination reaction to the condensation
products of phenols and hydroxy aromatic carbonyl compounds.

1 The phenolic compounds substituted by alkyl groups are expected to improve moisture performance and the compounds substituted by chlorine or bromine atom are expected to improve inflammability.

5 The reaction of the phenolic compound with an epichlorohydrin to produce the glycidyl ether compound is generally carried out in the presence of an alkali metal hydroxide. Among various improved techniques for obtaining high-purity glycidyl ethers, the
10 process of the present invention is characterized by reacting a phenolic compound as specified above with an epichlorohydrin in the presence of an aprotic polar solvent in addition to the alkali metal hydroxide, then removing the unreacted materials, the alkali metal
15 salt and water as the by-products, and the aprotic polar solvent, and treating the resulting crude glycidyl ether of the phenolic compound with an alkaline material in an organic solvent, thereby yielding a high-purity glycidyl ether of a phenolic compound.

20 For the reaction, epichlorohydrin is used in an amount of about 2.5 to 8 moles per mole of the phenolic hydroxyl groups.

 The use of epichlorohydrin in less amounts than the above lower limit is undesirable, because
25 this results in such industrial disadvantages that the intermolecular reaction produces a high polymer to cause a rise in the melt viscosity of the product glycidyl ether compound, the deterioration of product resin quality,

1 and further an increase in the amount of gel formed.
The use of more epichlorohidrin than the above upper
limit is also undesirable, since this merely increases
the volume of the reaction mixture to result in
5 industrial disadvantages such as lowering of the
productivity.

Suitable alkali metal hydroxides for use in
the present invention are, for example, sodium hydroxide
and potassium hydroxide, though not limited to these
10 hydroxides. The amount of alkali metal hydroxide used
is desired to be about one equivalent to the phenolic
hydroxyl groups. When the amount of alkali metal
hydroxide used is less than about one equivalent, some
of the phenolic hydroxyl groups remain unreacted and
15 hence the intermolecular reaction takes place to form
a high polymer, which is undesirable. When the amount
of alkali metal hydroxide used is more than about one
equivalent, an increased amount of gel is produced
to bring about disadvantages in the production process.

20 An aqueous solution of the alkali metal
hydroxide, higher concentrations of which are preferable,
is used since water must be removed from the reaction
mixture.

Suitable aprotic polar solvents for use in the
25 present invention include, for example, dimethylsulfoxide,
dimethyl sulfone, dimethylacetamide, tetramethylurea,
and hexamethylphosphorylamide.

These aprotic polar solvents are used in an

1 amount of 20 to 100 parts, preferably 40 to 80 parts,
by weight based on 100 parts by weight of epichloro-
hydrin used. When the solvent is used in too small
amounts, the content of hydrolyzable chlorine in the
5 product is not notably reduced and moreover phenolic
hydroxyl groups remain unreacted. This is undesirable
as stated above. When the solvent is used more than
the above amount, the intermolecular reaction proceeds
to result in low product quality as well as low produc-
10 tivity, which is undesirable.

In the present invention, the glycidyl ether-
ification of said phenolic compound can be carried out,
for instance, as follows:

First, a uniform solution is prepared by
15 mixing together said polyhydric phenol, epichlorohydrin,
and said aprotic polar solvent in proportions as stated
above. Then, said alkali metal hydroxide (dissolved
in water) is added to the solution with stirring to
initiate the reaction. This reaction is conducted in
20 the temperature range of 20 to 80°C, preferably 30 to
70°C.

In the case of the present invention, the
reaction temperature has large influences. That is,
in decreasing temperature, the selectivity of the reaction
25 rises and the content of hydrolyzable chlorine decreases.
At too low temperatures the reaction rate is, however,
undesirably low to decrease the productivity. At
temperatures exceeding 80°C, the effect of the present

1 invention is limited and the intermolecular reaction is undesirably promoted.

During this reaction, volatile matters are evaporated from the reaction mixture under reduced
5 pressure and condensed, the condensate is separated into an oil phase and a water phase, and the oil phase is returned to the reaction system, whereby the dehydration is performed. In this operation, the temperature and pressure are set under such conditions that the water
10 content in the reaction system may be from 0.5 to 5.0%, preferably from 0.5 to 3.0%, by weight. Excessive contents of water in the reaction system have such adverse effects that the product contains a large amount of hydrolyzable chlorine and has a high epoxy equivalent
15 weight and moreover that much epichlorohydrin is wasted by hydrolysis. The pressure is necessarily fixed when the temperature is set according to the composition of the reaction mixture.

