CURABLE RESIN COMPOSITION AND ELECTRONIC COMPONENT DEVICE

[Technical Field]

[0001] The invention relates to a curable resin composition and an electronic component device.

[Background Art]

[0002] In conjunction with recent trends in electronic devices, such as reductions in size or weight, and increased sophistication, the density of electronic components for mounting on electronic component devices is increasing. As a result, the mainstream trend of electronic component devices is changing from conventional pin-insertion packages to surface-mounted packages such as IC (integrated circuit) or LSI (large scale integration).

[0003] Surface-mounted packages are produced by a different method from the methods of producing conventional pin-insertion packages. Specifically, a pin-insertion package is not subjected to high temperature because soldering is performed after a process of inserting pins into a circuit board, from the backside of the circuit board. However, a surface-mounted package is directly exposed to a temperature for soldering (reflow temperature) because the entire body of the electronic component device is processed in a solder bath or a reflow machine. As a result, when the package includes water absorbed therein, the water may rapidly expand during the soldering, and the pressure of the generated steam may cause separation between an insert such as an element or a lead frame, and a sealing material, and may eventually cause package cracking, defective electronic properties or the like.

Therefore, development of a sealing material that exhibits excellent adhesion with respect to an insert and excellent thermal resistance during soldering (reflow resistance) is desired.

[0004] In order to meet the aforementioned demand, use of a silane coupling agent as a modifier of an inorganic filler included in a sealing material has been investigated. For example, use of an epoxy group-containing silane coupling agent or an amino group-containing silane coupling agent (see, for example, Patent Document 1) and use of a sulfur atom-containing silane coupling agent (see for example, Patent Document 2) have been investigated.

[Prior Art Documents]

[Patent Documents]

[0005] [Patent Document 1] Japanese Patent Application Laid-Open No. H11-147939

[Patent Document 2] Japanese Patent Application Laid-Open No. 2000-103940

[Summary of the Invention]

[Problem to be Solved by the Invention]

[0006] In the method of using an epoxy group-containing silane coupling agent or an amino group-

containing silane coupling agent, the effect of improving the adhesion of the sealing material with respect to a metal included in the surface of a lead frame may not be sufficient. In the method of using a sulfur atom-containing silane coupling agent, the effect of improving the adhesion of the sealing material with respect to metal of a specific kind, such as gold or silver, may not be sufficient.

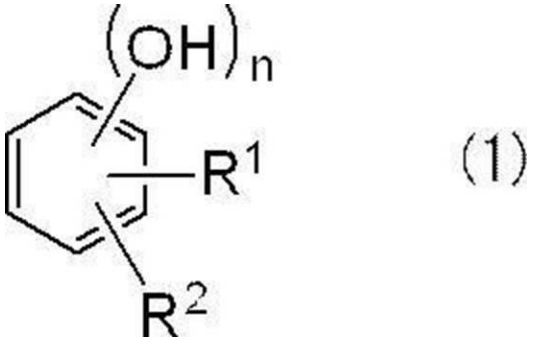
[0007] In view of the foregoing, the present invention aims to provide a curable resin composition that forms a sealed structure that exhibits excellent adhesion with respect to metal; and an electronic component device obtained by using the curable resin composition.

[Means for Solving the Problem]

[0008] The means for solving the problems include the following embodiments.

<1> A curable resin composition, comprising an epoxy resin and a curing agent, the curing agent comprising a phenol novolac resin having a structural unit derived from a phenol compound represented by the following Formula (1):

[0009]

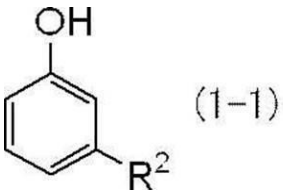


(1)

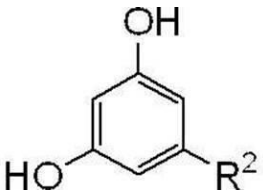
wherein, in Formula (1), R^1 represents a hydrogen atom or a methyl group, R^2 represents an aliphatic hydrocarbon group having 10 to 18 carbon atoms, and n represents an integer 1 or 2.

<2> The curable resin composition according to <1>, wherein the phenol novolac resin comprises, as the structural unit derived from the phenol compound represented by Formula (1), a structural unit derived from a phenol compound represented by at least one of the following Formula (1-1) to Formula (1-3):

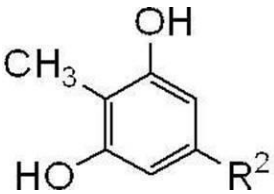
[0010]



(1-1)



(1-2)



(1-3)

wherein, in Formulae (1-1) to (1-3), R^2 is the same as R^2 in Formula (1).

<3> The curable resin composition according to <1> or <2>, wherein the phenol novolac

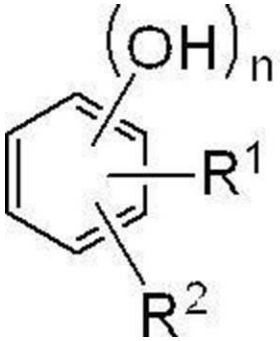
resin further comprises a structural unit derived from a phenol compound other than the phenol compound represented by Formula (1).

<4> The curable resin composition according to any one of <1> to <3>, wherein the curing agent further comprises a curing agent other than the phenol novolac resin having a structural unit derived from a phenol compound represented by Formula (1).

<5> The curable resin composition according to any one of <1> to <4>, which is used as a sealing material for an electronic component device.

<6> An electronic component device, comprising an element and a cured product of the curable resin composition according to any one of <1> to <5>.

Disclosed herein is a curable resin composition, which is in a solid state at 25°C in an atmospheric pressure and used as a sealing material for an electronic component device, comprising an epoxy resin and a curing agent, the curing agent comprising a phenol novolac resin having a structural unit derived from a phenol compound represented by the following Formula (1), the phenol novolac resin having a hydroxy equivalent of from 70 g/eq to 223 g/eq:



(1)

wherein, in Formula (1), R^1 represents a hydrogen atom or a methyl group, R^2 represents an aliphatic hydrocarbon group having 10 to 18 carbon atoms, and n represents an integer 1 or 2.

[Effect of the Invention]

[0011] According to the present invention, it is possible to provide a curable resin composition that forms a sealed structure that exhibits excellent adhesion with respect to metal; and an electronic component device obtained by using the curable resin composition.

[Embodiments for Implementing the Invention]

[0012] Embodiments for implementing the invention will now be described in detail. However, the invention is in no way limited to the following embodiments. In the following embodiments, constituent elements (including element steps and the like) of the embodiments are not essential, unless otherwise specified. Likewise, numerical values and ranges thereof are not intended to restrict the invention.

[0013] In the present disclosure, the definition of the term “step” includes not only an independent

step which is distinguishable from another step, but also a step which is not clearly distinguishable from another step, as long as the purpose of the step is achieved.

In the present disclosure, any numerical range described using the expression “to” represents a range in which numerical values described before and after the “to” are included in the range as a minimum value and a maximum value, respectively.

In a numerical range described in stages, in the present disclosure, an upper limit value or a lower limit value described in one numerical range may be replaced with an upper limit value or a lower limit value in another numerical range described in stages. Further, in a numerical range described in the present disclosure, the upper limit value or the lower limit value in the numerical range may be replaced with a value shown in the Examples.

In the present disclosure, each component may include plural kinds of substances corresponding to the component. In a case in which plural kinds of substances corresponding to each component are present in a composition, the content ratio or content of each component refers to the total content ratio or content of the plural kinds of substances present in the composition, unless otherwise specified.

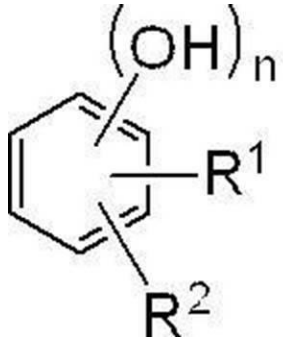
In the present disclosure, particles corresponding to each component may include plural kinds of particles. In a case in which plural kinds of particles corresponding to each component are present in a composition, the particle size of each component refers to the value of the particle size of a mixture of the plural kinds of particles present in the composition, unless otherwise specified.

The reference in this specification to any prior publication (or information derived from it), or to any matter which is known, is not, and should not be taken as an acknowledgment or admission or any form of suggestion that that prior publication (or information derived from it) or known matter forms part of the common general knowledge in the field of endeavour to which this specification relates.

[0014] <Curable resin composition>

The curable resin composition according to the disclosure includes an epoxy resin and a curing agent, and the curing agent includes a phenol novolac resin having a structural unit derived from a phenol compound represented by the following Formula (1):

[0015]



(1)

[0016] In Formula (1), R^1 represents a hydrogen atom or a methyl group, R^2 represents an aliphatic hydrocarbon group having 10 to 18 carbon atoms, and n represents an integer 1 or 2. Hereinafter, the phenol novolac resin as described above is also referred to as a specific phenol novolac resin.

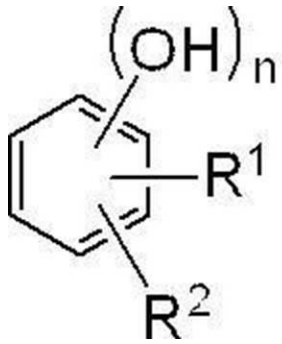
[0017] The curable resin composition including a specific phenol novolac resin exhibits excellent adhesion with respect to metal (especially gold) in a cured state. Although the reason for this is not exactly clear, it is thought to be that the aliphatic hydrocarbon group having 10 to 18 carbon atoms of the structural unit derived from a phenol compound included in the specific phenol novolac resin functions to improve the adhesion with respect to metal. Further, it is thought to be that the aliphatic hydrocarbon group having 10 to 18 carbon atoms of the structural unit derived from a phenol compound included in the specific phenol novolac resin functions to cause reduction in elasticity or reduction in water absorption of a cured product of the curable resin composition in the vicinity of an interface with respect to a metallic surface, thereby improving the reflow resistance.

[0018] The curable resin composition including a specific phenol novolac resin exhibits excellent adhesion with respect to metal in a cured state. Therefore, the curable resin composition is suitably used as a sealing material for a package including a lead frame including metal (especially gold) at least at a surface thereof. Examples of the lead frame including gold at least at a surface thereof include a lead frame referred to as PPF (Pre Plating Lead Frame), which is a copper lead frame with Ni-Pd-Au plating.

[0019] (Specific phenol novolac resin)

The specific phenol novolac resin is a phenol novolac resin having a structural unit derived from a phenol compound represented by the following Formula (1):

[0020]



(1)

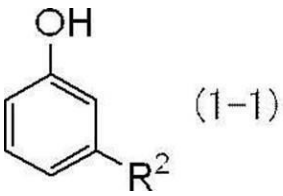
[0021] wherein, in Formula (1), R^1 represents a hydrogen atom or a methyl group, R^2 represents an aliphatic hydrocarbon group having 10 to 18 carbon atoms, and n represents an integer 1 or 2.

[0022] The specific phenol novolac resin may include a single kind of structural units derived from a phenol compound represented by Formula (1) or may include different kinds of structural units derived from a phenol compound represented by Formula (1). When the specific phenol novolac resin includes two or more kinds of structural units derived from a phenol compound represented by Formula (1), the structural units may be arranged in a regular manner or an irregular manner without particular limitation.

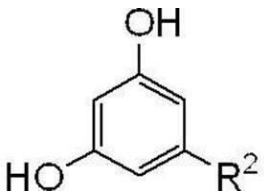
[0023] In an embodiment, the specific phenol novolac resin may include a structural unit derived from a phenol compound represented by Formula (1) in which n is 1 (i.e., monovalent phenol) and a structural unit derived from a phenol compound represented by Formula (1) in which n is 2 (i.e., divalent phenol). In an embodiment, the specific phenol novolac resin may include a structural unit derived from a phenol compound represented by Formula (1) in which n is 1 (i.e., monovalent phenol) and a structural unit derived from a phenol compound represented by Formula (1) in which n is 2 and one of the hydroxy groups is at a meta position with respect to the other hydroxy group.

[0024] The specific phenol novolac resin may include at least one of the structural units derived from the phenol compounds represented by the following Formulae (1-1) to (1-3). The specific phenol novolac resin may include each of the structural units derived from the phenol compounds represented by the following Formulae (1-1) to (1-3), respectively.

[0025]



(1-1)



(1-2)



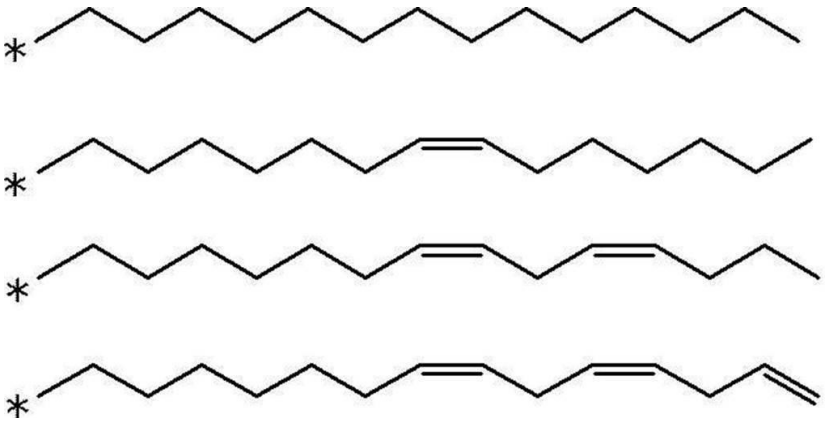
(1-3)

[0026] In Formulae (1-1) to (1-3), R^2 is the same as R^2 in Formula (1).

[0027] In Formula (1), the aliphatic hydrocarbon group having 10 to 18 carbon atoms represented by R^2 may be an aliphatic hydrocarbon group having 13 to 16 carbon atoms, and may be with or

without an unsaturated double bond. When the aliphatic hydrocarbon group having 10 to 18 carbon atoms represented by R^2 includes an unsaturated double bond, the number thereof is not particularly limited and may be selected from 1 to 5, for example. The aliphatic hydrocarbon group having 10 to 18 carbon atoms represented by R^2 may be branched or not branched, preferably not branched. Specific examples of the aliphatic hydrocarbon group having 10 to 18 carbon atoms represented by R^2 include the aliphatic hydrocarbon groups in the following Group (A), in which * represents a bonding site to an aromatic ring. The structure of the aliphatic hydrocarbon group having 10 to 18 carbon atoms represented by R^2 in the specific phenol novolac resin may be the same or different from each other.

