

Stabilized Cationically Polymerizable Composition, and Adhesive Film and Conductor Circuit Comprising the Same

Detailed Description of the Invention

Field of the Invention

5 The present invention relates to a stabilized cationically polymerizable composition, and an adhesive film and a conductor circuit comprising the same.

Description of the References

 An epoxy composition (hereinafter optionally referred to as "epoxy resin composition") which contains an organic compound having at least one epoxy
10 group (hereinafter optionally referred to as "epoxy resin", "epoxide" or "epoxy monomer") is widely used in adhesives.

 Such an organic compound having an epoxy group is generally cured or hardened by addition of a curing agent or a hardening agent. In general, a curing agent starts to act immediately or in short time even at room temperatures. In such
15 a case, one-pack type epoxy composition has an inherent problem in shelf stability. Therefore, many of epoxy compositions are provided in the form of two-pack type. In two-pack type, an epoxide and a curing agent are separately kept on the shelf, and they are mixed just before use.

 In many applications, it is desirable that one-pack type epoxy composition
20 prepared by mixing an epoxide and a curing agent should be stable before use and should be cured by heating when in use. If one-pack type epoxy composition can be stored stably until it is actually used, a large batch of such one-pack type epoxy composition can be prepared in advance, so that it becomes possible to take out small portions from the batch for use as required. In other words, the epoxy
25 composition can be stored as one-pack type if the shelf life of the epoxy composition in an uncured state can be prolonged.

 It is generally known that a prolonged shelf life of an epoxy composition leads to a decrease in curing rate in accordance with the prolongation. It becomes necessary to raise the curing temperature to complete the curing reaction after the
30 consumption of all the epoxy groups. However, in cases where the epoxy composition is applied to an adherent having little or no heat resistance, for

example, a general-purpose plastic, it is required that the epoxy composition be cured at a lower temperature to avoid degradation of the adherent material. It is therefore necessary to use a curing agent capable of exhibiting high activity at a low temperature. However, it is not desirable to sacrifice the shelf life of the epoxy composition prior to curing. Thus, achieving high activity at a lower temperature is in contradiction to having a practical long shelf life, and therefore, it is hard for the epoxy composition to have both advantages as above at the same time.

An UV-activated cationic polymerization initiator which exhibits a polymerization initiating activity upon irradiation with UV is used to improve the polymerizability of a cationically polymerizable monomer such as an epoxide at a lower temperature and also to obtain a practical pot life. One of such typical polymerization initiators, a bis-arene type metal complex salt is used. This polymerization initiator does not initiate the cationic polymerization of an epoxy monomer before the irradiation with UV, even when mixed with an epoxy composition. Therefore, it is expected that the epoxy composition will be able to have high shelf stability.

In some cases, thermocompression bonding is needed to the bonding between an epoxy composition and an adherent, as required. For example, thermocompression bonding is carried out where an epoxy composition is applied to an anisotropic conductive adhesive film which is used to electrically connect an electronic circuit substrate such as a flexible printed circuit (or FPC), carrier tape for tape automated bonding (or TAB), printed circuit board (or PCB), glass circuit substrate or the like so as to form a conductive circuit.

The above UV-activated cationic polymerization initiator, once activated upon irradiation with UV, quickly starts the curing of the epoxy composition at a relatively low temperature. After that, the thermocompression bonding is carried out normally at a temperature as relatively low as about 100°C, so that the composition is allowed to flow to form a conductive circuit, and the curing is completed in short time, that is, several tens seconds.

However, in practical use, thermocompression bonding is sometimes carried out after a relatively long period of time has passed since the start of curing

of the epoxy composition by UV. In such a case, a stabilizer must be further added to the epoxy composition so as to inhibit or delay the cationic polymerization of the epoxy monomer. The addition of stabilizers of this type is, of course, also effective to thermal cationic polymerization without UV irradiation.