To carry out the reaction uniformly, the alkali
20 metal hydroxide is added intermittently in small amounts or continuously at a low rate over 2-7 hours. Adding the alkali metal hydroxide momentarily or quickly causes the reaction to proceed locally, resulting in gel formation and/or making it impossible to maintain the
25 predetermined concentration of water, which is not desirable.

After finish of the reaction, the unreacted materials and by-products are removed in conventional

1 or well known methods. That is, the unreacted epichloro-
hydrin and remaining water are removed by distillation,
and the residue containing the glycidyl ether compound
is mixed with an organic solvent selected from ketone
5 solvents such as methyl isobutyl ketone and methyl
ethyl ketone and aromatic solvents such as benzene and
toluene to dissolve the glycidyl ether compound. The
alkali metal salt, which is insoluble, is removed by
filtration or washing with water. The aprotic polar
10 solvent is removed by washing with water.

While a crude glycidyl ether compound can be
obtained by evaporating the organic solvent from the
above solution, this solution containing a crude
glycidyl ether compound, according to the present inven-
15 tion, is further treated with an alkaline material.

Suitable alkaline materials for this treatment
include alkali metal hydroxides, alkaline earth metal
hydroxides, and alkali metal carbonates, for example,
sodium hydroxide, potassium hydroxide, calcium hydroxide,
20 sodium carbonate, and potassium carbonate.

The alkaline material is used in an amount of
0.01 to 0.10 mole per mole of the phenolic hydroxyl
groups.

When the amount of alkaline material used is
25 less than the above lower limit, the content of hydrolyz-
able chlorine is not reduced effectively. When the
amount exceeds the above upper limit, the polymerization
through the intermolecular reaction tends to take place.

1 The alkaline material in the form of fine
powders or aqueous solution is mixed with the solution
of the glycidyl ether compound in the organic solvent
and reacted at 40-100°C for 30 minutes to several hours.

5 At temperatures below 40°C the content of
hydrolyzable chlorine is not reduced effectively, while
at temperatures above 100°C the polymerization is
liable to take place.

 The excess alkaline material is neutralized
10 with phosphoric acid, carbon dioxide gas or the like,
and the resulting salt is removed by filtration or
washing with water, and then the organic solvent is
removed by distillation to recover the intended high-
purity glycidyl ether of a phenolic compound.

15 The glycidyl ether of a phenolic compound of
the present invention can be mixed with hardeners
to provide epoxy resin compositions. These compositions
can be used extensively to form epoxy resins having
high temperature performance, low hygroscopicity, and
20 good mechanical properties.

 The above hardeners include polyhydric phenols
such as phenol novolak, cresol novolak, polyvinylphenol
and the phenolic compound of the formula (IV); amine
type curing agents such as diaminodiphenylmethane and
25 diaminodiphenyl sulfone; and acid anhydride type curing
agents such as pyromellitic anhydride, trimellitic
anhydride, and benzophenonetetracarboxylic dianhydride.
In general, these hardeners are selected according to

1 the individual applications of cured epoxy resins.
Polyhydric phenols are fitted for encapsulation purposes
and amines are fitted for laminated board production.
These hardeners are used in amounts of 0.7 to 1.2
5 equivalents to the epoxy groups contained in the glycidyl
ether compound. When the amount is less than 0.7
equivalent or more than 1.2 equivalents to the epoxy
groups, the curing is imperfect and the cured product
will not be low hygroscopic.

10 Depending on the product applications, known
suitable additives can be incorporated into the epoxy
resin compositions. Such additives include fillers,
accelerators, flame retardants, mold-releasing agents,
surface treating agents and the like.

15 Fillers include silica, alumina, talc, clay,
and glass fiber; accelerators include imidazole compounds,
tertiary amines, and phosphoric compounds; and flame
retardants include brominated epoxy resins and antimony
trioxide. Mold-releasing agents include waxes and
20 metal salts of higher fatty acids including zinc stearate;
and surface treating agents include silane coupling
agents.