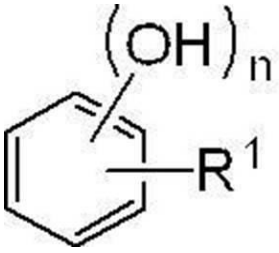
[0028]



(A)

[0029] The specific phenol novolac resin may include a structural unit derived from a phenol compound other than the phenol compound represented by Formula (1). Examples of the phenol compound other than the phenol compound represented by Formula (1) include a phenol compound represented by the following Formula (2).

[0030]



(2)

[0031] In Formula (2), R^1 represents a hydrogen atom or a methyl group, and n represents an integer 1 or 2. Examples of the phenol compound represented by Formula (2) includes monovalent phenol compounds such as phenol and cresol, and divalent phenol compounds such as resorcin, catechol and hydroquinone.

[0032] In an embodiment, the specific phenol novolac resin may include a structural unit derived from either one or both of phenol and cresol, as the structural unit derived from a phenol

compound represented by Formula (2). In an embodiment, the specific phenol novolac resin may include a structural unit derived from either one or both of phenol and ortho cresol, as the structural unit derived from a phenol compound represented by Formula (2).

[0033] When the specific phenol novolac resin includes a structural unit derived from a phenol compound other than the phenol compound represented by Formula (1), the proportion of the structural unit derived from a phenol compound represented by Formula (1) in the total specific phenol novolac resin is preferably 50% by mass or more, more preferably 60% by mass or more, further preferably 70% by mass or more.

[0034] The method for synthesizing the specific phenol novolac resin is not particularly limited. For example, the specific phenol novolac resin may be synthesized by allowing a phenol compound as a raw material for the specific phenol novolac resin to react with an aldehyde such as formaldehyde in the presence of an acidic catalyst.

[0035] The molecular weight of the specific phenol novolac resin is not particularly limited. For example, the specific phenol novolac resin may have a weight average molecular weight as measured by gel permeation chromatography of from 300 to 20,000.

[0036] The viscosity of the specific phenol novolac resin is not particularly limited. For example, the specific phenol novolac resin preferably has a viscosity at 25°C of 50 Pa·s or less, more preferably 30 Pa·s or less. The viscosity at 25°C of the specific phenol novolac resin is obtained by multiplying a measured value of the viscosity with a specific conversion factor (0.5). The measured value of the viscosity is obtained with an EHD rotation viscometer attached with a cone rotor at a cone angle of 3° and a cone diameter of 14 mm, rotating the same at a rate of 10 rotations per minute (10 rpm) for 1 minute at 25°C.

[0037] The hydroxy equivalent of the specific phenol novolac resin is not particularly limited. From the viewpoint of a balance of the properties such as moldability, reflow resistance and electrical reliability, the specific phenol novolac resin preferably has a hydroxy equivalent of from 70 g/eq to 1,000 g/eq, more preferably from 80 g/eq to 500 g/eq.

[0038] The specific phenol novolac resin is preferably used in combination with a curing agent other than the specific phenol novolac resin. Specifically, the curable resin composition preferably includes a specific phenol novolac resin and a curing agent other than the specific phenol novolac resin as the curing agent.

[0039] When the curable resin composition includes a specific phenol novolac resin and a curing agent other than the specific phenol novolac resin as the curing agent, the proportion based on the equivalent amount of the specific phenol novolac resin with respect to the total curing agent is preferably 50% or less, more preferably 30% or less, further preferably 20% or less, from the

viewpoint of curability. The proportion based on the equivalent amount of the specific phenol novolac resin with respect to the total curing agent is preferably 1% or more, more preferably 3% or more, further preferably 5% or more, from the viewpoint of improving the adhesion with respect to metal.

[0040] The curing agent other than the specific phenol novolac resin is not particularly limited, and may be selected according to the desired properties of the curable resin composition or the like. Specific examples of the curing agent are described later.

[0041] (Epoxy resin)

The type of the epoxy resin included in the curable resin composition is not particularly limited, and may be selected according to the desired properties of the curable resin composition and the like.

Specific examples of the epoxy resin include novolac epoxy resin (such as a phenol novolac epoxy resin or an ortho-cresol novolac epoxy resin) which is obtained by epoxidizing a novolac resin obtained by condensation or co-condensation of at least one phenolic compound selected from the group consisting of phenol compounds such as phenol, cresol, xylenol, resorcinol, catechol, bisphenol A and bisphenol F, and naphthol compounds such as α-naphthol, β-naphthol and dihydroxynaphthalene, with an aliphatic aldehyde compound such as formaldehyde, acetaldehyde or propionaldehyde, in the presence of an acidic catalyst; triphenylmethane epoxy resin which is obtained by epoxidizing a triphenylmethane phenol resin obtained by condensation or co-condensation of the above-described phenolic compound with an aromatic aldehyde compound such as benzaldehyde or salicylaldehyde in the presence of an acidic catalyst; copolymerized epoxy resins which is obtained by epoxidizing a novolac resin obtained by co-condensation of any of the above-described phenol compound and the naphthol compound with an aldehyde compound in the presence of an acidic catalyst; diphenylmethane epoxy resin which is a diglycidyl ether of bisphenol A, bisphenol F or the like; biphenyl epoxy resin which is a diglycidyl ether of an alkyl-substituted or unsubstituted biphenol; stilbene epoxy resin which is a diglycidyl ether of a stilbene phenol compound; sulfur atom-containing epoxy resin which is a diglycidyl ether of bisphenol S or the like; epoxy resin which is a glycidyl ether of an alcohol such as butanediol, polyethylene glycol or polypropylene glycol; glycidyl ester epoxy resin which is a glycidyl ester of a polyvalent carboxylic acid compound such as phthalic acid, isophthalic acid or tetrahydrophthalic acid; glycidyl amine epoxy resin which is obtained by substituting an active hydrogen bound to a nitrogen atom of aniline, diaminodiphenylmethane, isocyanuric acid or the like, with a glycidyl group; dicyclopentadiene epoxy resin which is obtained by epoxidizing a co-condensed resin of dicyclopentadiene with a phenol compound; alicyclic epoxy resin which is

obtained by epoxidizing an olefin bond in the molecule, such as vinylcyclohexene diepoxide, 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate or 2-(3,4-epoxy)cyclohexyl-5,5-spiro(3,4-epoxy)cyclohexane-m-dioxane; paraxylylene-modified epoxy resin which is a glycidyl ether of a paraxylylene-modified phenol resin; metaxylylene-modified epoxy resin which is a glycidyl ether of a metaxylylene-modified phenol resin; terpene-modified epoxy resin which is a glycidyl ether of a terpene-modified phenol resin; dicyclopentadiene-modified epoxy resin which is a glycidyl ether of a dicyclopentadiene-modified phenol resin; cyclopentadiene-modified epoxy resin which is a glycidyl ether of a cyclopentadiene-modified phenol resin; polycyclic aromatic ring-modified epoxy resin which is a glycidyl ether of a polycyclic aromatic ring-modified phenol resin; naphthalene epoxy resin which is a glycidyl ether of a naphthalene ring-containing phenol resin; halogenated phenol novolac epoxy resin; hydroquinone epoxy resin; trimethylolpropane epoxy resin; linear aliphatic epoxy resin which is obtained by oxidizing an olefin bond with a peracid such as peracetic acid; and aralkyl epoxy resin which is obtained by epoxidizing an aralkyl phenol resin such as a phenol aralkyl resin or a naphthol aralkyl resin. Epoxidized silicone resin, and epoxidized acrylic resin and the like are also included in the epoxy resin. The epoxy resin may be used singly, or in combination of two or more kinds thereof.

[0042] From the viewpoint of a balance between the reflow resistance and the fluidity, the epoxy resin is preferably an epoxy resin selected from a biphenyl epoxy resin, a stilbene epoxy resin, a diphenylmethane epoxy resin, a sulfur-atom containing epoxy resin, a novolac epoxy resin, a dicyclopentadiene epoxy resin, a triphenylmethane epoxy resin, a copolymeized epoxy resin and an aralkyl epoxy resin (hereinafter, these epoxy resins are referred to as a specific epoxy resin). The specific epoxy resin may be used singly or in combination of two or more kinds thereof.

[0043] When the epoxy resin includes a specific epoxy resin, the amount thereof is preferably 30% by mass or more, more preferably 50% by mass or more, of the total epoxy resin from the viewpoint of exhibiting the effect of the specific epoxy resin.

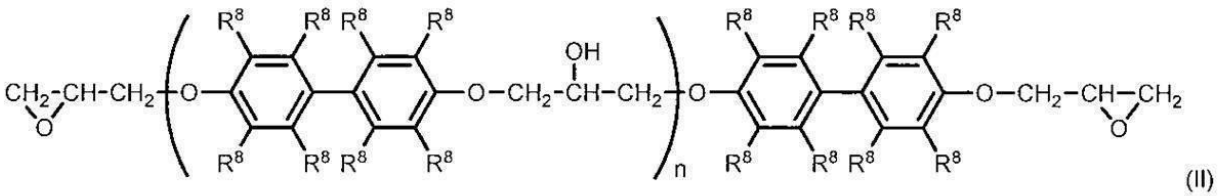
[0044] From the viewpoint of fluidity, the specific epoxy resin is preferably a biphenyl epoxy resin, a stilbene epoxy resin, a diphenylmethane epoxy resin or a sulfur atom-containing epoxy resin. From the viewpoint of heat resistance, the specific epoxy resin is preferably a dicyclopentadiene epoxy resin, a triphenylmethane epoxy resin or an aralkyl epoxy resin. In the following, specific examples of the preferred epoxy resins are described.

[0045] The biphenyl epoxy resin is not particularly limited, as long as it is an epoxy resin having a biphenyl structure. For example, an epoxy resin represented by the following Formula (II) is preferred.

Among the epoxy resin represented by the following Formula (II), an epoxy resin in which

each of R^8 at 3, 3', 5 and 5' positions, when an oxygen atom is substituted at 4 and 4' positions, is a methyl group and the rest of R^8 are a hydrogen atom (YX-4000H, trade name, Mitsubishi Chemical Corporation); an epoxy resin in which all of R^8 are a hydrogen atom (i.e., 4,4'-bis(2,3-epoxypropoxy)biphenyl); and a mixture of an epoxy resin in which all of R^8 are a hydrogen atom and an epoxy resin in which each of R^8 at 3, 3', 5 and 5' positions, when an oxygen is substituted at 4 and 4' positions, is a methyl group and the rest of R^8 are a hydrogen atom (YL-6121H, trade name, Mitsubishi Chemical Corporation); and the like are available as a commercial product.

[0046]



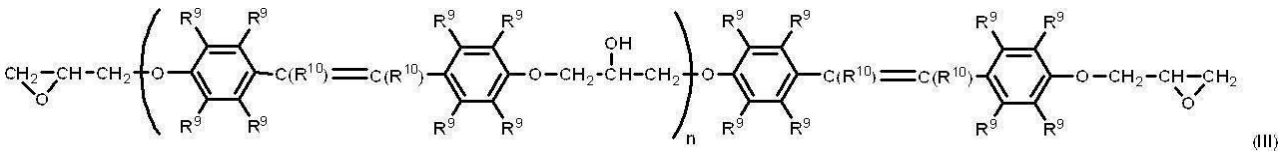
(II)

[0047] In Formula (II), each of R^8 represents a hydrogen atom, an alkyl group having 1 to 12 carbon atoms, or an aromatic group having 4 to 18 carbon atoms, which may be the same or different from each other; and n is an average value within a range of from 0 to 10.

[0048] The stilbene epoxy resin is not particularly limited, as long as it has a stilbene structure. For example, an epoxy resin represented by the following Formula (III) is preferred.

Among the epoxy resin represented by the following Formula (III), a mixture of an epoxy resin in which each of R^9 at 3, 3', 5 and 5' positions, when an oxygen atom is substituted at 4 and 4' positions, is a methyl group, the rest of R^9 are a hydrogen atom, and all of R^{10} are a hydrogen atom, and an epoxy resin in which three of R^9 at 3, 3', 5 and 5' positions, when an oxygen atom is substituted at 4 and 4' positions, is a methyl group and one of R^9 at 3, 3', 5 and 5' positions, when an oxygen is substituted at 4 and 4' positions, is a t-butyl group, the rest of R^9 are a hydrogen atom, and all of R^{10} are a hydrogen atom (ESLV-210, trade name, Sumitomo Chemical Co., Ltd.) and the like are available as a commercial product.

[0049]



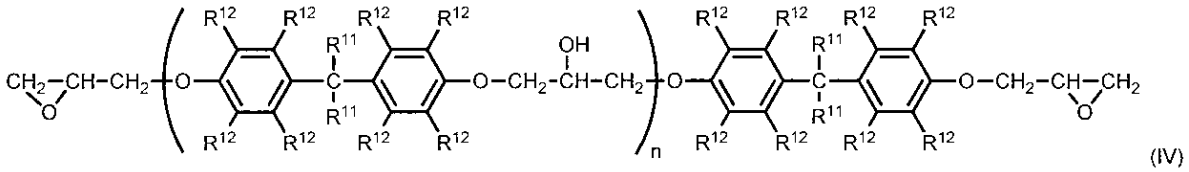
(III)

[0050] In Formula (III), each of R^9 and R^{10} represents a hydrogen atom or an organic group having 1 to 18 carbon atoms, which may be the same or different from each other; and n is an average value within a range of from 0 to 10.

[0051] The diphenylmethane epoxy resin is not particularly limited, as long as it has a diphenylmethane structure. For example, an epoxy resin represented by the following Formula (IV) is preferred.

Among the epoxy resin represented by the following Formula (IV), an epoxy resin in which all of R^{11} are a hydrogen atom and each of R^{12} at 3, 3', 5 and 5' positions, when an oxygen is substituted at 4 and 4' positions, is a methyl group, and the rest of R^{12} are a hydrogen atom (YSLV-80XY, trade name, Nippon Steel Chemical & Material Co., Ltd.) and the like are available as a commercial product.

