prepared in Example 1.

[Fig. 4] Fig. 4 is a GPC chart of a phenolic resin (A-2) prepared in Example 2.

[Fig. 5] Fig. 5 is a GPC chart of a phenolic resin (A-3) prepared in Example 3.

[Fig. 6] Fig. 6 is a GPC chart of a phenolic resin (A-4) prepared in Example 4.

[Fig. 7] Fig. 7 is a C^{13}-NMR chart of the phenolic resin (A-4) prepared in Example 4.

[Fig. 8] Fig. 8 is a MS spectrum of the phenolic resin (A-4) prepared in Example 4.

[Fig. 9] Fig. 9 is a GPC chart of a phenolic resin (E-1) prepared in Example 5.

[Fig. 10] Fig. 10 is a C^{13}-NMR chart of the epoxy resin (E-1) prepared in Example 5.

[Fig. 11] Fig. 11 is a MS spectrum of the epoxy resin (E-1) prepared in Example 5.

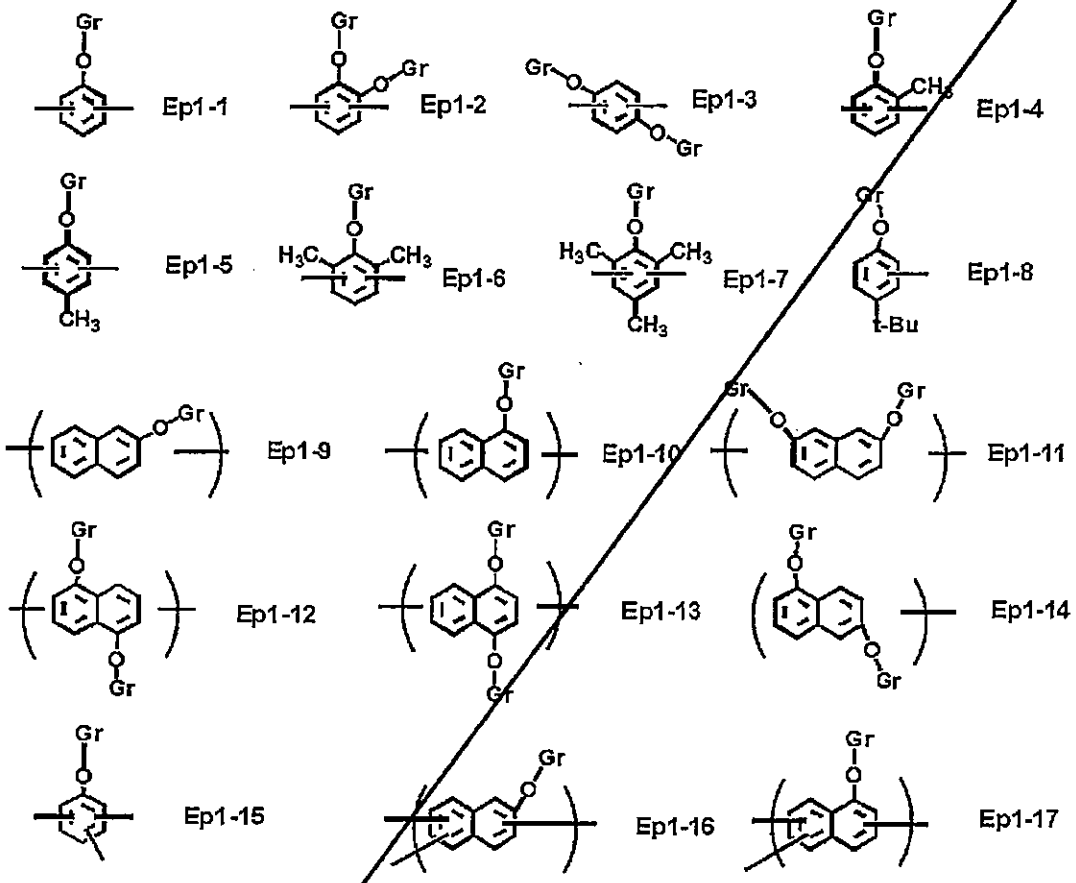
[Fig. 12] Fig. 12 is a GPC chart of an epoxy resin (E-2) prepared in Example 6.

[Fig. 13] Fig. 13 is a GPC chart of an epoxy resin (E-3) prepared in Example 7.