When used as an encapsulating material, the
epoxy resin composition may contain various elastomers
25 for the purpose of lowering the stress which will be
caused in the cured composition. Such elastomers include,
for example, polybutadiene rubber, butadiene-acrylonitrile
copolymer, and silicone rubber.

1 For encapsulating electronic components such
as semiconductor devices with the resin composition of
the present invention, the composition is cured according
to the conventional known molding method such as transfer
5 molding, compression molding, or injection molding.

For the fabrication of laminated boards by
using the resin composition of the present invention,
glass fibers or organic fibers are impregnated with a
uniform solution of the composition in a solvent such
10 as methyl ethyl ketone, toluene or ethylene glycol
monomethyl ether and then dried by heating to form
prepregs, which are then compression-molded.

The glycidyl ether compound of the present
invention can provide epoxy resin compositions which,
15 as encapsulants for electronic components and as laminated
board materials, can be cured into moldings having
low hygroscopicity and temperature performance durable
for use at higher temperatures. These compositions have
improved processability and can be molded into cured
20 products of higher reliability.

According to the process of the present inven-
tion, high-purity glycidyl ether compounds of low
hydrolyzable chlorine contents and small epoxy equivalent
weights can be obtained industrially with good produc-
25 tivity.

The present invention is illustrated with
reference to the following examples.

In the examples, the epoxy equivalent weight

- 1 is defined as the molecular weight of the epoxy resin per epoxy group.

The hydrolyzable chlorine content was determined by dissolving a sample of epoxy resin in dioxane, 5 adding an alcoholic solution of potassium hydroxide, heating the mixture under reflux for 30 minutes, and titrating the released chlorine ions with a silver nitrate solution. The found value was expressed in the parts per million based on the epoxy resin.

- 10 The water content in the reaction system was measured by the Karl Fischer's method.

The average number of repeating units was calculated from the average molecular weight determined by using a gel permeation chromatograph (TRIROTAR SR-II 15 manufactured by Japan Spectroscopic Co., Ltd.).

Properties of cured products were evaluated as follows:

- Glass transition temperature: Measured by using a thermal mechanical analyzer (Model TMA 10 20 manufactured by Daini Seikosha Co., Ltd.).

Flexural strength and flexural modulus: Measured in accordance with JIS K-6911 by using an Instron universal material tester (INSTRON Model 1122 [INSTRON is a registered Trade Mark]).

- Boiling water absorption: The change in the 25 weight of a test specimen was measured under the conditions: temperature 121°C, pressure 2 atm., and period 75 hours, by using a high-pressure steam environment tester (Model PC-305S manufactured by Hirayama Seisakusho Co., Ltd.).

1 Referential Examples 1-6 and Comparative Referential
Examples 1-6

Each of phenols, the names and amounts of which are shown in Table 1, 122 g of p-hydroxybenzal-
5 dehyde, and 3.8 g of p-toluene sulfonic acid (monohydrate) were reacted together in a reactor equipped with a thermometer, stirrer, and condenser under reflux with stirring at 95-105°C for 6 hours.

Thereafter, each of the reaction mixtures
10 was neutralized with a 10% aqueous sodium hydroxide solution, and washed twice with water. Then, the unreacted monomers were removed by distillation to yield a reddish brown phenolic compound. The average numbers of repeating units of the resulting phenolic compounds are shown in
15 Table 1.

Table 1

	Phenols		Average number of repeating units
	Name	Amount (g)	
Referential Example 1	3-Methyl-6-t-butylphenol	328	1.7
"	"	295.2	2.8
"	"	262.4	4.1
"	4-Methyl-2-t-butylphenol	328	1.9
"	5-Methyl-2-isopropylphenol	300	1.6
"	2-Methyl-4-n-hexylphenol	384	2.0
Comparative Referential Example 1	Phenol	1410	0.3
"	Phenol	188	3.3
"	O-Cresol	216	2.1
"	4-t-Butylphenol	300	2.3
"	3-Methyl-6-t-butylphenol	1640	0.2
"	2-Methyl-4-nonylphenol	468	2.4

1 Referential Example 7

A phenolic compound was prepared according to the procedures of Referential Example 1 except using 246 g of 3-methyl-6-t-butylphenol and 54 g of m-cresol
5 in place of 328 g of 3-methyl-6-t-butylphenol. The average number of repeating units of the resultant compound was 2.2.