[0052]



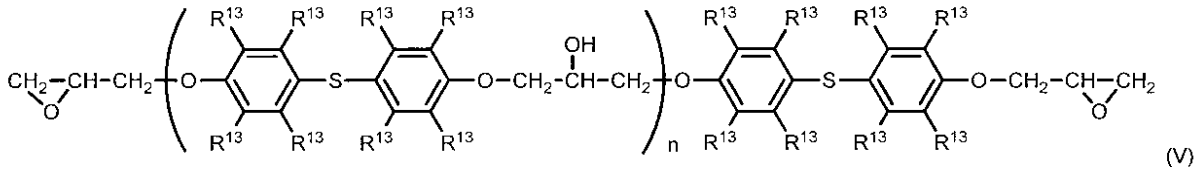
(IV)

[0053] In Formula (IV), each of R^{11} and R^{12} represents a hydrogen atom or an organic group having 1 to 18 carbon atoms, which may be the same or different from each other; and n is an average value within a range of from 0 to 10.

[0054] The sulfur atom-containing epoxy resin is not particularly limited, as long as it includes a sulfur atom. For example, an epoxy resin represented by the following Formula (V) is preferred.

Among the epoxy resin represented by the following Formula (V), an epoxy resin in which each of R^{13} at 3 and 3' positions, when an oxygen atom is substituted at 4 and 4' positions, is a t-butyl group, each of R^{13} at 6 and 6' positions, when an oxygen atom is substituted at 4 and 4' positions, is a methyl group, and the rest of R^{13} are a hydrogen atom (YSLV-120TE, trade name, Nippon Steel Chemical & Material Co., Ltd.) and the like are available as a commercial product.

[0055]



(V)

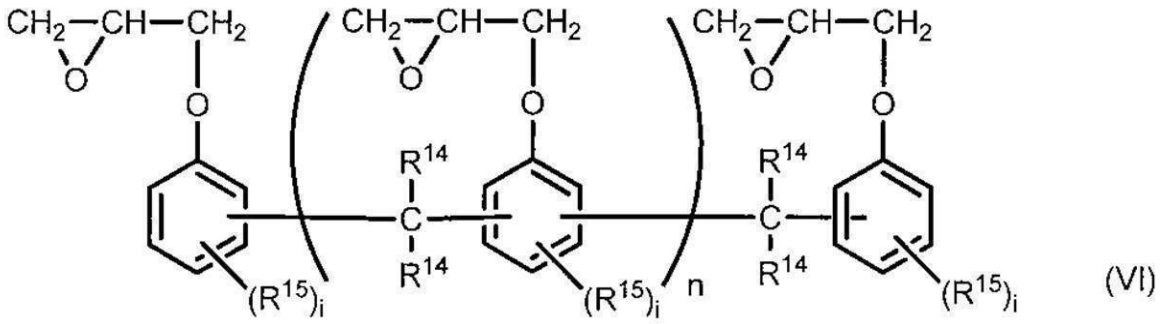
[0056] In Formula (V), each of R^{13} represents a hydrogen atom or an organic group having 1 to 18 carbon atoms, which may be the same or different from each other; and n is an average value within a range of from 0 to 10.

[0057] The novolac epoxy resin is not particularly limited, as long as it is obtained by epoxidizing a novolac phenol resin. For example, an epoxy resin obtained by epoxidizing a novolac phenol

resin, such as a phenol novolac resin, a cresol novolac resin or a naphthol novolac resin, by glycidyletherification or the like is preferred, and an epoxy resin represented by the following Formula (VI) is more preferred.

Among the epoxy resin represented by the following Formula (VI), an epoxy resin in which each of R^{14} is a hydrogen atom, each of R^{15} is a methyl group and i is 1 (ESCN-190 and ESCN-195, trade names, Sumitomo Chemical Co., Ltd.); an epoxy resin in which each of R^{14} is a hydrogen atom and i is 0 (N-770 and N-775, trade names, DIC Corporation); a styrene-modified phenol novolac epoxy resin in which each of R^{14} is a hydrogen atom, part of i is 0, and part of i is 1 with R^{15} being -CH(CH_3)-Ph (YDAN-1000-10C, trade name, Nippon Steel Chemical & Material Co., Ltd.); and a benzyl-modified cresol novolac epoxy resin, in which each of R^{14} is a hydrogen atom, part of i is with R^{15} being a methyl group, and part of i is 2 with either one of R^{15} being a methyl group and the other being a benzyl group (HP-5600, trade name, DIC Corporation) and the like are available as a commercial product.

[0058]



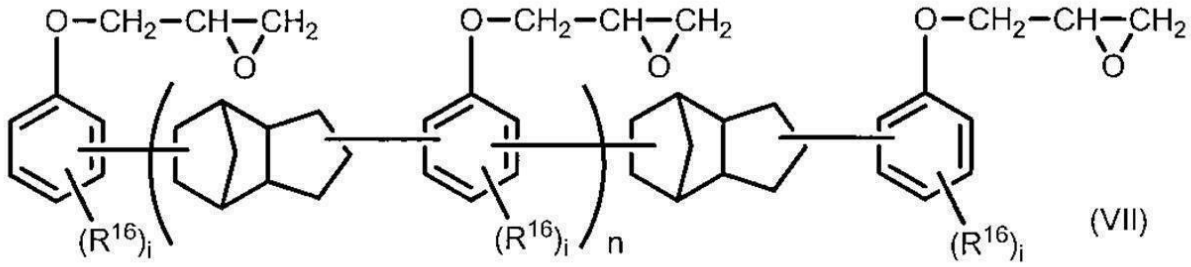
(VI)

[0059] In Formula (VI), each of R^{14} represents a hydrogen atom or a monovalent organic group having 1 to 18 carbon atoms, which may be the same or different from each other; each of R^{15} represents an organic group having 1 to 18 carbon atoms, which may be the same or different from each other; each of i independently represents an integer from 0 to 3; and n is an average value within a range of from 0 to 10.

[0060] The dicyclopentadiene epoxy resin is not particularly limited, as long as it is obtained by epoxidizing a compound having a dicyclopentadiene structure. For example, an epoxy resin represented by the following Formula (VII) is preferred.

Among the epoxy resin represented by Formula (VII), an epoxy resin in which i is 0 (HP-7200, trade name, DIC Corporation) and the like is available as a commercial product.

[0061]



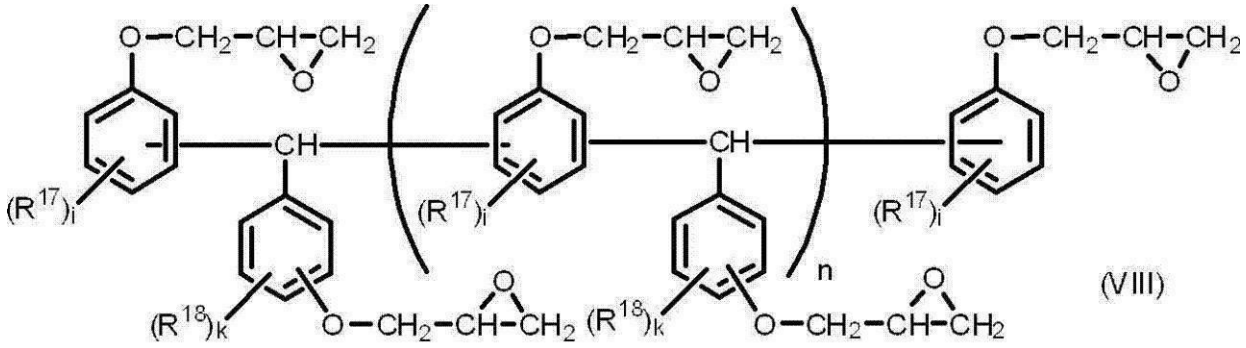
(VII)

[0062] In Formula (VII), each of R^{16} represents an organic group having 1 to 18 carbon atoms, which may be the same or different from each other; each of i independently represents an integer from 0 to 3; and n is an average value within a range of from 0 to 10.

[0063] The triphenylmethane epoxy resin is not particularly limited, as long as it is an epoxy resin obtained from a compound having a triphenylmethane structure. For example, an epoxy resin obtained by glycidylesterification of a triphenylmethane phenol resin, such as a novolac phenol resin obtained from a compound having a triphenylmethane compound and a compound having a phenollic hydroxy group, is preferred, and an epoxy resin represented by the following Formula (VIII) is more preferred.

Among the epoxy resin represented by the following Formula (VIII), an epoxy resin in which i is 0 and k is 0 (1032H60, trade name, Mitsubishi Chemical Corporation and EPPN-502H, trade name, Nippon Kayaku Corporation) and the like are available as a commercial product.

[0064]



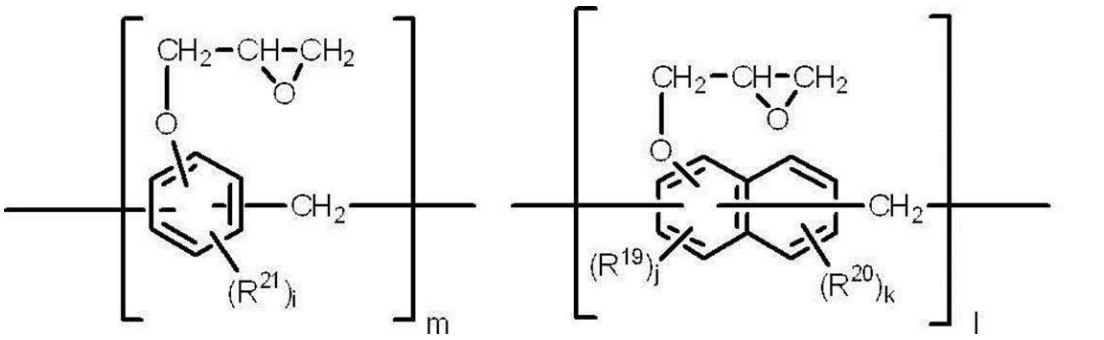
(VIII)

[0065] In Formula (VIII), each of R^{17} and R^{18} represents a monovalent organic group having 1 to 18 carbon atoms, which may be the same or different from each other; each of i independently represents an integer form 0 to 3; each of k independently represents an integer from 0 to 4; and n is an average value within a range of from 0 to 10.

[0066] The copolymerized epoxy resin, which is obtained by epoxydizing a novolac resin obtained from a naphthol compound and a phenol compound with an aldehyde compound, is not particularly limited as long as it is an epoxy resin obtained from a compound having a naphthol

structure and a phenol structure. For example, an epoxy resin obtained by glycidyletherification of a novolac phenol resin using a compound having a naphthol structure and a compound having a phenol structure is preferred, and an epoxy resin represented by the following Formula (IX) is more preferred. Among the epoxy resin represented by the following Formula (IX), an epoxy resin in which R^{21} is a methyl group, i is 1, j is 0 and k is 0 (NC-7300, trade name, Nippon Kayaku Corporation) and the like is available as a commercial product.

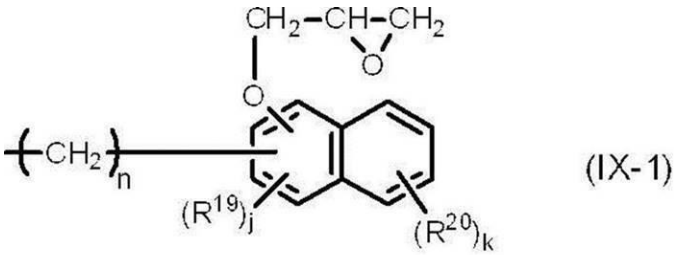
[0067]



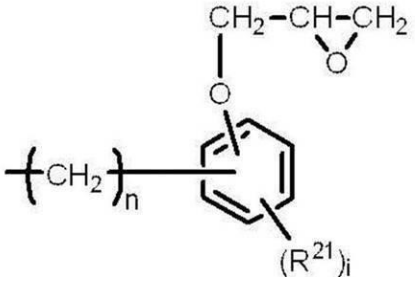
(IX)

[0068] In Formula (IX), each of R^{19} to R^{21} represents a monovalent organic group having 1 to 18 carbon atoms, which may be the same or different from each other; each of i independently represents an integer from 0 to 3, each of j independently represents an integer from 0 to 2, and each of k independently represents an integer form 0 to 4. Each of l and m is an average value within a range of from 0 to 10, and (l+m) is a number from 0 to 10. The terminal of the epoxy resin represented by Formula (IX) has a structure represented by the following Formula (IX-1) or Formula (IX-2). In Formulae (IX-1) and (IX-2), the definitions of R^{19} to R^{21}, i, j and k are the same as the definitions of R^{19} to R^{21}, i, j and k in Formula (IX), and n is either 1 (the structure is bonded with a methylene group) or 0 (the structure is bonded without a methylene group).

[0069]



(IX-1)

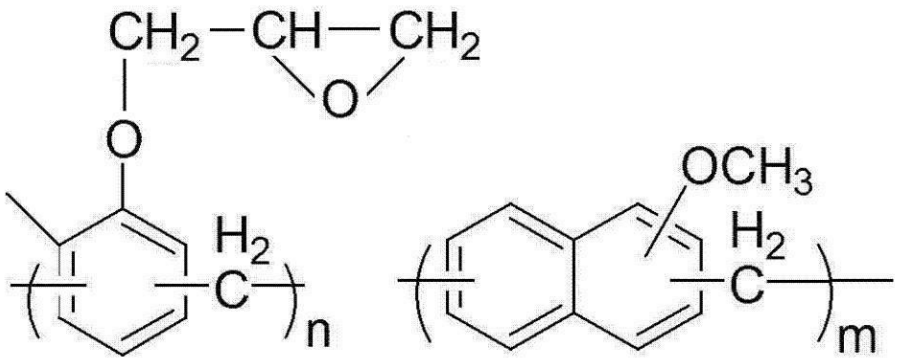


(IX-2)

[0070] Examples of the epoxy resin represented by Formula (IX) include a random copolymer including the structural unit by the number of l and the structural unit by the number of m in a random manner, an alternate copolymer including these structural units in an alternating manner, a copolymer including these structural units in a regular manner, and a block copolymer including these structural units in a manner of blocks. The copolymer may be used singly or two or more types may be used in combination.