[Fig. 14] Fig. 14 is a GPC chart of an epoxy resin (E-4) prepared in Example 8.

[Fig. 15] Fig. 15 is a C^{13}-NMR chart of the epoxy resin (E-4) prepared in Example 8.

[Chem. 30]



In the above structural formulae, "Gr" represents a glycidyloxy group. Among these structures, regarding those having two or more positions of bonding to other structural moieties on a naphthalene skeleton, the bonding positions may be located on the same nucleus or different nuclei.

[0094]

In the present invention, among these, the aromatic hydrocarbon group represented by structural formula Ep1-1 is particularly preferable from the standpoint of good

curability, and the aromatic hydrocarbon group represented by structural formula Ep1-4 is particularly preferable from the standpoint of good resistance to moisture and solder.

[0095]

Next, as in the phenolic resin (B) in the thermosetting resin composition (I), examples of the divalent aralkyl group (X) included in the resin structure of the epoxy resin (A') include groups having structures represented by X1 to X5 above.

[0096]

The epoxy resin (A') used in the thermosetting resin composition (II) of the present invention has a resin structure in which plural aromatic hydrocarbon groups selected from the group consisting of a naphthylmethyloxy group- or anthrylmethyloxy group-containing aromatic hydrocarbon group (ph1) and a glycidyloxy group-containing aromatic hydrocarbon group (ep) are bonded through a divalent aralkyl group phenylene alkylidene group (X). The form of these bonds may be any combination. When the naphthylmethyloxy group- or anthrylmethyloxy group-containing aromatic hydrocarbon group (ph1) is represented by "Ph1", the glycidyloxy group-containing aromatic skeleton (ep) is represented by "Ep1", and the divalent aralkyl group (X) is represented by "X", examples of the molecular structure of the epoxy resin constituted by these structural

naphthalene, and 300.0 g of methyl isobutyl ketone were charged while nitrogen gas was purged, and the resulting mixture was stirred at room temperature while nitrogen was blown. The temperature was increased to 60 degrees (Celsius), and 23.3 g (0.29 moles) of an aqueous 49% sodium hydroxide solution was then added dropwise to the mixture over a period of one hour. After the completion of the addition, the temperature was increased, and the mixture was allowed to react at 70 degrees (Celsius) for two hours, at 95 degrees (Celsius) for two hours, and further for five hours while the mixture was refluxed. After the completion of the reaction, the temperature was decreased to 80 degrees (Celsius), the organic layer was washed with 100 g of water, and this water washing was repeated four times. Subsequently, methyl isobutyl ketone was removed by heating under reduced pressure. Thus, a phenolic resin (A-1) was prepared. The resulting phenolic resin had a softening point of 72 degrees (Celsius) (B & R method), a melt viscosity (measuring method: ICI viscometer method, measuring temperature: 150 degrees (Celsius)) of 1.3 dPa·s, and a hydroxyl equivalent of 276 g/eq.

A GPC chart of the prepared phenolic resin is shown in Fig. 1, a C^{13}-NMR chart of the phenolic resin is shown in Fig. 2, and a MS spectrum of the phenolic resin is shown in Fig. 3. The presence of a methylnaphthyloxy group was confirmed

measuring temperature: 150 degrees (Celsius)) of 1.0 dPa·s, and a hydroxyl equivalent of 195 g/eq.
A GPC chart of the prepared phenolic resin is shown in Fig. 5. The ratio of a phenolic hydroxyl group to a naphthylmethyloxy group or an anthrylmethyloxy group was 92:8.

[0167]

EXAMPLE 4 [Synthesis of phenolic resin (A-4)]

A phenolic resin (A-4) was prepared as in Example 1 except that 200.0 g (hydroxyl group: 1 equivalent) of a biphenyl novolac resin ("MEH-7851SS" manufactured by Meiwa Plastic Industries, Ltd.) was used instead of the phenol aralkyl resin ("XLC-4L" manufactured by Mitsui Chemicals, Inc.), and 53.0 g (0.3 moles) of 1-chloromethyl naphthalene was used. The resulting phenolic resin had a softening point of 76 degrees (Celsius) (B & R method), a melt viscosity (measuring method: ICI viscometer method, measuring temperature: 150 degrees (Celsius)) of 1.4 dPa·s, and a hydroxyl equivalent of 351 g/eq. A GPC chart of the prepared phenolic resin is shown in Fig. 6, a C^{13}-NMR chart of the phenolic resin is shown in Fig. 7, and a MS spectrum of the phenolic resin is shown in Fig. 8. The presence of a methylnaphthyloxy group was confirmed by the above analysis. The ratio of a phenolic hydroxyl group to a naphthylmethyloxy group or an anthrylmethyloxy group was

70:30.