Referential Example 8

246 g of 3-methyl-6-t-butylphenol, 54 g of
10 o-cresol, and 3.8 g of p-toluenesulfonic acid (mono-hydrate) were mixed in the same reactor as Referential Example 1, and then 16.7 g of a 36% aqueous solution of formaldehyde was added dropwise for an hour at a temperature of 95-105°C, the mixture being maintained
15 for one hour with stirring.

97.5 g of p-hydroxybenzaldehyde was added into the mixture and reacted for six hours under reflux. Then the same after-treatment as Referential Example 1 was carried out to obtain a phenolic compound.

20 The average number of repeating units was 2.2 (each of the numbers of repeating units derived from p-hydroxybenzaldehyde and formaldehyde was 1.8 and 0.4 respectively.).

Examples 1-10 and Comparative Examples 1-6

25 Each of the phenolic compounds was reacted with an epichlorohydrin (names and amounts of the phenolic compounds

1 and amounts of epichlorohydrin are shown in Table 2)
in a separable flask equipped with a baffle, thermo-
meter, stirrer, and further a dropping funnel for
continuous addition of a 40% aqueous sodium hydroxide
5 solution and a condenser-equipped tubular separator for
cooling and liquefying the water and epichlorohydrin
vaporized from the reaction system, separating the
condensed liquids into an organic layer and a water
layer by utilizing the specific gravity difference,
10 and returning the organic layer into the reaction system
while excluding the water layer.

This reaction was carried out in the presence
of dimethylsulfoxide as an aprotic polar solvent,
while adding continuously said sodium hydroxide solution
15 over 4 hours, the amounts of said solvent and sodium
hydroxide solution being shown in Table 2.

After finish of the reaction, the unreacted
epichlorohydrin was removed by distillation under
reduced pressure, and the residue was dissolved in 500 g
20 of methyl isobutyl ketone. This solution was washed
three times with 120 g of water to remove the by-product
salt and the aprotic polar solvent.

Further, a 10% aqueous sodium hydroxide solu-
tion, the amount of which is shown in Table 2, was
25 added in about 10 minutes to the methyl isobutyl ketone
solution while keeping the temperature at 80°C. After
2 hours' standing, the resulting mixture was neutralized
by blowing carbon dioxide gas thereinto. The resultant

1 by-product salt was removed by filtration and then the
solvent was removed by distillation. Thus, glycidyl
ethers of the polyhydric phenols were obtained. Table
2 shows properties (hydrolyzable chlorine contents
5 and epoxy equivalent weights) of these products.

Comparative Example 7

A glycidyl ether compound was prepared according to the procedures of Example 1 except that, after glycidyl etherification, the solvent was immediately
10 removed from the methyl isobutyl ketone solution of the crude glycidyl ether compound without adding the 10% aqueous sodium hydroxide solution.

Results of evaluation on properties of the product are shown in Table 2.

15 Comparative Example 8

A glycidyl ether compound was prepared according to the procedures of Example 1 except using no aprotic polar solvent.

Results of evaluation on properties of the
20 product are shown in Table 2.

Comparative Example 9

Glycidyl etherification of the phenolic compound prepared in Referential Example 1 was carried out according to the method described in Example 3 of
25 U.S. Patent No. 4,394,496.

- 1 That is, 144.0 g of the phenolic compound prepared in Referential Example 1 and 925 g of epichlorohydrin were charged into a separable flask equipped with a baffle, thermometer, stirrer, and condenser.
- 5 After dissolution of the phenolic compound, the solution was heated to the reflux temperature, and further 1.44 g of a 60% aqueous solution of benzyltrimethylammonium chloride was added. The mixture was maintained at the same temperature (119-120°C) for 1 hour and then cooled
- 10 to 50°C. At this temperature, 333.3 ml of 3 molar NaOH in saturated Na_2CO_3 aqueous solution was added and reacted for 1 hour.

The resulting mixture was allowed to stand, and then the separated aqueous layer was removed, and

15 further 166.7 ml of 3 molar NaOH in saturated Na_2CO_3 aqueous solution was added and reacted at 50°C for 1 hour..