[0071] Another preferred example of the copolymerized epoxy resin is a methoxynaphthalene-cresol formaldehyde co-condensed epoxy resin, having the structural units as described below in a manner of random, alternate or blocks (EPICLON HP-5000, DIC Corporation). In the following formula, each of n and m is an average value in a range of from 0 to 10, and (n+m) is a number from 0 to 10; preferably, each of n and m is an average value in a range of from 1 to 9, and (n+m) is a number from 2 to 10.

[0072]



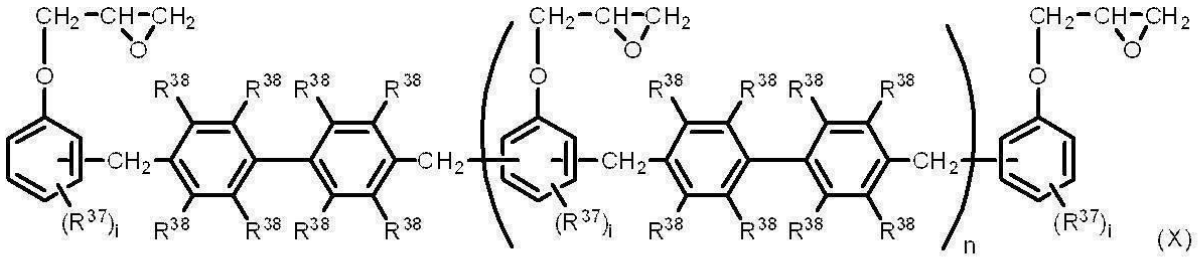
[0073] The aralkyl epoxy resin is not particularly limited, as long as it is an epoxy resin obtained from at least one selected from the group consisting of a phenol compound such as phenol or cresol and a naphthol compound such as naphthol or dimethylnaphthol, and a phenol resin synthesized from dimethoxyparaxylene, bis(methoxymethyl)biphenyl or a derivative thereof. For example, an epoxy resin obtained by glycidylertherification of a phenol resin synthesized from at least one selected from the group consisting of a phenol compound such as phenol or cresol and a naphthol compound such as naphthol or dimethylnaphthol, and dimethoxyparaxylene, bis(methoxymethyl)biphenyl or a derivative thereof is preferred, and an epoxy resin represented by the following Formula (X) or Formula (XI) is more preferred.

[0074] Among the epoxy resin represented by the following Formula (X), an epoxy resin in which i is 0 and R^{38} is a hydrogen atom (NC-3000S, trade name, Nippon Kayaku Corporation) and a mixture of an epoxy resin in which i is 0 and R^{38} is a hydrogen atom and an epoxy resin represented by Formula (II) in which each of R^{8} is a hydrogen atom, mixed at a mass ratio of 80:20

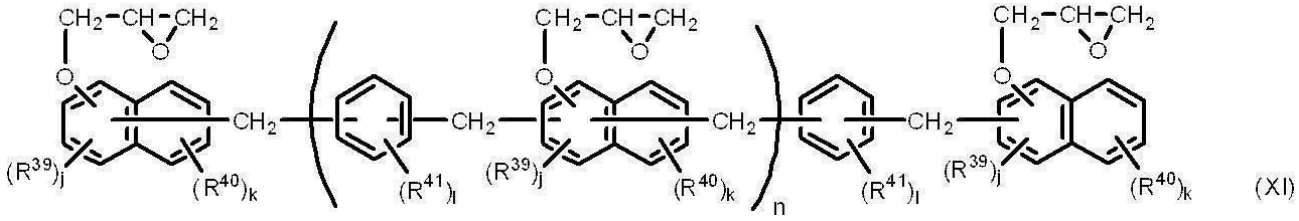
(CER-3000, trade name, Nippon Kayaku Corporation) and the like are available as a commercial product.

Among the epoxy resin represented by the following Formula (XI), an epoxy resin in which i, j and k are 0, respectively (ESN-175, trade name, Nippon Steel Chemical Co., Ltd.) and the like is available as a commercial product.

[0075]



(X)



(XI)

[0076] In Formula (X) and Formula (XI), each of R^{38} represents a hydrogen atom or a monovalent organic group having 1 to 18 carbon atoms, which may be the same or different from each other; each of R^{37}, R^{39}, R^{40} and R^{41} represents a hydrogen atom or a monovalent organic group having 1 to 18 carbon atoms, which may be the same or different from each other; each of i independently represents an integer from 0 to 3; each of j independently represents an integer from 0 to 2; each of k independently represents an integer from 0 to 4; each of l independently represents an integer from 0 to 6; and n is an average value within a range of from 0 to 10.

[0077] In the Formulae (II) to (XI), the expression "may be the same or different from each other" regarding R^8 to R^{21} and R^{37} to R^{41} refers to, for example, that R^8 in Formula (II) by the number of 8 to 88 may be the same or different from each other, and the same applies to R^9 to R^{21} and R^{37} to R^{41}. Further, each of R^8 to R^{21} and R^{37} to R^{41} may be the same or different from each other. For example, all of R^9 and all of R^{10} may be the same or different from each other.

The organic group having 1 to 18 carbon atoms in Formulae (III) to (XI) is preferably an alkyl group or an aryl group.

[0078] The n in Formulae (II) to (XI) is an average value and is preferably independently within a range of from 0 to 10. When n is not more than 10, the melt viscosity of the resin component is not too high and the viscosity of the curable resin composition during the molding is kept low,

thereby suppressing the occurrence of injection defects, deformation of bonding wires (metallic lines connecting an element to a lead) and the like. The range of n in one molecule is preferably within a range of from 0 to 4.

[0079] The functional group equivalent of the curable resin (epoxy equivalent in case of epoxy resin) is not particularly limited. From the viewpoint of a valance of the properties such as moldability, reflow resistance and electrical reliability, the functional group equivalent of the curable resin is preferably from 100 g/eq to 1000 g/eq, more preferably from 150 g/eq to 500 g/eq.

[0080] The softening point or the melting point of the curable resin is not particularly limited. From the viewpoint of moldability and reflow resistance, the softening point or the melting point of the curable resin is preferably from 40°C to 180°C. From the viewpoint of handleability during the preparation of the curable resin composition, the softening point or the melting point of the curable resin is preferably from 50°C to 130°C.

[0081] The content of the curable resin in the curable resin composition is preferably from 0.5% by mass to 50% by mass, more preferably from 2% by mass to 30% by mass, from the viewpoint of strength, fluidity, heat resistance and moldability.

[0082] (Curing agent other than specific phenol novolac resin)

The type of the curing agent other than the phenol novolac resin included in the curable resin composition is not particularly limited, and may be selected depending on the type of the epoxy resin to be used in combination, desired properties of the curable resin composition, and the like.

Examples of the curing agent include a phenol curing agent, an amine curing agent, an acid anhydride curing agent, a polymercaptan curing agent, a polyaminoamide curing agent, an isocyanate curing agent, and a block isocyanate curing agent. From the viewpoint of achieving both of the curability and pot life, at least one selected from the group consisting of a phenol curing agent, an amine curing agent and an acid anhydride curing agent is preferred. From the viewpoint of electrical reliability, a phenol curing agent is more preferred.

[0083] Examples of the phenol curing agent include a phenol resin or a polyvalent phenol compound, having two or more phenolic hydroxy groups in one molecule.

Specific examples of the phenol curing agent include a polyvalent phenol compound, such as resorcin, catechol, bisphenol A, bisphenol F and a substituted or unsubstituted biphenol; a novolac phenol resin obtained by condensation or co-condensation of at least one phenollic compound selected from the group consisting of a phenol compound such as phenol, cresol, xylenol, resorcin, catechol, bisphenol A, bisphenol F, phenylphenol, and aminophenol, and a naphthol compound such as α-naphthol, β-naphthol and dihydroxynaphthalene, and an aldehyde

compound such as formaldehyde, benzaldehyde or salicylaldehyde, in the presence of an acidic catalyst; an aralkyl phenol resin such as a phenol aralkyl resin and a naphthol aralkyl resin, synthesized from the phenollic compound as described above and dimethoxy-p-xylene or bis(methoxymethyl)biphenyl; a phenol resin modified with p-xylylene and/or m-xylylene; a melamine-modified phenol resin; a terpene-modified phenol resin; a dicyclopentadiene-modified phenol resin and a dicyclopentadiene-modified naphthol resin, which is a copolymer synthesized from the phenollic compound as described above and dicyclopentadiene; a cyclopentadiene-modified phenol resin; a polycyclic aromatic ring-modified phenol resin; a biphenyl phenol resin; a triphenylmethane phenol resin, which is obtained by condensation or co-condensation of the phenollic compound as described above with an aromatic aldehyde compound such as benzaldehyde or salicylaldehyde; and a phenol resin obtained by copolymerizing two or more of the phenol resins as described above. The phenol curing agent may be used singly or in combination of two or more kinds.

[0084] From the viewpoint of reflow resistance, the phenol curing agent is preferably at least one selected from the group consisting of an aralkyl phenol resin, a cyclopentadiene phenol resin, a triphenylmethane phenol resin, a copolymerized phenol resin of a benzaldehyde phenol resin and an aralkyl phenol resin, and a novolac phenol resin (hereinafter, these phenol curing agents are also referred to as a specific phenol curing agent). The specific phenol curing agent may be used singly or in combination of two or more kinds.

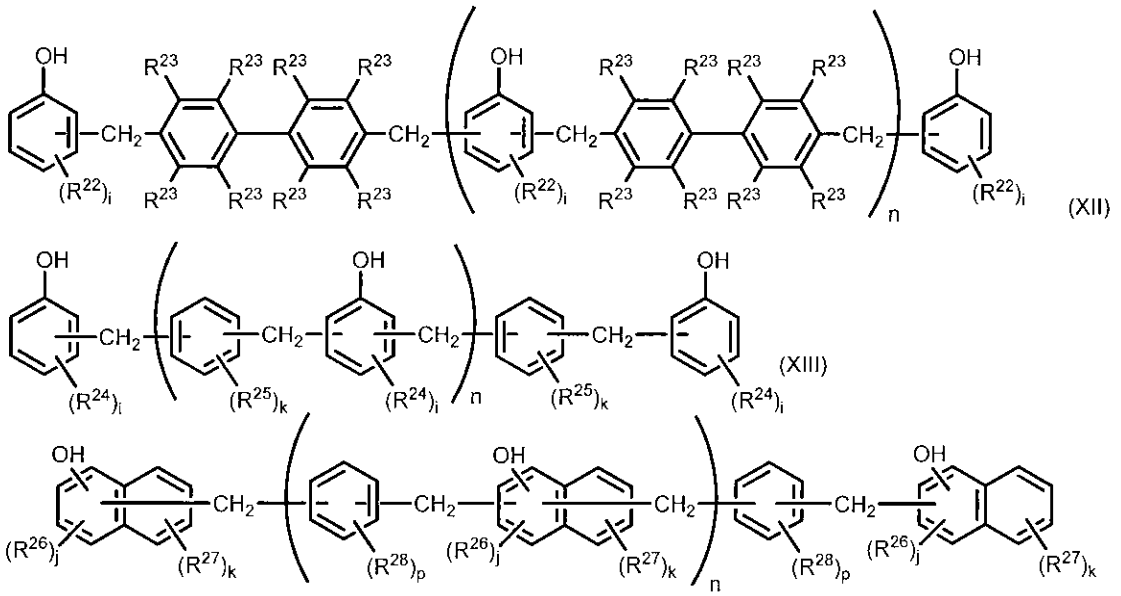
[0085] When the curing agent includes a specific phenol curing agent, the content thereof with respect to the total curing agent is preferably 30% by mass or more, more preferably 50% by mass or more, from the viewpoint of exhibiting the effect of the specific curing agent.

[0086] Example of the aralkyl phenol resin include a phenol aralkyl resin and a naphthol aralkyl resin, synthesiezed from a phenollic compound and dimethoxy-p-xylene or bis(methoxymethyl)biphenyl. The aralkyl phenol resin may be copolymerized with a different phenol resin. Examples of the copolymerized aralkyl phenol resin include a copolymerized phenol resin of a benzaldehyde phenol resin and an aralkyl phenol resin, a copolymerized phenol resin of a salicylaldehyde phenol resin and an aralkyl phenol resin; and a copolymerized phenol resin of a novolac phenol resin and an aralkyl phenol resin.

[0087] The aralkyl phenol resin is not particularly limited, as long as it is a phenol resin synthesized from at least one selected from the group consisting of a phenol compound and a naphthol compound and dimethoxy-p-xylene, bis(methoxymethyl)biphenyl or a derivative thereof.

For example, the aralkyl phenol resin is preferably phenol resins represented by the following Formulae (XII) to (XIV).

[0088]



(XII)

(XIII)

(XIV)

[0089] In Formulae (XII) to (XIV), each of R^{23} represents a hydrogen atom or a monovalent organic group having 1 to 18 carbon atoms, which may be the same or different from each other; each of R^{22}, R^{24}, R^{25} and R^{28} represents a monovalent organic group having 1 to 18 carbon atoms, which may be the same or different from each other; each of R^{26} and R^{27} represents a hydrogen atom or a monovalent organic group having 1 to 18 carbon atoms, which may be the same or different from each other; each of i independently represents an integer of 0 to 3; each of j independently represents an integer from 0 to 2; each of k independently represents an integer of 0 to 4; each of p independently represents an integer from 0 to 4; and each of n is an average value within a range of 0 to 10.

[0090] Among the phenol resin represented by Formula (XII), a phenol resin in which i is 0 and each of R^{23} is a hydrogen atom (MEH-7851, trade name, Meiwa Plastic Industries, Ltd.) and the like are available as a commercial product.

[0091] Among the phenol resin represented by Formula (XIII), a phenol resin in which i is 0 and k is 0 (XL-225 and XLC, trade names, Mitsui Chemicals, Inc. and MEH-7800, trade name, Meiwa Plastic Industries, Ltd.) and the like are available as a commercial product.