5 For example, Japanese Kokai Patent Publication No. 10-152600/1998 discloses a resin composition for sealing a semiconductor. The resin composition is prepared by adding a crown ether as a stabilizer to an epoxy monomer. In this publication, it is disclosed that the crown ether stabilizer acts to inhibit the deterioration of the semiconductor which is stored under a high temperature
10 atmosphere. However, the crown ether is typically very hydrophilic because of the presence of oxygen, and thus accelerates an increase in water absorption of the semiconductor-sealing resin composition. As a result, this resin composition has a danger of becoming poor in crack resistance.

 Japanese Kokai Patent Publication No. 4-227625/1992, JPA 8-
15 511570/1996, JPA 8-511572/1996 and EPO 66132241 disclose stabilizers which comprise compounds having coordination nitrogen atoms.

 Japanese Kokai Patent Publication No. 4-227625/1992 discloses a specific stabilizer of extra pure amine added to an epoxy resin composition. JPA 8-
20 511570/1996 discloses a stabilizer of an aromatic amine added to a conductive adhesive composition. EP06613241 discloses a stabilizer having oxygen as coordination atom in addition to nitrogen, which comprises 8-hydroxyquinoline or a 8 position-substitution product thereof.

 However, any of these stabilizers show a tendency to dramatically inhibit the cationic polymerization of the epoxy monomer at a low temperature.
25 Therefore, relatively high temperature and long time frames are required for thermocompression bonding. When thermocompression bonding is performed at a high temperature for long time there is an adverse influence on the productivity and the electrical connection. On the other hand, thermocompression bonding at a relatively low temperature for relatively short time makes it impossible to complete
30 the curing of the composition, and thus, the composition is unstable.

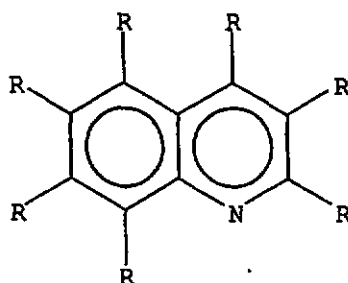
 Therefore, an object of the present invention is to provide a stabilized cationically polymerizable composition which overcomes the foregoing problems.

Another object of the present invention is to provide an adhesive film and a conductor circuit both comprising such cationically polymerizable compositions.

Summary of the Invention

According to the present invention, the foregoing problems can be overcome by providing the following a composition, an adhesive film, and a conductive circuit.

Specifically, the invention provides a cationically polymerizable composition comprising a cationically polymerizable monomer, a cationic polymerization initiator, and a stabilizer comprising a quinoline which is a compound of the formula:



wherein each R is selected independently from a hydrogen atom or an alkyl group, preferably an alkyl group having 1 to 10 carbon atoms;

The invention further provides an adhesive film comprising a thermoplastic material having an epoxy group in the molecule, a cationically polymerizable monomer, a cationic polymerization initiator, and a stabilizer comprising a quinoline of the above formula, and if necessary, an electrically conductive material dispersed therein;

Finally, the invention provides a conductor circuit comprising two adherents carrying conductors on their surfaces, respectively, and the adherents are bonded with the adhesive film of the present invention which contains an electrically conductive material dispersed therein, and are in electrically connection with each other by allowing the conductive materials to contact with each other between the conductors.

Modes for Carrying out the Invention:

Hereinafter, the present invention will be described by way of a preferred embodiment, with reference to the accompanying drawing. However, the following embodiment should not be construed as limiting the scope of the present invention, any way.

Fig. 1 shows a conductor circuit (20) which comprises a pair of electronic circuit substrates (12, 18) (adherents) which are mechanically and electrically connected to each other.

In detail, an adhesive layer (16) is provided between each of the electronic circuit substrates (12, 18) to connect and bond them to each other. According to the present invention, the adhesive layer is formed from a cationically polymerizable composition which essentially comprises a cationically polymerizable monomer, a cationic polymerization initiator, a stabilizer comprising a quinoline of the above formula, and electrically conductive materials (24, 28).