The resulting mixture was again allowed to stand, and the separated aqueous layer was removed,

20 and then the organic layer was washed with 300 ml of a 1 wt.% aqueous acetic acid solution and further 5 times with 300 ml of pure water. Then, the unreacted epichlorohydrin was removed by distillation under reduced pressure to produce a glycidyl ether compound.

25 The epoxy equivalent weight of this product was 216 and the hydrolyzable chlorine content therein was 1080 ppm.

Table 2

	Phenolic compound		Amount of Epichloro- hydrin (g)	Amount of dimethyl- sulfoxide (g)	Amount of 40% aq. NaOH soln. (g)	Reaction temp./ pressure (°C/Torr)
	Source	Amount (g)				
Ex. 1	Referential Example 1	144.0*1	370*2	148	100*3	45/38
2	" 2	"	"	"	"	"
3	" 3	"	"	"	"	"
4	" 4	"	"	"	"	"
5	" 5	134.7	"	"	"	"
6	" 6	162.7	"	"	"	"
7	" 7	135	"	"	"	"
8	" 8	138	"	"	"	"
9	" 1	144.0	"	222	"	45/36
10	" 1	"	555	"	"	45/39

- Cont'd. -

Table 2 (Cont'd.)

Water content in reaction system (%)	Amount of 10% aq. NaOH soln. (g)	Hydrolyzable chlorine content (ppm)	Epoxy equivalent weight
1.9	20 ^{*4}	140	219
2.0	"	150	216
1.9	"	140	217
1.8	"	160	215
1.9	"	180	209
1.9	"	150	228
1.8	"	190	209
2.0	"	190	207
1.8	"	150	215
1.7	"	130	217

- Cont'd. -

Table 2 (Cont'd.)

Comparative Ex. 1	Comparative Referential Example 1	97.3	370	148	100*3	45/38
2	" 2	97.3	"	"	"	"
3	" 3	106.7	"	"	"	"
4	" 4	134.7	"	"	"	"
5	" 5	144.0	"	"	"	"
6	" 6	190.6	"	"	"	"
7	Referential Example 1	144.0	"	"	"	"
8	" 1	"	"	-	"	45/90

- Cont'd. -

Notes: *1: Amount containing 1 mole of phenolic hydroxy groups.

*2: Amount corresponding to 4 moles of epichlorohydrin.

*3: Amount corresponding to 1 mole of NaOH.

*4: Amount corresponding to 0.05 mole of NaOH.

Table 2 (Cont'd.)

1.8	20 ^{*4}	180	157
1.9	"	200	159
2.0	"	190	170
2.0	"	170	205
1.9	"	150	212
2.0	"	190	258
1.7	-	310	215
2.4	20	800	225

1 Examples 11-20 and Comparative Examples 10-16

Various glycidyl ether compounds shown in Table 3 were blended each with a phenol novolak (used as a hardener, softening point 95°C), triphenyl phosphine 5 (used as an accelerator), and fused silica (used as a filler) in proportions (g) as shown in Table 3. Each blend was heated and kneaded on a roll mill, and molded by pressing at 175°C for 5 minutes. Further, each molded product was post-cured for 5 hours in a 180°C oven to 10 produce a cured material.

Table 3 shows the glass transition temperature, boiling water absorption (%), flexural strength, and flexural modulus of each of the cured materials.

Table 3

	Glycidyl ether compound		Phenol novolak (g)	Triphenyl phosphine (g)	Silica (g)	Glass transition temperature (°C)
	Source	Amount (g)				
Example 11	Example 1	214	110	3.21	756	210
" 12	" 2	216	"	3.24	761	216
" 13	" 3	217	"	3.26	763	220
" 14	" 4	215	"	3.23	758	208
" 15	" 5	209	"	3.14	744	213
" 16	" 6	228	"	3.42	789	200
" 17	" 7	209	"	3.14	744	221
" 18	" 8	207	"	3.11	740	214
" 19	" 9	215	"	3.23	758	209
" 20	" 10	217	"	3.26	763	208

- Cont'd. -

Table 3 (Cont'd.)