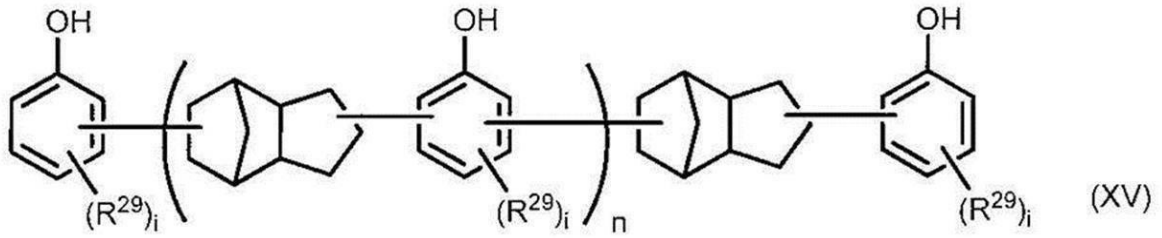
[0092] Among the phenol resin represented by Formula (XIV), a phenol resin in which j is 0, k is 0 and p is 0 (SN-170, trade name, Nippon Steel Chemical & Material Co., Ltd.) and a phenol resin in which j is 0, k is 1, R^{27} is a hydroxy group and p is 0 (SN-395, trade name, Nippon Steel Chemical & Material Co., Ltd.) and the like are available as a commercial product.

[0093] The dicyclopentadiene phenol resin is not particularly limited, as long as it is a phenol resin obtained from a compound having a dicyclopentadiene structure. For example, a phenol resin

represented by the following Formula (XV) is preferred.

Among the phenol resin represented by Formula (XV), a phenol resin in which i is 0 (DPP, trade name, Nippon Petrochemicals, Co., Ltd.) and the like are available as a commercial product.

[0094]



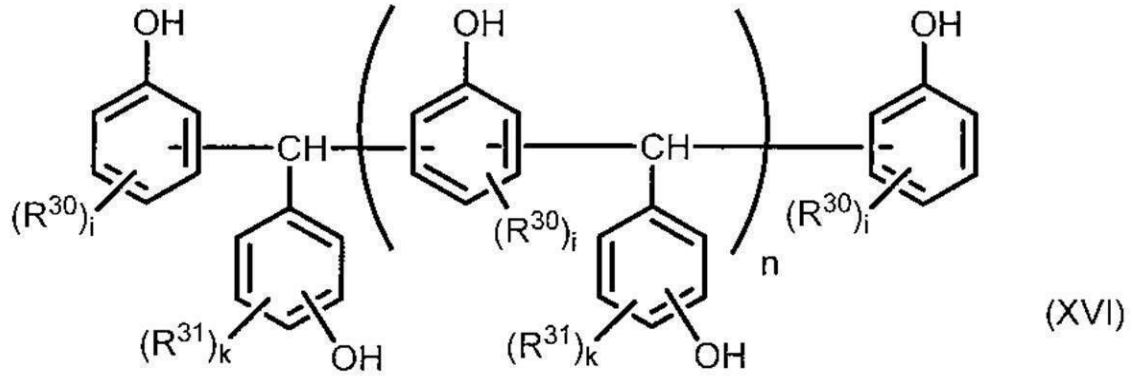
(XV)

[0095] In Formula (XV), each of R^{29} is a monovalent organic group having 1 to 18 carbon atoms, which may be the same or different from each other; each of i independently represents an integer from 0 to 3; and n is an average value within a range of from 0 to 10.

[0096] The triphenylmethane phenol resin is not particularly limited, as long as it is a phenol resin obtained from a compound having a triphenylmethane structure. For example, a phenol resin represented by the following Formula (XVI) is preferred.

[0097] Among the phenol resin represented by Formula (XVI), a phenol resin in which i is 0 and k is 0 (MEH-7500, trade name, Meiwa Plastic Industries, Ltd.) and the like is available as a commercial product.

[0098]



(XVI)

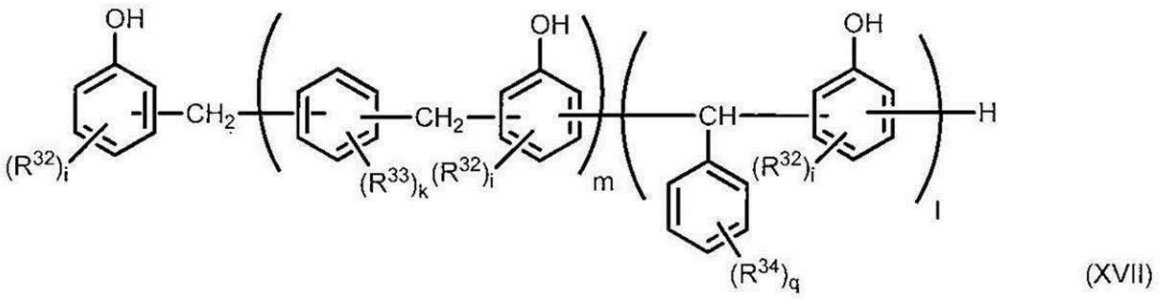
[0099] In Formula (XVI), each of R^{30} and R^{31} represents a monovalent organic group having 1 to 18 carbon atoms, which may be the same or different from each other; each of i independently represents an integer from 0 to 3; each of k independently represents an integer from 0 to 4; and n represents an average value within a range of 0 to 10.

[0100] The copolymerized phenol resin of a benzaldehyde phenol resin and an aralkyl phenol resin

is not particularly limited, as long as it is a copolymerized phenol resin obtained by copolymerizing a phenol resin that is obtained from a compound having a benzaldehyde structure and an aralkyl phenol resin. For example, a phenol resin represented by the following Formula (XVII) is preferred.

[0101] Among the phenol resin represented by Formula (XVII), a phenol resin in which i is 0, k is 0 and q is 0 (HE-510, trade name, Air Water Chemical, Inc.) and the like are available as a commercial product.

[0102]



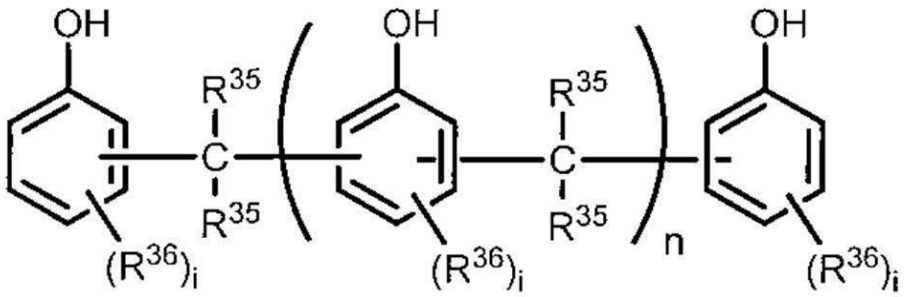
(XVII)

[0103] In Formula (XVII), each of R^{32} to R^{34} represents a monovalent organic group having 1 to 18 carbon atoms, which may be the same or different from each other; each of i independently represents an integer from 0 to 3; each of k independently represents an integer from 0 to 4; each of q independently represents an integer from 0 to 5; and each of l and m is independently an average value within a range of 0 to 11, wherein the total of l and m is from 1 to 11.

[0104] The novolac phenol resin is not particularly limited, as long as it is a phenol resin obtained by condensation or co-condensation of a phenollic compound, which is at least one selected from the group consisting of a phenol compound and a naphthol compound, and an aldehyde compound in the presence of an acid catalyst. For example, a phenol resin represented by the following (XVIII) is preferred.

[0105] Among the phenol resin represented by the following (XVIII), a phenol resin in which i is 0 and each of R^{35} is a hydrogen atom (TAMANOL 758 and 759, trade names, Arakawa Chemical Industries, Ltd. and HP-850N, trade name, Hitachi Chemicals, Co., Ltd.) and the like are available as a commercial product.

[0106]



(XVIII)

[0107] In Formula (XVIII), each of R^{35} represents a hydrogen atom or a monovalent organic group having 1 to 18 carbon atoms, which may be the same or different from each other; each of R^{36} represents a monovalent organic group having 1 to 18 carbon atoms, which may be the same or different from each other; each of i independently represents an integer of 0 to 3; and n represents an average value within a range of from 0 to 10.

[0108] In the Formulae (XII) to (XVIII), the expression "may be the same or different from each other" regarding R^{22} to R^{36} refers to, for example, that R^{22} in Formula (XII) by the number of i may be the same or different from each other, and the same applies to R^{23} to R^{36}. Further, each of R^{22} to R^{36} may be the same or different from each other. For example, all of R^{22} and all of R^{23} may be the same or different from each other, and all of R^{30} and all of R^{31} may be the same or different from each other.

[0109] The n in Formulae (XII) to (XVIII) is an average value and is preferably independently within a range of from 0 to 10. When n is not more than 10, the melt viscosity of the resin component is not too high and the viscosity of the curable resin composition during the molding is kept low, thereby suppressing the occurrence of injection defects, deformation of bonding wires (metallic lines connecting an element to a lead) and the like. The range of n in one molecule is preferably within a range of from 0 to 4.

[0110] The functional group equivalent of the curing agent (hydroxy equivalent in case of phenol curing agent) is not particularly limited. From the viewpoint of a balance of the properties such as moldability, reflow resistance and electrical reliability, the functional group equivalent of the curing agent is preferably from 70 g/eq to 1000 g/eq, more preferably from 80 g/eq to 500 g/eq.

[0111] The softening point or the melting point of the curing agent is not particularly limited. From the viewpoint of moldability and reflow resistance, the softening point or the melting point of the curing agent is preferably from 40°C to 180°C. From the viewpoint of handleability during the preparation of the curable resin composition, the softening point or the melting point of the curing agent is preferably from 50°C to 130°C.

[0112] The equivalent ratio of the curable resin and the curing agent, i,e., the ratio of the number

of functional groups in the curable resin and the number of functional groups in the curing agent (number of functional groups in curing agent/number of functional groups in curable resin) is not particularly limited. From the viewpoint of suppressing the amount of unreacted components, the ratio is preferably from 0.5 to 2.0, more preferably from 0.6 to 1.3. From the viewpoint of moldability and reflow resistance, the ratio is further preferably from 0.8 to 1.2.

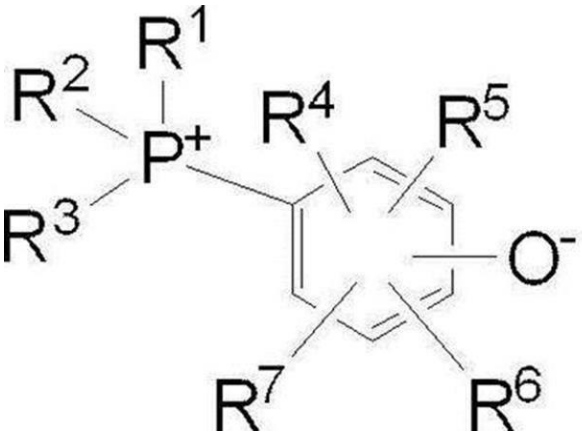
[0113] (Curing accelerator)

The curable resin composition may include a curing accelerator. The type of the curing accelerator is not particularly limited, and may be selected depending on the type of the curable resin, desired properties of the curable resin composition, and the like.

[0114] From the viewpoint of curability and fluidity, the curing accelerator preferably includes a phosphonium compound. Specific examples of the phosphonium compound include a compound having intramolecular polarization obtained by adding, to a tertiary phosphine such as triphenylphosphine, diphenyl(p-tolyl)phosphine, tris(alkylphenyl)phosphine, tris(alkoxyphenyl)phosphine, tris(alkyl-alkoxyphenyl)phosphine, tris(dialkylphenyl)phosphine, tris(trialkylphenyl)phosphine, tris(tetraalkylphenyl)phosphine, tris(dialkoxyphenyl)phosphine, tris(trialkoxyphenyl)phosphine, tris(tetraalkoxyphenyl)phosphine, trialkylphosphine, dialkylarylphosphine or alkyldiarylphosphine, a compound having a π bond such as maleic anhydride, a quinone compound such as 1,4-benzoquinone, 2,5-toluquinone, 1,4-naphthoquinone, 2,3-dimethylbenzoquinone, 2,6-dimethylbenzoquinone, 2,3-dimethoxy-5-methyl-1,4-benzoquinone, 2,3-dimethoxy-1,4-benzoquinone or phenyl-1,4-benzoquinone, or a diazophenylmethane; a compound having intramolecular polarization obtained by the reaction of the tertiary phosphine or the phosphine compound as described above with a halogenated phenol compound such as 4-bromophenol, 3-bromophenol, 2-bromophenol, 4-chlorophenol, 3-chlorophenol, 2-chrolophenol, 4-iodophenol, 3-iodophenol, 2-iodophenol, 4-bromo-2-methylphenol, 4-bromo-3-methylphenol, 4-bromo-2,6-dimethylphenyl, 4-bromo-3,5-dimethylphenol, 4-bromo-2,6-di-tert-butylphenyl, 4-chloro-1-naphthol, 1-bromo-2-naphthol, 6-bromo-2-naphthol or 4-bromo-4'-hydroxybiphenyl, and the subsequent dehydrohalogenation; tetra-substituted phosphonium or tetra-substituted borate not having a phenyl group bonded to a boron atom, such as tetraphenylphosphonium or tetra-p-tolyl borate; a salt of tetra-substituted phosphonum and an anion which is a phenol compound from which a proton is desorbed; and a salt of tetra-substituted phosphonium and an anion which is a carboxylic acid compound from which a proton is desorbed.

[0115] Among the phosphonium compounds, a compound represented by the following Formula (I-1) (hereinafter, also referred to as a specific curing accelerator) is preferred.

[0116]



(I-1)

[0117] In Formula (I-1), each of R^1 to R^3 independently represents a hydrocarbon group having 1 to 18 carbon atoms, and at least two of R^1 to R^3 may bond to form a ring structure. Each of R^4 to R^7 independently represents a hydrogen atom, a hydroxy group or an organic group having 1 to 18 carbon atoms, and at least two of R^4 to R^7 may bond to form a ring structure.

[0118] Examples of the hydrocarbon group having 1 to 18 carbon atoms, represented by R^1 to R^3 in Formula (I-1), include an aliphatic hydrocarbon group having 1 to 18 carbon atoms and an aromatic hydrocarbon group having 6 to 18 carbon atoms.

[0119] From the viewpoint of fluidity, the aliphatic hydrocarbon group having 1 to 18 carbon atoms preferably has 1 to 8 carbon atoms, more preferably 2 to 6 carbon atoms, further preferably 4 to 6 carbon atoms.