The cationically polymerizable monomer is polymerized to form the matrix of the adhesive layer (16) for bonding and securing the electronic circuit substrates (12, 18) of the conductor circuit (20) to each other.

The cationically polymerizable monomer is generally at least one epoxy resin and/or a material containing vinyl ether. Such a monomer is polymerized in the presence of a cationic polymerization initiator to form a thermocurable resin excellent in adhesion, heat resistance, etc.

Preferable examples of the epoxy resin include cycloaliphatic epoxy resins, bisphenol A epoxy resins, phenolnovolak epoxy resins and the like.

The cycloaliphatic epoxy resins are commercially available under the trade names of ERL-4221 and ERL-4229 from Union Carbide Co., Ltd., and under the trade name of Epoleed GT401 from Daisel Kagaku Kogyo Co., Ltd.

The bisphenol A epoxy resins are commercially available under the trade names of Epicoat 828 and YL 980 from Yuka Shell Epoxy Co., Ltd. The phenolnovolak epoxy resins are commercially available under the trade names of Epicoat 152, Epicoat 154 and CT 128 from Yuka Shell Epoxy Co., Ltd. The vinyl

ether-containing materials are commercially available under the trade names of Rapi-Cure DVE-3 and Rapi-Cure CHVE from I.S.P Japan Co., Ltd.

The cationic polymerization initiator is activated by heat or UV, or electronic beams or other radiation to initiate the polymerization of the cationically polymerizable monomer. Preferred examples of the cationic polymerization initiator include bis-arene metal complex salts such as cyclopentadienyl iron (II) (xylene) hexafluoroantimonate (CpFeXySbF_6) and cyclopentadienyl iron (II) (cumene) hexafluorophosphate (CpFeCmPF_6) because these can initiate the polymerization at low temperatures upon irradiation with UV. The cyclopentadienyl iron (II) (cumene) hexafluorophosphate is commercially available, for example, under the trade name of Ilgacure 261 from Chiba Gaigi, Japan.

In addition, a bis-arene metal complex salt such as bismesitylene iron (II) bis (tris(trifluoromethyl-sulfonylmethide)) (MeFeMeMtd) is included in the preferable cationic polymerization initiators, because this polymerization initiator allows polymerization also by heat.

Among those, the UV-activated cationic polymerization initiators such as cyclopentadienyl iron (II) (xylene) hexafluoroantimonate, even when mixed with cationically polymerizable monomers, do not initiate the cationic polymerization of epoxy monomers, if not irradiated with UV. Therefore, a cationically polymerizable composition containing an UV-activated cationic polymerization initiator can have high shelf stability at room temperatures.

The UV-activated cationic polymerization initiator is not limited to the above examples, and it also include the UV-activated cationic polymerization initiators described in Japanese Kokai Patent Publication No. 8-511572, specifically, $(\eta^5\text{-cyclopentadienyl})(\eta^6\text{-arene})$ complexes as preferred ones.

The curing rate of the cationically polymerizable composition can be properly controlled by addition of the stabilizer.

Generally, the stabilizer traps the cationic polymerization initiator by the coordination atom to thereby prevent the initiation of polymerization of the cationically polymerizable monomer, and thus prolongs the curing time (in other words, open time) of the cationically polymerizable composition. According to the

present invention, the stabilizer comprises a quinoline of the formula described above.

The open time referred to herein means time spent from UV irradiation to thermocompression bonding, in case of the UV-irradiation type cationic polymerization initiator, and it also means time spent from the mixing of the initiator with the cationically polymerizable monomer to the thermocompression bonding, in case of the thermal cationic polymerization initiator.

A quinoline of the above formula has only one nitrogen atom as a coordination atom, differently from 8-hydroxyquinoline described in the part of the prior art. As a result, this quinoline immediately liberates the cationic polymerization initiator which has been trapped by heat having a relatively lower temperature of 90 to 150°C, so that the polymerization of the cationically polymerizable monomer is started in short time. Thus, the cationically polymerizable composition can be cured in short time.