Flexural strength (Kg/mm ²)	Flexural modulus (Kg/mm ²)	Boiling water absorption (%)
13.7	1210	0.78
13.9	1250	0.81
14.1	1320	0.83
13.7	1200	0.81
14.0	1270	0.84
13.0	1170	0.75
14.2	1280	0.83
13.8	1230	0.81
13.6	1200	0.77
13.7	1220	0.77

- Cont'd. -

Table 3 (Cont'd.)

Comparative Example 10	(*5)	175	110	2.93	712	175
" 11	Comparative Example 1	157	"	2.36	623	203
" 12	" 2	159	"	2.39	628	223
" 13	" 3	170	"	2.55	653	198
" 14	" 4	205	"	3.08	735	193
" 15	" 5	212	"	3.18	751	193
" 16	" 6	258	"	3.87	859	124

Note; *5: Glycidyl ether of o-cresol novolak (manufactured by Sumitomo Chemical Co., Ltd. under the tradename of Sumi Epoxy ESCN-195, epoxy equivalent weight; 195).

- Cont'd. -

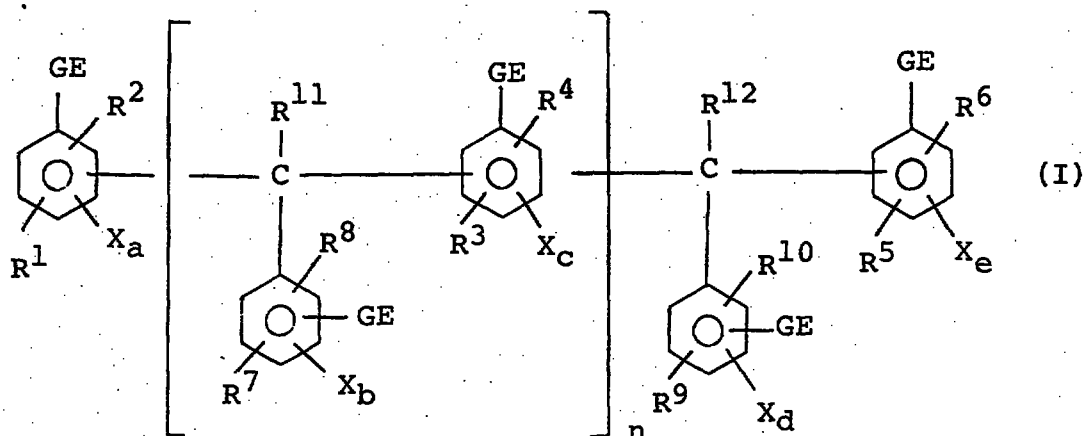
Table 3 (Cont'd.)

15.0	1320	0.81
13.3	1230	1.03
13.7	1250	1.10
13.9	1300	0.94
14.1	1280	0.87
13.2	1200	0.76
12.7	1110	0.74