[0168]

COMPARATIVE EXAMPLE 1 [Synthesis of phenolic resin (A-5): phenolic resin described in PTL1]

In a flask equipped with a thermometer, a dropping funnel, a condenser tube, a distilling tube, and a stirrer, 520 g (5.0 moles) of a phenol novolac resin ("PHENOLITE TD-2131" manufactured by DIC Corporation), 209 g (1.65 moles) of benzyl chloride, 1,094 g of methyl isobutyl ketone, and 7 g of tetraethylammonium chloride were charged, and the resulting mixture was stirred at room temperature while nitrogen was blown. Next, 149 g (1.82 moles) of an aqueous 49% sodium hydroxide solution was added to the mixture at 70 degrees (Celsius) over a period of one hour. After the completion of the addition, the mixture was further stirred at 100 degrees (Celsius) for three hours. After the completion of the reaction, the reaction mixture was neutralized by adding 10 g of sodium dihydrogen phosphate, and the aqueous layer was then removed. Furthermore, the organic layer was washed with 300 parts of water, and this water washing was repeated three times. Subsequently, methyl isobutyl ketone was removed by heating under reduced pressure. Thus, 626 g of a compound (A-5) was prepared. The resulting compound (A-1) had a softening point of 66 degrees (Celsius) (B & R method), a melt viscosity (measuring

crude epoxy resin in the solvent. Furthermore, 10 g of an aqueous 10% sodium hydroxide solution was added to this solution, and the resulting mixture was allowed to react at 80 degrees (Celsius) for two hours. Subsequently, the reaction mixture was washed with 150 g of water, and this water washing was repeated three times until the pH of the washing liquid became neutral. Next, the reaction system was dehydrated by azeotrope. Microfiltration was conducted, and the solvent was then distilled off under reduced pressure. Thus, 299 g of an epoxy resin (E-1) was prepared. The resulting epoxy resin had a softening point of 62 degrees (Celsius) (B & R method), a melt viscosity (measuring method: ICI viscometer method, measuring temperature: 150 degrees (Celsius)) of 1.2 dPa·s, and an epoxy equivalent of 363 g/eq.

[0170]

A GPC chart of the prepared phenolic resin is shown in Fig. 9, a C^{13}-NMR chart of the resin is shown in Fig. 10, and a MS spectrum of the resin is shown in Fig. 11. The presence of a methylnaphthyloxy group was confirmed by the above analysis. The ratio of a glycidyloxy group to a naphthylmethyloxy group or an anthrylmethyloxy group was 74:26.

[0171]

EXAMPLE 6 Epoxidation of phenolic resin (A-2), Epoxy

anthrylmethyloxy group was 92:8.

[0173]

EXAMPLE 8 Epoxidation of phenolic resin (A-4), Epoxy resin (E-4)

An epoxidized product (E-4) (380 g) was prepared as in Example 5 except that 351 g (hydroxyl group: 1 equivalent) of the phenolic resin (A-4) was used instead of the phenolic resin (A-1). The resulting epoxy resin had a softening point of 69 degrees (Celsius) (B & R method), a melt viscosity (measuring method: ICI viscometer method, measuring temperature: 150 degrees (Celsius)) of 1.7 dPa·s, and an epoxy equivalent of 463 g/eq. A GPC chart of the prepared epoxy resin is shown in Fig. 14, a C^{13}-NMR chart of the epoxy resin is shown in Fig. 15, and a MS spectrum of the epoxy resin is shown in Fig. 16. The presence of a methylnaphthyloxy group was confirmed by the above analysis. The ratio of a glycidyloxy group to a naphthylmethyloxy group or an anthrylmethyloxy group was 70:30.