In contrast, 8-hydroxyquinoline liberates the cationic polymerization initiator only by heating at a high temperature of 200 to 250°C because of its very high stability.

According to the present invention, the use of a quinoline of the above formula in combination with the UV-activated cationic polymerization initiator allows the cationically polymerizable composition to be cured at a relatively low temperature and in relatively short time. Also, it is found that the adhesive layer containing this quinoline prevents an increase in connection resistance between each of the substrates through the film and maintains the connection resistance constant.

Specific examples of the quinoline to be used in the present invention are 2-methylquinoline, 3-methylquinoline, 4-methylquinoline, 6-methylquinoline, 7-methylquinoline and 8-methylquinoline. Particularly in case where the quinoline frame has an alkyl group, it is expected that the stabilizing effect for the composition is further improved because of the electron donor effect.

In the present invention, the above quinoline is added as a stabilizer in an adequate amount to the cationic polymerization initiator. Preferably, the amount of the quinoline is 0.001 to one mole based on one mole of the cationic

polymerization initiator. If this amount is less than about 0.001 mole based on one mole of the cationic polymerization initiator, the resultant cationically polymerizable composition tends to have poor shelf stability at room temperatures. On the other hand, if it exceeds about one mole, the resultant cationically polymerizable composition can not be cured at a relatively low temperature and in relatively short time.

Such tendencies of the compositions can be confirmed by using a differential scanning calorimeter (DSC). That is, anyway, a cationically polymerizable composition containing a quinoline in an amount outside the above adequate range tends to show an exothermic peak on the higher temperature side when heated while the temperature being scanned by the DCS.

In the conductor circuit (20) shown in Fig. 1, the conductive particles (28) are generally dispersed in the cationically polymerizable composition. Such conductive particles (the conductive substance (24) in Fig. 1) contact one another between the conductors (10, 14) functioning as electrodes, thereby electrically connecting the electrodes to each other while the cationically polymerizable composition is being cured. In other words, the adhesive layer has conductivity (anisotropic conductivity) in the thickness direction.

The conductive substance is generally in the form of particles of a conductive metal or alloy (e.g., silver, copper, nickel, gold, tin, zinc, platinum, palladium, iron, tungsten, molybdenum, solder or the like) or graphite or graphitized carbon. The conductive substance is not limited to the above examples, and it may be a non-conductive particle coated with the above metal, alloy, graphite or graphitized carbon.

The proportion of the conductive substance to the cationically polymerizable composition of the present invention is not particularly limited, however, it is generally 0.1 to 30 vol. %, preferably 0.5 to 10 vol. %, more preferably 1 to 5 vol. % based on the volume of the composition.

When this proportion is smaller than about 0.1 vol. %, there is a tendency that no conductive particle may be present on the electrodes in the course of bonding. On the other hand, when it exceeds about 30 vol. %, there is a tendency that a short circuit often may occur between each of the adjacent electrodes.

The cationically polymerizable composition of the present invention generally has relatively high flowability. Thus, a thermoplasticizer may be added to the composition, as required, so as to mold an adhesive film having plasticity and flexibility.

5 It is desirable to use a thermoplastic elastomer as the thermoplasticizer in order to improve the film-forming property of the composition and the impact resistance of the resultant adhesive film and to relieve the internal stress which occurs because of the curing reaction. A styrene thermoplastic elastomer is particularly preferred, because it can impart heat resistance to the adhesive film.

10 Further, it is preferable that a styrene thermoplastic elastomer has an epoxy group in the molecule, because the epoxy group participates in the curing reaction of the cationically polymerizable monomer to improve the cohesion of the resultant adhesive film. The styrene thermoplastic elastomers having epoxy groups in the molecules are commercially available under the trade names of Epofriend A1010

15 and CT128 from Daisel Kagaku Kogyo Co., Ltd.