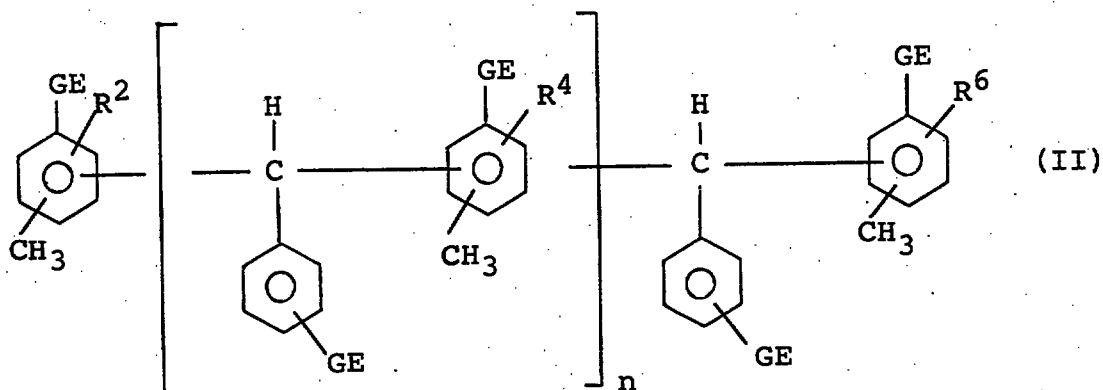
CLAIMS:-

1. A glycidyl ether of a phenolic compound of the formula (I):



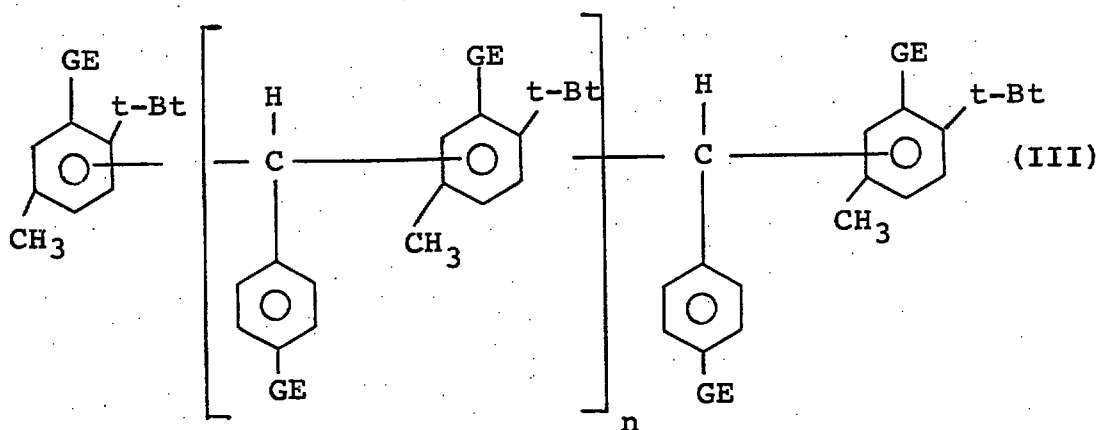
, wherein each of R^1 through R^6 represents an alkyl group of from 1 to 6 carbon atoms; each of R^7 through R^{12} represents a hydrogen atom, an alkyl group of from 1 to 4 carbon atoms or an alkoxy group of from 1 to 4 carbon atoms; X represents a chlorine or bromine atom; GE represents a glycidyl ether group; a, b, c, d, and e are 0 or 1; and n is an average number of from 0.5 to 5.

2. A glycidyl ether of a phenolic compound of the formula (II):



, wherein each of R^2 , R^4 , and R^6 represents an alkyl group of from 3 to 6 carbon atoms; GE represents a glycidyl ether group; and n is an average number of from 0.5 to 5.

3. A glycidyl ether of a phenolic compound of the formula (III):

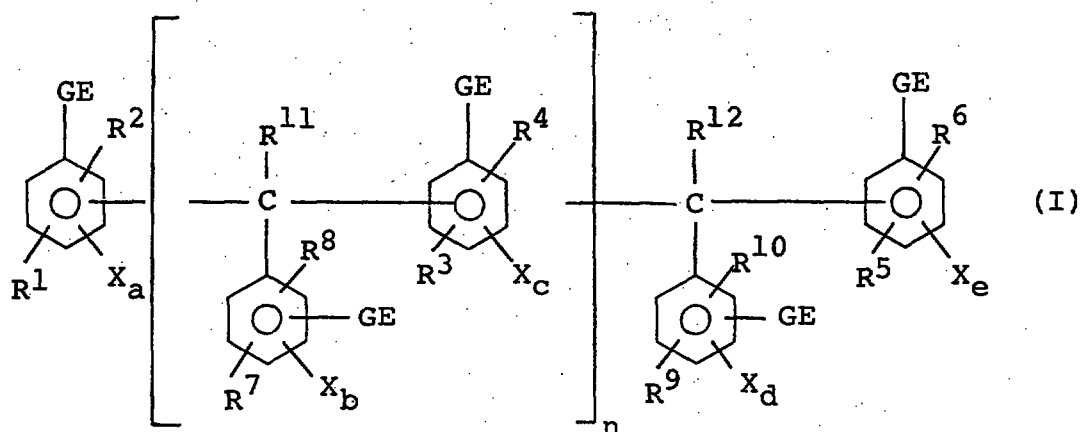


, wherein t-Bt represents tertiary butyl; GE represents a glycidyl ether group; and n is an average number of from 0.5 to 5.