[0174]

COMPARATIVE EXAMPLE 2 [Synthesis of epoxy resin (E-5)]

Epoxidation was conducted as in Example 5 except that 189 g (hydroxyl group: 1 equivalent) of the phenolic resin (A-5) was used instead of the phenolic resin (A-1). The resulting epoxy resin (E-1) had a softening point of 43 degrees (Celsius) (B & R method), a melt viscosity

added to the resulting crude epoxy resin to dissolve the crude epoxy resin in the solvent. Furthermore, 10 g of an aqueous 10 mass% sodium hydroxide solution was added to this solution, and the resulting mixture was allowed to react at 80 degrees (Celsius) for two hours. Subsequently, the reaction mixture was washed with 150 g of water, and this water washing was repeated three times until the pH of the washing liquid became neutral. Next, the reaction system was dehydrated by azeotrope. Microfiltration was conducted, and the solvent was then distilled off under reduced pressure. Thus, an epoxy resin (E-8) was prepared. The resulting epoxy resin had a melt viscosity (measuring method: ICI viscometer method, measuring temperature: 150 degrees (Celsius)) of 0.8 dPa·s and an epoxy equivalent of 250 g/eq.

[0177]

EXAMPLES 9 to 18 and COMPARATIVE EXAMPLES 1 to 3

The epoxy resins (E-1) to (E-5), YX-4000H manufactured by Japan Epoxy Resin Co., Ltd. (tetramethylbiphenol-type epoxy resin, epoxy equivalent: 195 g/eq.), NC-3000 manufactured by Nippon Kayaku Co., Ltd. (biphenyl novolac-type epoxy resin, epoxy equivalent: 274 g/eq.), and NC-2000L manufactured by Nippon Kayaku Co., Ltd. (phenol aralkyl-type epoxy resin, epoxy equivalent: 236 g/eq.), all of which serve as epoxy resins; the phenolic resins (A-1) to (A-5),

manufactured by Nippon Kayaku Co., Ltd., epoxy equivalent: 274 g/eq.)

YX-4000H: tetramethylbiphenol-type epoxy resin, "YX-4000H" manufactured by Japan Epoxy Resin Co., Ltd., epoxy equivalent: 195 g/eq.)

N-655-EXP-S: cresol novolac-type epoxy resin ("Epiclon N-655-EXP-S", epoxy equivalent: 200 g/eq.)

MEH-7851SS: biphenyl novolac resin ("MEH-7851SS" manufactured by Meiwa Plastic Industries, Ltd., hydroxyl equivalent: 200 g/eq.)

XLC-3L: phenol aralkyl resin ("XLC-3L" manufactured by Mitsui Chemicals, Inc., hydroxyl equivalent: 172 g/eq.)

TD-2131: phenol novolac-type phenolic resin ("TD-2131" manufactured by DIC Corporation, hydroxyl equivalent: 104 g/eq.)

TPP: triphenylphosphine

prepared in Example 1.

[Fig. 4] Fig. 4 is a GPC chart of a phenolic resin (A-2) prepared in Example 2.

[Fig. 5] Fig. 5 is a GPC chart of a phenolic resin (A-3) prepared in Example 3.

[Fig. 6] Fig. 6 is a GPC chart of a phenolic resin (A-4) prepared in Example 4.

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[Fig. 8] Fig. 8 is a MS spectrum of the phenolic resin (A-4) prepared in Example 4.

[Fig. 9] Fig. 9 is a GPC chart of an epoxy resin (E-1) prepared in Example 5.

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[Fig. 11] Fig. 11 is a MS spectrum of the epoxy resin (E-1) prepared in Example 5.