[0120] The aliphatic hydrocarbon group having 1 to 18 carbon atoms may be a linear or branched aliphatic hydrocarbon group having 1 to 18 carbon atoms or an alicyclic hydrocarbon group having 3 to 18 carbon atoms. From the viewpoint of ease of production, the aliphatic hydrocarbon group is preferably a linear or branched aliphatic hydrocarbon group.

[0121] Specific examples of the linear or branched aliphatic hydrocarbon group having 1 to 18 carbon atoms include an alkyl group such as a methyl group, an ethyl group, a propyl group, an isopropyl group, an n-butyl group, a sec-butyl group, a t-butyl group, a pentyl group, a hexyl group, an octyl group, a decyl group or a dodecyl group, an allyl group and a vinyl group. The linear or branched aliphatic hydrocarbon group may have a substituent or may not have a substituent. Examples of the substituent include an alkoxy group such as a methoxy group, an ethoxy group, a butoxy group and a t-butoxy group, an aryl group such as a phenyl group and a naphthyl group, a hydroxy group, an amino group, and a halogen atom. The linear or branched aliphatic hydrocarbon group may have two or more substituents. In that case, the substituents may be the same or different from each other. When the linear or branched aliphatic hydrocarbon group has a substituent, the total number of carbon atoms in the aliphatic hydrocarbon group and

the substituent is preferably from 1 to 18. From the viewpoint of curability, the aliphatic hydrocarbon group is preferably an unsubstituted alkyl group, more preferably an unsubstituted alkyl group having 1 to 8 carbon atoms, further preferably an n-butyl group, an isobutyl group, an n-pentyl group, an n-hexyl group and an n-octyl group.

[0106] Specific examples of the alicyclic hydrocarbon group having 3 to 18 carbon atoms include a cycloalkyl group such as a cyclopentyl group, a cyclohexyl group and a cycloheptyl group, and a cycloalkenyl group such as a cyclopentenyl group and a cyclohexenyl group. The alicyclic hydrocarbon group may have a substituent or may not have a substituent. Examples of the substituent include an alkyl group such as a methyl group, an ethyl group, a butyl group and a tert-butyl group, an alkoxy group such as a methoxy group, an ethoxy group, a butoxy group and a t-butoxy group, an aryl group such as a phenyl group and a naphthyl group, a hydroxy group, an amino group and a halogen atom. The alicyclic hydrocarbon group may have two or more substituents. In that case, the substituents may be the same or different from each other. When the alicyclic hydrocarbon group has a substituent, the total number of carbon atoms in the alicyclic hydrocarbon group and the substituent is preferably from 3 to 18. When the alicyclic hydrocarbon group has a substituent, the position thereof is not particularly limited. From the viewpoint of curability, the alicyclic hydrocarbon group is preferably an unsubstituted cycloalkyl group, more preferably an unsubstituted cycloalkyl group having 4 to 10 carbon atoms, further preferably a cyclohexyl group, a cyclopentyl group or a cycloheptyl group.

[0123] The aromatic hydrocarbon group having 6 to 18 carbon atoms preferably has 6 to 14 carbon atoms, more preferably 6 to 10 carbon atoms. The aromatic hydrocarbon group may have a substituent or may not have a substituent. Examples of the substituent include an alkyl group such as a methyl group, an ethyl group, a butyl group and a t-butyl group, an alkoxy group such as a methoxy group, an ethoxy group, a butoxy group and a t-butoxy group, an aryl group such as a phenyl group and a naphthyl group, a hydroxy group, an amino group and a halogen atom. The aromatic hydrocarbon group may have two or more substituents. In that case, the substituents may be the same or different from each other. When the aromatic hydrocarbon group has a substituent, the total number of carbon atoms in the aromatic hydrocarbon group and the substituent is preferably from 6 to 18. When the aromatic hydrocarbon group has a substituent, the position thereof is not particularly limited.

[0124] Specific examples of the aromatic hydrocarbon group having 6 to 18 carbon atoms include a phenyl group, a 1-naphthyl group, a 2-naphthyl group, a tolyl group, a dimethylphenyl group, an ethylphenyl group, a butylphenyl group, a t-butylphenyl group, a methoxyphenyl group, an ethoxyphenyl group, a butoxyphenyl group and a t-butoxyphenyl group. The position for a

substituent in these aromatic hydrocarbon groups may be any one of ortho, meta and para positions. From the viewpoint of fluidity, the aromatic hydrocarbon group is preferably an unsubstituted aryl group having 6 to 12 carbon atoms or a substituted aryl group having 6 to 12 carbon atoms including the number of carbon atoms in the substituent; more preferably an unsubstituted aryl group having 6 to 10 carbon atoms or a substituted aryl group having 6 to 10 carbon atoms including the number of carbon atoms in the substituent; further preferably a phenyl group, a p-tolyl group or a p-methoxyphenyl group.

[0125] The expression "two or more of R^1 to R^3 may bond to form a ring structure" in Formula (I-1) refers to a case in which the two or three of R^1 to R^3 may bond to form a divalent or trivalent hydrocarbon group. In that case, examples of R^1 to R^3 include a substituent that can form a ring structure by bonding with a phosphorus atom, including an alkylene group such as an ethylene group, a propylene group, a butylene group, a pentylene group and a hexylene group, an alkenylene group such as ethenylene group, a propenylene group and a butenylene group, an aralkylene group such as a methyelnephenylene group, and an arylene group such as a phenylene group and an anthracenylene group. The substituent may be substituted by an alkyl group, an alkoxy group, an aryl group, an aryloxy group, an amino group, a hydroxy group, a halogen atom or the like.

[0126] The "organic group having 1 to 18 carbon atoms" regarding R^4 to R^7 in Formula (I-1) includes an aliphatic hydrocarbon group, an aromatic hydrocarbon group, an aliphatic hydrocarbon oxy group, an aromatic hydrocarbon oxy group, an acyl group, a hydrocarbon oxycarbonyl group and an acyloxy group, which may be substituted or unsubstituted.

[0127] Examples of the aliphatic hydrocarbon group and the aromatic hydrocarbon group represented by R^4 to R^7 include the aliphatic hydrocarbon groups and the aromatic hydrocarbon groups represented by R^1 to R^3 as described above.

[0128] Examples of the aliphatic hydrocarbon oxy group include an oxy group having a structure in which an oxygen atom is bonded to the aliphatic hydrocarbon group as described above, such as a methoxy group, an ethoxy group, a propoxy group, an isopropoxy group, an n-butoxy group, a 2-butoxy group, a t-butoxy group, a cyclopropyloxy group, a cyclohexyloxy group, a cyclopentyloxy group, an allyloxy group and a vinyloxy group; and a group having a structure in which any of these aliphatic hydrocarbon oxy groups is substituted by an alkyl group, an alkoxy group, an aryl group, an aryloxy group, an amino group, a hydroxy group, a halogen atom or the like.

[0129] Examples of the aromatic hydrocarbon oxy group include a phenoxy group, a methylphenoxy group, an ethylphenoxy group, a methoxyphenoxy group, a butoxyphenoxy group, a phenoxyphenoxy group, an oxy group having a structure in which an oxygen is bonded to the

aromatic hydrocarbon group as described above, and a group having a structure in which any of these aromatic hydrocarbon groups is substituted by an alkyl group, an alkoxy group, an aryl group, an aryloxy group, an amino group, an halogen atom or the like.

[0130] Examples of the acyl group include an aliphatic hydrocarbon carbonyl group such as a formyl group, an acetyl group, an ethylcarbonyl group, a butylyl group, a cyclohexylcarbonyl group and an allylcarbonyl group, an aromatic hydrocarbon carbonyl group such as a phenylcarbonyl group and a methylphenylcarbonyl group, and a group having a structure in which any of these aliphatic hydrocarbon carbonyl groups or aromatic hydrocarbon carbonyl groups is substituted by an alkyl group, an alkoxy group, an aryloxy group, an amino group, a halogen atom or the like.

[0131] Examples of the hydrocarbon oxycarbonyl group include an aliphatic hydrocarbon oxycarbonyl group such as a methoxycarbonyl group, an ethoxycarbonyl group, a butoxycarbonyl group, an allyloxycarbonyl group and a cyclohexyloxycarbonyl group; an aromatic hydrocarbon oxycarbonyl group such as a phenoxycarbonyl group and a methylcarbonyloxy group, and a group having a structure in which any of these aliphatic hydrocarbon oxycarbonyl group and aromatic hydrocarbon oxycarbonyl groups is substituted by an alkyl group, an alkoxy group, an aryloxy group, an amino group, a halogen atom or the like.

[0132] Examples of the acyloxy group include an aliphatic hydrocarbon carbonyloxy group such as a methylcarbonyloxy group, an ethylcarbonyloxy group, a butylcarbonyloxy group, an allylcarbonyloxy group and a cyclohexylcarbonyloxy group, an aromatic hydrocarbon carbonyloxy group such as a phenylcarbonyloxy group and a methylphenylcarbonyloxy group, and a group having a structure in which any of these aliphatic hydrocarbon carbonyloxy groups and aromatic hydrocarbon carbonyloxy groups is substituted by an alkyl group, an alkoxy group, an aryloxy group, an amino group, a halogen atom or the like.

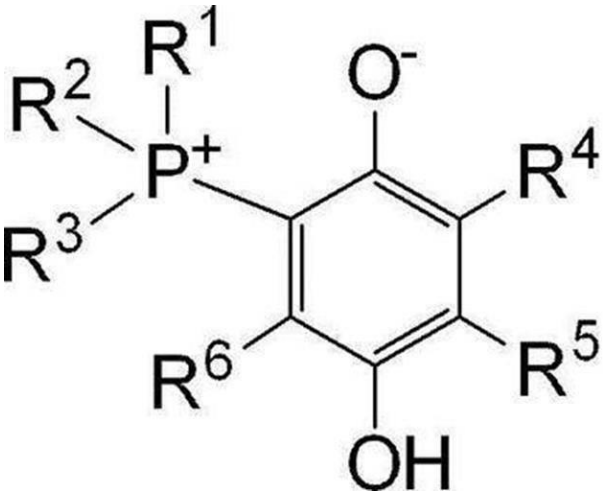
[0133] The expression "two or more of R^4 to R^7 may bond to form a ring structure" in Formula (I-1) refers to that the two to four of R^4 to R^7 may bond to form a divalent to tetravalent organic group. In that case, examples of R^4 to R^7 include a substituent that can form a ring structure, including an alkylene group such as an ethylene group, a propylene group, a butylene group, a pentylene group and a hexylene group, an alkenylene group such as ethenylene group, a propenylene group and a butenylene group, an aralkylene group such as a methylenephenylene group, an arylene group such as a phenylene group and an anthracenylene group, and an oxy group or a dioxy group of these substituents. The substituent may be substituted by an alkyl group, an alkoxy group, an aryl group, an aryloxy group, an amino group, a hydroxy group, a halogen atom or the like.

[0134] The R^4 to R^7 in Formula (I-1) are not particularly limited. For example, each of R^4 to R^7 is preferably independently selected from a hydrogen atom, a hydroxy group, a substituted or unsubstituted alkyl group, a substituted or unsubstituted alkoxy group, or a substituted or unsubstituted aryloxy group. From the viewpoint of commercial availability, each of R^4 to R^7 is preferably independently selected from a hydrogen atom, a hydroxy group, an unsubstituted aryl group, an aryl group substituted by at least one selected from the group consisting of an alkyl group and an alkoxy group, or a linear or cyclic alkyl group. Examples of the unsubstituted aryl group and the aryl group substituted by at least one selected from the group consisting of an alkyl group and an alkoxy group include a phenyl group, a p-tolyl group, a m-tolyl group, an o-tolyl gorup and a p-methoxyphenyl group. Examples of the linear or cyclic alkyl group include a methyl group, an ethyl group, a propyl group, an isopropyl group, a butyl group, a 2-butyl group, a t-butyl group, an octyl group and a cyclohexyl group. From the viewpoint of curability, a case in which all of R^4 to R^7 are a hydrogen atom and a case in which at least one of R^4 to R^7 is a hydroxy group and the rest are a hydrogen atom are preferred.

[0135] In Formula (I-1), in a preferred embodiment, at least two of R^1 to R^3 are an alkyl group having 1 to 18 carbon atoms or a cycloalkyl group having 3 to 18 carbon atoms, and all of R^4 to R^7 are a hydrogen atom or at least one of R^4 to R^7 is a hydroxy group and the rest are a hydrogen atom. In a more preferred embodiment, all of R^1 to R^3 are an alkyl group having 1 to 18 carbon atoms or a cycloalkyl group having 3 to 18 carbon atoms, and all of R^4 to R^7 are a hydrogen atom or at least one of R^4 to R^7 is a hydroxy group and the rest are a hydrogen atom.

[0136] From the viewpoint of rapid curability, the specific curing accelerator is preferably a compound represented by the following Formula (I-2).

[0137]



(I-2)

[0138] In Formula (I-2), each of R^1 to R^3 is independently represents a hydrocarbon group having 1 to 18 carbon atoms and two or more of R^1 to R^3 may bond to form a ring structure. Each of R^4 to

R^6 independently represents a hydrogen atom or an organic group having 1 to 18 carbon atoms, and two or more of R^4 to R^6 may bond to form a ring structure.

[0139] Specific examples and preferred examples of R^1 to R^6 in Formula (I-2) are the same as the specific examples and preferred examples of R^1 to R^6 in Formula (I-1).

[0140] Specific examples of the specific curing accelerator include an adduct of triphenylphosphine and 1,4-benzoquinone, an adduct of tri-n-butylphosphine and 1,4-benzoquinone, an adduct of tricyclohexylphosphine and 1,4-benzoquinone, an adduct of dicyclohexylphenylphosphine and 1,4-benzoquinone, an adduct of cyclohexyldiphenylphosphine and 1,4-benzoquinone, an adduct of triisobutylphosphione and 1,4-benzoquinone, and an adduct of tricyclopentylphosphine and 1,4-benzoquinone.

[0141] The specific curing accelerator may be obtained by, for example, as an adduct of a tertiary phosphine compound and a quinone compound.