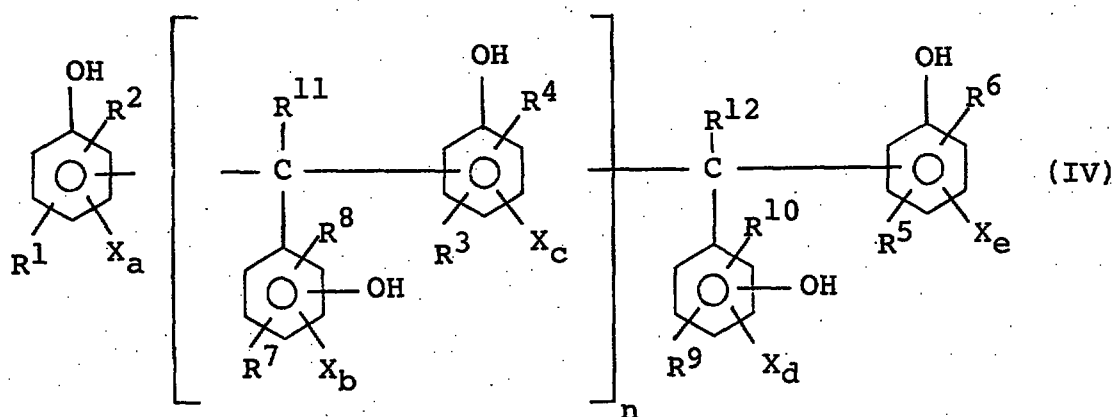
4. An epoxy composition comprising a glycidyl ether of claim 1 and a hardener.



5. An epoxy composition comprising a glycidyl ether of claim 1 and a polyhydric phenol.
6. An encapsulating composition comprising a glycidyl ether of claim 1 and a polyhydric phenol.
7. A process of preparing a glycidyl ether of the formula (I):



, wherein each of R^1 through R^6 represents an alkyl group of from 1 to 6 carbon atoms; each of R^7 through R^{12} represents a hydrogen atom, an alkyl group of from 1 to 4 carbon atoms or an alkoxy group of from 1 to 4 carbon atoms; X represents a chlorine or bromine atom; GE represents a glycidyl ether group; a, b, c, d, and e are 0 or 1; and n is an average number of from 0.5 to 5, which comprises reacting a phenolic compound of the formula (IV):



, wherein each of R^1 through R^6 represents an alkyl group of from 1 to 6 carbon atoms; each of R^7 through R^{12} represents a hydrogen atom, an alkyl group of from 1 to 4 carbon atoms, or an alkoxy group of from 1 to 4 carbon atoms; X represents a chlorine or bromine atom; GE represents a glycidyl ether group; a, b, c, d, and e are 0 or 1; and n is an average number of from 0.5 to 5,

with an epichlorohydrin in the presence of an alkali metal hydroxide and an aprotic polar solvent, then treating the resulting crude glycidyl ether of the phenolic compound with an alkaline material in an organic solvent.

8. A process of claim 7, wherein said aprotic polar solvent is dimethylsulfoxide, dimethylsulfone, dimethylacetoamide, tetramethylurea, or hexamethylphosphorylamide.

9. A process of claim 7, wherein said aprotic polar solvent is used in an amount of 20 to 100 parts by weight per 100 parts by weight of an epichlorohydrin.



10. A process of claim 7, wherein an epichlorohydrin is used in an amount of 2.5 to 8 equivalents per the phenolic hydroxyl groups.

11. A process of claim 7, wherein said alkali metal hydroxide is sodium hydroxide, potassium hydroxide, or a mixture of them and used in an amount of about one equivalent per the phenolic hydroxyl groups.

12. A process of claim 7, wherein said phenolic compound is reacted with an epichlorohydrin at a temperature of from 20 to 80°C.

13. A process of claim 7, wherein said phenolic compound is reacted with an epichlorohydrin keeping the water content of the reaction system in the range of from 0.5 to 5.0 weight %.

14. A process of claim 7, wherein said alkaline material is selected from alkali metal hydroxides, alkaline earth metal hydroxides, and alkali metal carbonates.

15. A process of claim 7, wherein said alkaline material is used in an amount of 0.01 to 0.10 equivalent per the phenolic hydroxyl groups.

16. A process of claim 7, wherein the crude glycidyl ether of the phenolic compound is treated with said alkaline material in an organic solvent at a temperature of from 40 to 100°C.