In this regard, a thermoplastic resin having a glass transition temperature (T_g) lower than the thermocompression bonding temperature (e.g., a polystyrene resin) may be used instead of the elastomer, in view of flowability.

The cationically polymerizable composition of the present invention may

20 contain the components which have been added to conventional cationically polymerizable compositions, in addition to the above components. Such components are a cationic polymerization accelerator, antioxidant, additives such as silane coupling agent and the like, modifier such as diol and viscosity builder, and the like.

25 The conductor circuit of the present invention is formed as follows by a known method.

First, an anisotropic conductive adhesive film in which conductive particles are dispersed is applied to one of a pair of electronic circuit substrates and bonded thereto under thermocompression. Next, the anisotropic conductive adhesive film

30 bonded to the above substrate is irradiated with UV, and the other electronic circuit substrate is applied to the exposed surface of the adhesive film, and the lead wires of both electronic circuit substrates are aligned with each other. Then, both

electronic circuit substrates are further subjected to thermocompression bonding through the anisotropic conductive adhesive film. Thus, the conductor circuit is provided. According to the present invention, the thermocompression bonding is completed at a relatively low temperature and in relatively short time as mentioned
5 above, because a quinoline of the above formula is added to the composition.

Examples

Hereinafter, the present invention will be described in more detail by way of Examples, which should not be construed as limiting the scope of the present invention, any way.

10 Preparation of Cationically Polymerizable Composition

Example 1

First, cyclopentadienyl iron (II) (xylene) hexafluoroantimonate (CpFeXySbF_6) (an UV-activated cationic polymerization initiator) (0.01 g) was added to γ -butyrolactone (solvent) (0.03 g) on a cylindrical aluminum pan, and
15 thoroughly dissolved therein to prepare a solution for an initiator. A liquid multi-functional cycloaliphatic epoxy resin having an epoxy equivalent of 176 (under the trade name of ERL-4221 from Union Carbide Co., Ltd.) (2 g) was mixed with a quinoline (stabilizer) (0.001 g, 0.36 moles based on one mole of the initiator) to prepare a monomer solution. Then, the monomer solution was added to the
20 initiator solution on the aluminum pan, and the mixture was sufficiently stirred to prepare a cationically polymerizable composition.

Comparative Example 1

Example 1 was repeated to prepare a cationically polymerizable composition, except that no quinoline was added.

25 Evaluation of Cationically Polymerizable Composition

The cationically polymerizable compositions prepared in Example 1 and Comparative Example 1 were evaluated as follows.

Thermal Analysis

The cationically polymerizable composition (about 10 mg) was placed on a
30 cylindrical aluminum pan for use in DCS measurement, and the composition was

evenly irradiated with UV having a central wavelength at 365 nm, for 15 secs., using an UV irradiating machine having an output of 400 mW/cm² (manufactured by Hamamatsu Photonix Co., Ltd., equipped with an UV spot light source L5662-01 and an infrared cut filter), so as to activate the initiator.

- 5 In the course of curing, the surface temperature of the cationically polymerizable composition was kept at 30°C or lower, using dry air. This is done to prevent the acceleration of curing of the cationically polymerizable composition due to heat generated by infrared rays.

 The behavior of the cationically polymerizable composition to heat was
10 found as follows.

 Using a DSC (differential scanning calorimeter) (DSC 7 and a thermal analysis calorimeter TAC 7/DX) manufactured by PERKIN ELMER, the cationically polymerizable composition was heated from 10°C to 300°C at a heating rate of 10°C/min.,

- 15 1) immediately after the irradiation with UV,
 2) after left to stand alone at 25°C for 30 mins. in the dark after the irradiation with UV, or
 3) after left to stand alone at 100°C for 10 mins. in the dark after the irradiation with UV.

20 Then, the following a), b) and c) under the above conditions 1), 2) and 3) were found:

- a) the reaction-initiating temperature called the onset temperature of an exothermic peak (T_{onset} (°C)),
 b) the peak temperature (T_{peak} (°C)) of an exothermic peak, and
25 c) a value of integration of an exothermic peak (ΔH (J/g)) which indicates the calorific value of the cationically polymerizable composition.