Specific examples of the tertiary phosphine include triphenylphosphine, tributylphosphine, dibutylphenylphosphine, butyldiphenylphosphine, ethyldiphenylphosphine, tris(4-methylphenyl)phosphine, tris(4-ethylphenyl)phosphine, tris(4-propylphenyl)phosphine, tris(4-butylphenyl)phosphine, tris(isopropylphenyl)phosphine, tris(t-butylphenyl)phosphine, tris(2,4-dimethylphenyl)phosphine, tris(2,6-dimethylphenyl)phosphine, tris(2,4,6-trimethylphenyl)phosphine, tris(2,6-dimethyl-4-ethoxyphenyl)phosphine, tris(4-methoxyphenyl)phosphine and tris(4-ethoxyphenyl)phosphine. From the viewpoint of moldability, triphenylphosphine and tributylphosphine are preferred.

[0142] Specific examples of the quinone compound include o-benzoquinone, p-benzoquinone, diphenoquinone, 1,4-naphthoquinone and anthraquinone. From the viewpoint of moisture resistance and storage stability, p-benzoquinone is preferred.

[0143] The curable resin composition may include a curing accelerator other than a phosphonium compound.

Examples of the curing accelerator other than a phosphonium compound include diazabicycloalkenes such as 1,5-diazabicyclo[4.3.0]nonene-5 (DBN) and 1,8-diazabicyclo[5.4.0]undecene-7 (DBU); cyclic amidine compounds such as 2-methylimidazole, 2-phenylimidazole, 2-phenyl-4-methylimidazole and 2-heptadecylimidazole; derivatives of the cyclic amidine compounds; phenol novolac salts of the cyclic amidine compounds or the derivatives thereof; compounds having intramolecular polarization, obtained by adding, to the above-mentioned compounds, a compound having a π bond, such as maleic anhydride, a quinone compound such as 1,4-benzoquinone, 2,5-toluquinone, 1,4-naphthoquinone, 2,3-dimethylbenzoquinone, 2,6-dimethylbenzoquinone, 2,3-dimethoxy-5-methyl-1,4-benzoquinone,

2,3-dimethoxy-1,4-benzoquinone or phenyl-1,4-benzoquinone, or diazophenylmethane; cyclic amidinium compounds such as a tetraphenyl boric acid salt of DBU, a tetraphenyl boric acid salt of DBN, a tetraphenyl boric acid salt of 2-ethyl-4-methylimidazole, and a tetraphenyl boric acid salt of N-methylmorpholine; tertiary amine compounds such as pyridine, triethylamine, triethylenediamine, benzyldimethylamine, triethanolamine, dimethylaminoethanol, and tris(dimethylaminomethyl)phenol; derivatives of the above-mentioned tertiary amine compounds; and ammonium salt compounds such as tetra-n-butylammonium acetate, tetra-n-butylammonium phosphate, tetraethylammonium acetate, tetra-n-hexylammonium benzoate and tetrapropylammonium hydroxide.

[0144] When the curable resin composition includes a specific curing accelerator as the curing accelerator, the content thereof with respect to the total curing accelerator is preferably 30% by mass or more, more preferably 50% by mass or more, further preferably 70% by mass or more.

[0145] When the curable resin composition includes a curing accelerator, the amount thereof with respect to 100 parts by mass of the resin component is preferably from 0.1 parts by mass to 30 parts by mass, more preferably from 1 part by mass to 15 parts by mass. When the amount of the curing accelerator is 0.1 parts by mass or more with respect to 100 parts by mass of the resin component, the curable resin composition tends to cure within a short period in a favorable manner. When the amount of the curing accelerator is 30 parts by mass or less with respect to 100 parts by mass of the resin component, the rate of curing is not too high and a favorable molded product tends to be obtained.

[0146] (Inorganic filler)

The curable resin composition may include an inorganic filler. In particular, in a case of using the curable resin composition for a sealing material of a semiconductor package, the curable resin composition preferably includes an inorganic filler

[0147] The type of the inorganic filler is not particularly limited. Specific examples of the inorganic filler include inorganic materials such as fused silica, crystalline silica, glass, alumina, calcium carbonate, zirconium silicate, calcium silicate, silicon nitride, aluminum nitride, boron nitride, beryllia, zirconia, zircon, forstelite, steatite, spinel, mullite, titania, talc, clay and mica. It is also possible to use an inorganic filler having a fire-retardant effect, and examples thereof include aluminum hydroxide, magnesium hydroxide, a composite metallic hydroxide such as a composite hydroxide of magnesium and zinc, and zinc borate. From the viewpoint of reducing the linear expansion coefficient, the inorganic filler is preferably fused silica. From the viewpoint of increasing the thermal conductivity, the inorganic filler is preferably alumina. The inorganic filler may be used singly or in combination of two or more kinds. Example of the configuration of the

inorganic filler include a powder, beads obtained by spheronization of a powder, fibers and the like.

[0148] When the curable resin composition includes an inorganic filler, the content thereof is not particularly limited. From the viewpoint of fluidity and strength, the content of the inorganic filler with respect to the total curable resin composition is preferably from 30% by volume to 90% by volume, more preferably from 35% by volume to 80% by volume, further preferably from 40% by volume to 70% by volume. When the content of the inorganic filler is 30% by volume or more of the total curable resin composition, properties of a cured product such as the thermal expansion coefficient, thermal conductivity and elastic modulus tend to be further improved. When the content of the inorganic filler is 90% by volume or less of the total curable resin composition, moldability of the curable resin composition tends to become more favorable by suppressing the increase in viscosity and improving the fluidity.

[0149] The average particle size of the inorganic filler is not particularly limited. For example, the volume average particle size of the inorganic filler is preferably from 0.2 μm to 10 μm, more preferably from 0.5 μm to 5 μm. When the volume average particle size of the inorganic filler is 0.2 μm or more, an increase in the viscosity of the curable resin composition tends to be more suppressed. When the volume average particle size of the inorganic filler is 10 μm or less, the ability to fill a narrow gap tends to be further improved. The volume average particle size of the inorganic filler may be a volume average particle diameter (D50) measured by a laser diffraction scattering method using a particle size distribution analyzer.

[0150] The volume average particle size of the inorganic filler included in the curable resin composition or a cured product thereof may be measured by a known method. For example, the volume average particle size of the inorganic filler may be measured by preparing a dispersion of the inorganic filler by extracting the inorganic filler from the curable resin composition or a cured product thereof with an organic solvent, nitric acid or aqua regia, and dispersing the extraction with an ultrasonic disperser or the like, and performing the measurement of the volume-based particle size distribution using a laser diffraction scattering particle size distribution analyzer. Alternatively, the average particle size may be measured by embedding the cured product in a transparent epoxy resin and the like and observing a section thereof, obtained by polishing, with a scanning electron microscope, and measuring the volume average particle size from the volume-based particle size distribution. Further, the volume average particle size of the inorganic filler may be measured using a FIB apparatus (focused ion beam SEM) by observing a two-dimensional section of the cured product in a continuous manner and analyzing the three-dimensional structure thereof.

[0151] From the viewpoint of fluidity of the curable resin composition, the particle shape of the inorganic filler is preferably spherical rather than rectangular. Further, the inorganic filler preferably has a wide particle size distribution.

[0152] [Additives]

The curable resin composition may include an additive such as a coupling agent, an ion exchanger, a mold release agent, a fire retardant, a colorant or a stress relaxation agent. The curable resin composition may include an additive that is known in the technical field, other than the additives as mentioned below, as necessary.

[0153] (Coupling agent)

When the curable resin composition includes an inorganic filler, a coupling agent may be included in order to improve the adhesion between the resin component and the inorganic filler. Examples of the coupling agent include silane compounds such as epoxysilane, mercaptosilane, aminosilane, ureidosilane and vinylsilane, titaniuom compounds, aluminum chelate compounds and aluminum/zirconium compounds.

[0154] When the curable resin composition includes a coupling agent, the amount thereof with respect to 100 parts by mass of the inorganic filler is preferably from 0.05 parts by mass to 5 parts by mass, more preferably from 0.1 parts by mass to 2.5 parts by mass. When the amount of the coupling agent is 0.05 parts by mass or more with respect to 100 parts by mass of the inorganic filler, adhesion with respect to a lead frame tends to be further improved. When the amount of the coupling agent is 5 parts by mass or less with respect to 100 parts by mass of the inorganic filler, moldability of a package tends to be further improved.

[0155] (Ion exchanger)

The curable resin composition may include an ion exchanger. In particular, in a case of using the curable resin composition as a molding material for sealing, an ion exchanger is preferably included for the purpose of improving the resistance to moisture and high temperature of an electronic component device, in which an element is sealed with the curable resin composition. The ion exchanger is not particularly limited, and may be selected from known products. Specific examples of the ion exchanger include hydrotalcites and hydrous oxides including at least one element selected from the group consisting of magnesium, aluminum, titanium, zirconium and bismuth. The ion exchanger may be used singly or in combination of two or more kinds. Among the ion exchangers, a hydrotalcite represented by the following Formula (A) is preferred. In Formula (A), X is a number that satisfies $0<X \leqq 0.5$, and m is a positive number.

[0156] $Mg_{(1-X)}Al_X(OH)_2(CO_3)_{X/2}\cdot mH_2O$ ……(A)

[0157] When the curable resin composition includes an ion exchanger, the content thereof is not particularly limited as long as it is enough to trap ions such as halogen ions. For example, the amount of the ion exchanger with respect to 100 parts by mass of the resin component is preferably from 0.1 parts by mass to 30 parts by mass, more preferably from 1 part by mas to 15 parts by mass.

[0158] (Mold release agent)

The curable resin composition may include a mold release agent for the purpose of achieving a favorable releasability from a mold during the molding. The mold release agent is not particularly limited, and may be selected from known products. Specific examples of the mold release agent include higher fatty acids such as carnauba wax, motanic acid and stearic acid, metal salts of higher fatty acid, ester waxes such as montanic acid ester, and polyolefin waxes such as oxidized polyethylene and non-oxidized polyethylene. The mold release agent may be used singly or in combination of two or more kinds.

[0159] When the curable resin composition includes a mold release agent, the amount thereof with respect to 100 parts by mass of the resin component is preferably from 0.01 parts by mass to 15 parts by mass, more preferably from 0.1 parts by mass to 10 parts by mass. When the amount of the mold release agent is 0.01 pats by mass or more with respect to 100 parts by mass of the resin component, a sufficient degree of releasability tends to be achieved. When the amount of the mold release agent is 15 pats by mass or less with respect to 100 parts by mass of the resin component, a more favorable adhesion tends to be achieved.

[0160] (Fire retardant)

The curable resin composition may include a fire retardant. The fire retardant is not particularly limited, and may be selected from known products. Specific examples of the fire retardant include organic or inorganic compounds including a halogen atom, an antimony atom, a nitrogen atom or a phosphorous atom, and metallic hydroxides. The fire retardant may be used singly or in combination of two or more kinds.

[0161] When the curable resin composition includes a fire retardant, the amount thereof is not particularly limited as long as it is enough to achieve a desired fire-retardant effect. For example, the amount of the fire retardant with respect to 100 parts by mass of the resin component is preferably from 1 part by mass to 300 parts by mass, more preferably from 2 parts by mass to 150 parts by mass.

[0162] (Colorant)

The curable resin composition may include a colorant. Examples of the colorant include carbon black, organic dyes, organic pigments, titanium oxide, minium and colcothar. The amount of the colorant may be selected depending on the purposes and the like. The colorant may be used singly or in combination of two or more kinds.

[0163] (Stress relaxation agent)

The curable resin composition may include a stress relaxation agent such as silicone oil and silicone rubber particles. By including a stress relaxation agent, occurrence of warpage or cracking of a package may be reduced. Examples of the release relaxation include thermoplastic elastomers such as silicone elastomer, styrene elastomer, olefin elastomer, urethane elastomer, polyester elastomer, polyether elastomer, polyamide elastomer and polybutadiene elastomer, NR (natural rubber), NBR (acrylonitrile-butadiene rubber), acrylic rubber, urethane rubber, rubber particles such as silicone powder, and rubber particles having a core-shell structure such as methyl methacrylate-styrene-butadiene copolymer (MBS), methyl methacrylate-silicone copolymer, and methyl methacrylate-butyl acrylate copolymer. The stress relaxation agent may be used singly or in combination of two or more kinds. Among the stress relaxation agents, a silicone-based stress relaxation agent is preferred. Examples of the silicone-based stress relaxation agent include those having an epoxy group or an amino group, or those modified with a polyether.

[0164] (Method for preparing curable resin composition)

The method for preparing the curable resin composition is not particularly limited. A typical example thereof is a method in which predetermined amounts of the components are sufficiently mixed with a mixer or the like, the mixture is melt-kneaded with a mixing roll, an extruder or the like, and then cooled and pulverized. More specifically, the curable resin composition may be prepared by mixing the predetermined amounts of the components, kneading the mixture with a kneader, a roll an extruder or the like that has been heated at 70°C to 140°C, and cooling and pulverizing the kneaded product.

[0165] The curable resin composition is preferably in a solid state under ordinary temperature and pressure (for example, 25°C and the atmospheric pressure). When the curable resin composition is in a solid state, the configuration thereof is not particularly limited and may be a powder, particles, tablets and the like. When the curable resin composition is in a form of tablets, the size and the mass of the tablets are preferably adjusted according to the molding conditions of the package, from the viewpoint of handleability.

[0166] <Electronic component device>

The electronic component device according to the disclosure includes an element and a cured product of the curable resin composition as mentioned above, the cured product sealing the

element.

Examples of the electronic component device include those having, on a support such as a lead frame, a wired tape carrier, a wiring board, a glass or a silicon wafer, an element portion that is formed by mounting an element on the support and sealing the same with the curable resin composition. Examples of the element include active elements such as a semiconductor chip, a transistor, a diode and a thyristor and passive elements such as a capacitor, a resistor or a coil.