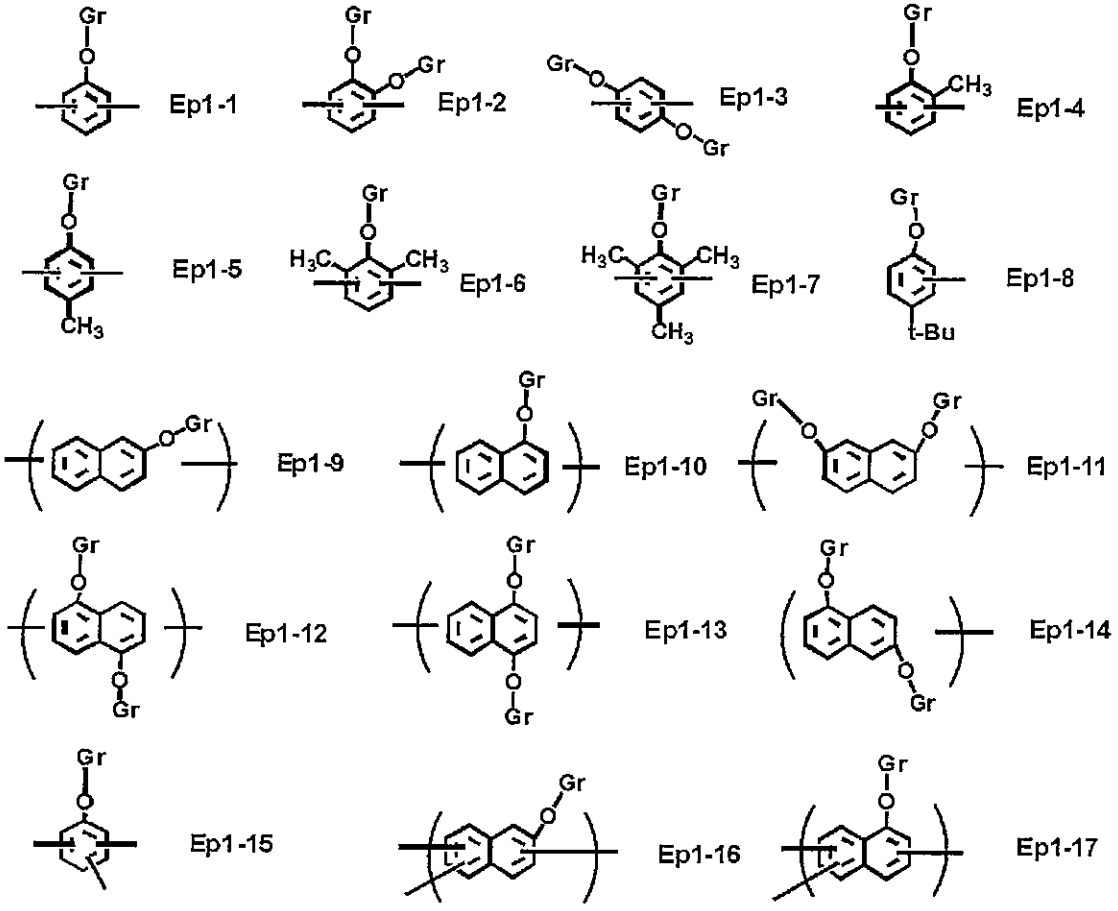
[Fig. 12] Fig. 12 is a GPC chart of an epoxy resin (E-2) prepared in Example 6.

[Fig. 13] Fig. 13 is a GPC chart of an epoxy resin (E-3) prepared in Example 7.

[Fig. 14] Fig. 14 is a GPC chart of an epoxy resin (E-4) prepared in Example 8.

[Fig. 15] Fig. 15 is a C^{13}-NMR chart of the epoxy resin (E-4) prepared in Example 8.

[Chem. 30]



In the above structural formulae, "Gr" represents a glycidyl group. Among these structures, regarding those having two or more positions of bonding to other structural moieties on a naphthalene skeleton, the bonding positions may be located on the same nucleus or different nuclei.

[0094]

In the present invention, among these, the aromatic hydrocarbon group represented by structural formula Ep1-1 is particularly preferable from the standpoint of good

curability, and the aromatic hydrocarbon group represented by structural formula Ep1-4 is particularly preferable from the standpoint of good resistance to moisture and solder.

[0095]

Next, as in the phenolic resin (B) in the thermosetting resin composition (I), examples of the divalent aralkyl group (X) included in the resin structure of the epoxy resin (A') include groups having structures represented by X1 to X5 above.

[0096]

The epoxy resin (A') used in the thermosetting resin composition (II) of the present invention has a resin structure in which plural aromatic hydrocarbon groups selected from the group consisting of a naphthylmethyloxy group- or anthrylmethyloxy group-containing aromatic hydrocarbon group (ph1) and a glycidyloxy group-containing aromatic hydrocarbon group (ep) are bonded through a divalent aralkyl group (X). The form of these bonds may be any combination. When the naphthylmethyloxy group- or anthrylmethyloxy group-containing aromatic hydrocarbon group (ph1) is represented by "Ph1", the glycidyloxy group-containing aromatic skeleton (ep) is represented by "Ep1", and the divalent aralkyl group (X) is represented by "X", examples of the molecular structure of the epoxy resin constituted by these structural

naphthalene, and 300.0 g of methyl isobutyl ketone were charged while nitrogen gas was purged, and the resulting mixture was stirred at room temperature while nitrogen was blown. The temperature was increased to 60 degrees (Celsius), and 23.3 g (0.29 moles) of an aqueous 49% sodium hydroxide solution was then added dropwise to the mixture over a period of one hour. After the completion of the addition, the temperature was increased, and the mixture was allowed to react at 70 degrees (Celsius) for two hours, at 95 degrees (Celsius) for two hours, and further for five hours while the mixture was refluxed. After the completion of the reaction, the temperature was decreased to 80 degrees (Celsius), the organic layer was washed with 100 g of water, and this water washing was repeated four times. Subsequently, methyl isobutyl ketone was removed by heating under reduced pressure. Thus, a phenolic resin (A-1) was prepared. The resulting phenolic resin had a softening point of 72 degrees (Celsius) (B & R method), a melt viscosity (measuring method: ICI viscometer method, measuring temperature: 150 degrees (Celsius)) of 1.3 dPa·s, and a hydroxyl equivalent of 276 g/eq.

A GPC chart of the prepared phenolic resin is shown in Fig. 1, a C^{13}-NMR chart of the phenolic resin is shown in Fig. 2, and a MS spectrum of the phenolic resin is shown in Fig. 3. The presence of a naphthylmethyloxy group was confirmed

measuring temperature: 150 degrees (Celsius)) of 1.0 dPa·s, and a hydroxyl equivalent of 195 g/eq.

A GPC chart of the prepared phenolic resin is shown in Fig. 5. The ratio of a phenolic hydroxyl group to a naphthylmethyloxy group or an anthrylmethyloxy group was 92:8.

[0167]

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[0168]

COMPARATIVE EXAMPLE 1 [Synthesis of phenolic resin (A-5): phenolic resin described in PTL1]

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[0170]

A GPC chart of the prepared epoxy resin is shown in Fig. 9, a C^{13}-NMR chart of the resin is shown in Fig. 10, and a MS spectrum of the resin is shown in Fig. 11. The presence of a naphthylmethyloxy group was confirmed by the above analysis. The ratio of a glycidyloxy group to a naphthylmethyloxy group or an anthrylmethyloxy group was 74:26.

[0171]

EXAMPLE 6 Epoxidation of phenolic resin (A-2), Epoxy

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[0173]

EXAMPLE 8 Epoxidation of phenolic resin (A-4), Epoxy resin (E-4)

An epoxidized product (E-4) (380 g) was prepared as in Example 5 except that 351 g (hydroxyl group: 1 equivalent) of the phenolic resin (A-4) was used instead of the phenolic resin (A-1). The resulting epoxy resin had a softening point of 69 degrees (Celsius) (B & R method), a melt viscosity (measuring method: ICI viscometer method, measuring temperature: 150 degrees (Celsius)) of 1.7 dPa·s, and an epoxy equivalent of 463 g/eq. A GPC chart of the prepared epoxy resin is shown in Fig. 14, a C^{13}-NMR chart of the epoxy resin is shown in Fig. 15, and a MS spectrum of the epoxy resin is shown in Fig. 16. The presence of a naphthylmethyloxy group was confirmed by the above analysis. The ratio of a glycidyloxy group to a naphthylmethyloxy group or an anthrylmethyloxy group was 70:30.

[0174]

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Epoxidation was conducted as in Example 5 except that 189 g (hydroxyl group: 1 equivalent) of the phenolic resin (A-5) was used instead of the phenolic resin (A-1). The resulting epoxy resin (E-5) had a softening point of 43 degrees (Celsius) (B & R method), a melt viscosity

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[0177]

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XLC-3L: phenol aralkyl resin ("XLC-3L" manufactured by Mitsui Chemicals, Inc., hydroxyl equivalent: 172 g/eq.)

TD-2131: phenol novolac-type phenolic resin ("TD-2131" manufactured by DIC Corporation, hydroxyl equivalent: 104 g/eq.)

TPP: triphenylphosphine