Specific examples of the electronic component device include ordinary resin-sealed ICs such as a DIP (dual inline package), a PLCC (plastic leaded chip carrier), a QFP (quad flat package), an SOP (small outline package), an SOJ (small outline J-lead package), a TSOP (thin small outline package) and a TQFP (thin quad flat package), which have a structure in which an element is fixed on a lead frame and a terminal portion of the element, such as a bonding pad, is connected to a lead portion with wires or bumps, and sealed with the curable resin composition by transfer molding or the like; a TCP (tape carrier package), having a structure in which an element is connected to a tape carrier with bumps, and sealed with the curable resin composition; a COB (chip on board) module, a hybrid IC and a multichip module, having a structure in which an element is connected to a wiring formed on a support by wire bonding, flip-chip bonding, soldering or the like, and sealed with the curable resin composition; and a BGA (ball grid array) and a CSP (chip size package), having a structure formed by mounting an element on a support having, at a rear surface thereof, a terminal to be connected to a wiring board, connecting the element to a wiring formed on the support with bumps or wires, and sealing the same with the curable resin composition. The curable resin composition may also be suitably used for a printed circuit board.

[0167] Examples of the method for sealing the electronic component device with the curable resin composition include low-pressure transfer molding, injection molding and compression molding. Among these methods, low-pressure transfer molding is most commonly used.

[Examples]

[0168] In the following, the embodiments are descried in further detail by referring to the Examples. However, the Examples do not limit the scope of the embodiments.

[0169] (Preparation of curable resin composition)

Curable resin compositions of Examples 1 to 15 and Comparative Examples 1 to 8 were prepared from the following materials in the amounts (part by mass) as described in Tables 1 and 2, by mixing with a roll mill at 80°C for 15 minutes.

[0170] (Epoxy resins)

Epoxy resin 1: biphenyl epoxy resin, epoxy equivalent: 196 g/eq, melting point: 106°C

(Mitsubishi Chemical Corporation, YX-4000H)

Epoxy resin 2: styrene-modified phenol novolac epoxy resin, epoxy equivalent: 282 g/eq, softening point: 59°C (Nippon Steel Chemical & Material Co., Ltd., YDAN-1000-10C)

Epoxy resin 3: methoxynaphthalene-cresol formaldehyde co-condensed epoxy resin, epoxy equivalent: 250 g/eq, softening point: 58°C (DIC Corporation, HP-5000)

Epoxy resin 4: aralkyl epoxy resin having a biphenylene structure, epoxy equivalent: 282 g/eq, softening point: 56°C (Nippon Kayaku Co., Ltd., NC-3000)

[0171] (Curing agents for Comparative Examples)

Curing agent A: phenol aralkyl resin, hydroxy equivalent: 176 g/eq, softening point: 70°C (Meiwa Plastic Industries, Ltd., MEH-7800)

Curing agent B: biphenyl skeleton-type phenol aralkyl resin, hydroxy equivalent: 199 g/eq, softening point: 89°C (Meiwa Plastic Industries, Ltd., MEH-7851)

[0172] (Curing agents for Examples)

Specific phenol novolac resin 1: novolac resin obtained by polycondensation of cashew nut shell liquid for industrial use and phenol with formaldehyde, hydroxy equivalent: 223 g/eq, viscosity at 25°C: 19.3 Pa·s (Gun-ei Chemical Industry Co., Ltd, ELP83H). The cashew nut shell liquid is a mixture of compounds represented by Formulae (1-1) to (1-3) respectively, in which R^2 is an aliphatic hydrocarbon group represented by Group (A).

Specific phenol novolac resin 2: novolac resin obtained by polycondensation of cashew nut shell liquid for industrial use, cresol and phenol with formaldehyde, hydroxy equivalent: 209 g/eq, viscosity at 25°C: 14.0 Pa·s (Gun-ei Chemical Industry Co., Ltd, ELPC80). The cashew nut shell liquid is a mixture of compounds represented by Formulae (1-1) to (1-3) respectively, in which R^2 is an aliphatic hydrocarbon group represented by Group (A).

Specific phenol novolac resin 3: novolac resin obtained by polycondensation of cashew nut shell liquid for industrial use, cresol and phenol with formaldehyde, hydroxy equivalent: 204 g/eq, viscosity at 25°C: 23.6 Pa·s (Gun-ei Chemical Industry Co., Ltd, ELPC75). The cashew nut shell liquid is a mixture of compounds represented by Formulae (1-1) to (1-3) respectively, in which R^2 is an aliphatic hydrocarbon group represented by Group (A).

Specific phenol novolac resin 4: novolac resin obtained by polycondensation of cashew nut shell liquid for industrial use and cresol with formaldehyde, hydroxy equivalent: 204 g/eq, viscosity at 25°C: 20.2 Pa·s (Gun-ei Chemical Industry Co., Ltd, ELC75). The cashew nut shell liquid is a mixture of compounds represented by Formulae (1-1) to (1-3) respectively, in which R^2 is an aliphatic hydrocarbon group represented by Group (A).

[0173] (Curing accelerator)

Curing accelerator: adduct of triphenylphosphine and 1,4-benzoquinone

(Inorganic filler)

Spherical fused silica (average particle diameter: 17.5 μm, specific surface area: 3.8 m^2/g)

(Coupling agent)

Epoxysilane (γ-glycidoxypropyltrimethoxysilane)

(Colorant)

Carbon black (Mitsubishi Chemical Corporation, MA-100)

(Releasing agent)

Carnauba wax (Cerarica Noda Co., Ltd.)

[0174] Table 1

			Examples														
			1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Composition	Epoxy resin	1	100														
		2		100		100		100	100	100	100	100	100	100	100	100	100
		3					100										
		4			100												
	Curing agent	A	76.3	53.0			59.8	56.2	59.3	60.5	43.7	53.0	53.0	53.0	53.0	53.0	53.0
		B			60.0	60.0											
		1	17.1	11.9	11.9	11.9	13.4	7.9	4.0	2.4	23.7	11.9	11.9	11.9			
		2													11.1		
		3														10.9	
		4															10.9
	Coupling agent		7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5
	Curing accelerator		3	3	3	3	3	3	3	3	3	3	3	3	3	3	3
	Carnauba wax		1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
	Carbon black		3	3	3	3	3	3	3	3	3	3	3	3	3	3	3
	Fused silica		1682	1452	1508	1508	1519	1445	1439	1435	1472	1017	1201	1814	1445	1443	1443
	Amount of fused silica (% by mass)		89	89	89	89	89	89	89	89	89	85	87	91	89	89	89

[0175] Table 2

			Comparative Examples							
			1	2	3	4	5	6	7	8
Composition	Epoxy resin	1	100							
		2		100		100		100	100	100
		3					100			
		4			100					
	Curing agent	A	89.8	62.4			70.4	62.4	62.4	62.4
		B			70.6	70.6				
	Coupling agent		7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5
	Curing accelerator		3	3	3	3	3	3	3	3
	Carnauba wax		1	1	1	1	1	1	1	1
	Carbon black		3	3	3	3	3	3	3	3
	Fused silica		1653	1431	1498	1498	1496	1002	1184	1789
	Amount of fused silica (% by mass)		89	89	89	89	89	85	87	91

[0176] (Evaluation of curable resin compositions)

The properties of the curable resin compositions prepared in Examples 1 to 15 and Comparative Examples 1 to 8 were evaluated by performing the following tests. The results are shown in Tables 3 and 4.

The molding was performed with a transfer molding machine with the molding temperature of 175°C, the molding pressure of 6.9 MPa, and the curing time of 90 seconds, unless otherwise specified. As necessary, post curing was performed at 175°C for 5 hours.

[0177] (1) Spiral flow

The curable resin composition was molded under the conditions as described above, and the distance of flow (cm) was measured using a mold for spiral flow measurement according to EMMI-1-66.

[0178] (2) Hardness at heat

The curable resin composition was molded under the conditions as described above to a shape of a circular disk having a diameter of 50 mm and a thickness of 3 mm, and the hardness of the disk was measured immediately after the molding using a Shore D durometer (Ueshima Seisakusho Co., Ltd., HD-1120, type D).

[0179] (3) Shear bond strength at 260°C

The curable resin composition was molded under the conditions as described above, on a copper alloy plate (Pd-PPF), into a shape having a bottom diameter of 4 mm, a top diameter of 3 mm and a height of 4 mm. The molded product was subjected to post curing under the conditions as described above. Thereafter, the shear bond strength (MPa) was measured at a shear rate of 50

μm/s using a bond tester (Nordson Advanced Technology K.K., Series 4000) while maintaining the temperature of the plate at 260°C.

[0180] (4) Water absorption

The disk obtained in (2) as describe above was subjected to the post curing under the conditions as described above. Thereafter, a test of subjecting the disk to an environment of 85°C and 60%RH (relative humidity) for 168 hours was performed. The mass of the disk before and after the test was measured, and the water absorption was calculated by the following formula.

Water absorption (% by mass) = (mass of disk after test - mass of disk before test) / mass of disk before test × 100

[0181] (5) Reflow resistance

A 80-pin flat package (QFP) with a copper-alloy (Pd-PPF) lead frame having a size of 20 mm ×14 mm ×2 mm, on which a silicon chip having a size of 8 mm ×10 mm× 0.4 mm was mounted, was used for the evaluation of reflow resistance.

The package was molded using the epoxy resin molding material for sealing under the conditions as described above, and subjected to post curing under the conditions as described above.

Thereafter, the package was subjected to a moist environment of 85°C and 60%RH for 168 hours. Thereafter, a reflow process was performed at predetermined temperatures (250°C, 260°C and 270°C) for 10 seconds, respectively. Thereafter, the existence or non-existence of cracking at an outer surface of the package was visually observed, and the existence or non-existence of the separation inside the package was observed with an ultrasonic flaw detector (Hitachi Construction Machinery Co., Ltd., HYE-FOCUS). The reflow resistance was evaluated based on the total number of packages in which either the clacking or the separation occurred, with respect to the number of the packages tested (10).

[0182] Table 3

		Examples														
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Evaluation	Spiral flow (cm)	145	125	108	116	119	123	120	118	132	146	135	115	128	122	121
	Hardness at heat	76	73	71	71	73	76	78	79	71	70	71	76	73	74	74
	Shear bond strength at 260℃	0.48	0.49	0.47	0.45	0.43	0.39	0.35	0.29	0.53	0.45	0.47	0.51	0.51	0.45	0.47
	Water absorption (%)	0.23	0.19	0.18	0.16	0.19	0.19	0.17	0.18	0.17	0.23	0.20	0.16	0.18	0.20	0.19
	Reflow resistance (250℃)	0/10	0/10	0/10	0/10	0/10	0/10	0/10	6/10	0/10	0/10	0/10	0/10	0/10	0/10	0/10
	Reflow resistance (260℃)	7/10	0/10	2/10	3/10	4/10	5/10	9/10	10/10	0/10	5/10	2/10	0/10	0/10	1/10	0/10
	Reflow resistance (270℃)	10/10	3/10	8/10	7/10	9/10	10/10	10/10	10/10	0/10	10/10	6/10	0/10	2/10	7/10	6/10

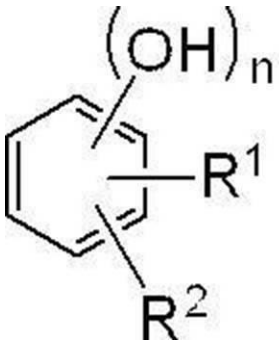
[0183] Table 4

		Comparative Examples							
		1	2	3	4	5	6	7	8
Evaluation	Spiral flow (cm)	135	117	102	109	108	140	129	108
	Hardness at heat	81	79	77	77	78	76	77	80
	Shear bond strength at 260℃	0.22	0.24	0.21	0.23	0.25	0.19	0.22	0.26
	Water absorption (%)	0.24	0.19	0.19	0.18	0.21	0.24	0.22	0.17
	Reflow resistance (250℃)	10/10	10/10	10/10	10/10	10/10	10/10	10/10	10/10
	Reflow resistance (260℃)	10/10	10/10	10/10	10/10	10/10	10/10	10/10	10/10
	Reflow resistance (270℃)	10/10	10/10	10/10	10/10	10/10	10/10	10/10	10/10

[0184] As shown in Tables 3 and 4, Examples 1 to 15, in which the curable resin composition includes any of specific phenol novolac resins 1 to 4, exhibit improved adhesion with respect to metal (Pd-PPF) as compared with Comparative Examples 1 to 8, in which the curable resin composition does not include a specific phenol novolac resin. Further, Examples 1 to 15 exhibit improved reflow resistance.

CLAIMS

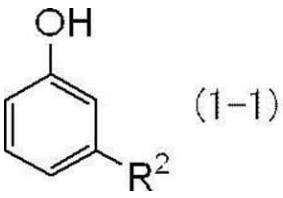
1. A curable resin composition, which is in a solid state at 25°C in an atmospheric pressure and used as a sealing material for an electronic component device, comprising an epoxy resin and a curing agent, the curing agent comprising a phenol novolac resin having a structural unit derived from a phenol compound represented by the following Formula (1), the phenol novolac resin having a hydroxy equivalent of from 70 g/eq to 223 g/eq:



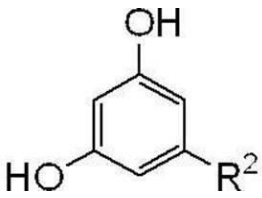
(1)

wherein, in Formula (1), R^1 represents a hydrogen atom or a methyl group, R^2 represents an aliphatic hydrocarbon group having 10 to 18 carbon atoms, and n represents an integer 1 or 2.

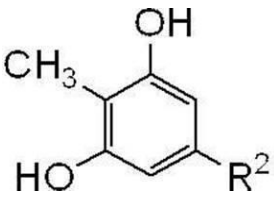
2. The curable resin composition according to claim 1, wherein the phenol novolac resin comprises, as the structural unit derived from the phenol compound represented by Formula (1), a structural unit derived from a phenol compound represented by at least one of the following Formula (1-1) to Formula (1-3):



(1-1)



(1-2)



(1-3)

wherein, in Formulae (1-1) to (1-3), R^2 is the same as R^2 in Formula (1).

3. The curable resin composition according to claim 1 or claim 2, wherein the phenol novolac resin further comprises a structural unit derived from a phenol compound other than the phenol compound represented by Formula (1).

4. The curable resin composition according to any one of claim 1 to claim 3, wherein the curing agent further comprises a curing agent other than the phenol novolac resin having a

structural unit derived from a phenol compound represented by Formula (1).

5. An electronic component device, comprising an element and a cured product of the curable resin composition according to any one of claim 1 to claim 4.