 The results are shown in Table 1.

Table 1

Example 1	Condition	T _{onset} (°C)	T _{peak} (°C)	ΔH(J/g)
	1)	67	81	568
	2)	67	81	567
	3)	No exothermic peak		
Comparative Example 1	Condition	T _{onset} (°C)	T _{peak} (°C)	ΔH(J/g)
	1)	35	57	564
	2)	44	67	376
	3)	No exothermic peak		

It was found from the results of Table 1 that the cationically polymerizable composition of Example 1 maintained substantially the initial calorific value after left to stand alone at 25°C for 30 mins. after the UV-activated cationic polymerization initiator had been activated by UV. Therefore, it was revealed that the cationically polymerizable composition of Example 1 was kept stable because the polymerization thereof was inhibited. In addition, no exothermic peak was observed by the DSC after the cationically polymerizable composition had been left to stand alone at 100°C for 10 mins. Therefore, it was known that the cationically polymerizable composition was sufficiently cured at 100°C. Further, the cationically polymerizable composition of Example 1 had an exothermic peak temperature 20°C or more higher than that of the cationically polymerizable composition of Comparative Example 1, immediately after the irradiation with UV. This result indicates that the addition of the quinoline was effective to improve the stability of the cationically polymerizable composition at room temperatures.

In contrast, it was revealed that the calorific value of the cationically polymerizable composition of Comparative Example 1 decreased after the composition had been left to stand alone at 25°C for 30 mins. after the activation of the UV-activated cationic polymerization initiator by the irradiation with UV, as compared with that found immediately after the irradiation with UV. Therefore, it was known that addition of no quinoline allowed the polymerization of the polymerizable composition, and that the composition had poor shelf stability.

Measurement of Gelling Time

The time required for the cationically polymerizable composition to form gel by heating (gelling time) was measured as follows.

The cationically polymerizable composition (2 g) was irradiated with UV in the same manner as in the test of thermal analysis as above. Then, the cationically polymerizable composition was placed on a cylindrical aluminum pan.

Next, the aluminum pan was put on a hot plate of 40°C to measure the time in which gel was formed at this temperature. The formation of gel was estimated by an increase in the viscosity of the cationically polymerizable composition. In case where no increase in the viscosity of the composition was observed at 40°C even after one hour had passed, the hot plate was heated to 100°C, and the time in which gel was formed at this temperature was measured. The gelling time is shown in Table 2.

Table 2

	Gelling time	
	40°C	100°C
Example 1	One hr. or more	one min.
Comparative Example 1	one min.	-

15

It was found from the results of Table 2 that the cationically polymerizable composition of Example 1 did not form gel even after the heating at 40°C for one hour but started to form gel at 100°C. On the other hand, it was found that the cationically polymerizable composition of Comparative Example 1 started to form gel at 40°C.

20

Therefore, it was revealed that, according to the present invention, the addition of an adequate amount of quinoline in combination with an UV-activated polymerization initiator is effective to prolong the open time from the UV irradiation to the thermal curing by heat treatment, and that the quinoline did not inhibit the polymerization while the composition was being cured by heat treatment.

25

The following Example and Comparative Example illustrate the effects of the present invention in thermal cationic polymerization.

Example 2

Example 1 was repeated to prepare a cationically polymerizable composition, except that bis-mesitylene iron (II) bis(tris(trifluoromethylsulfonylmethide)) (MeFeMeMtd) as a thermal cationic polymerization initiator was used instead of the cyclopentadienyl iron (II) (xylene) hexafluoroantimonate (CpFeXySbF₆) as an UV-activated cationic polymerization initiator, and that bisphenol A epoxy resin (2 g) having an epoxy equivalent of 189 (under the trade name of YL 980, manufactured by Yuka Shell Epoxy Co., Ltd.) was used instead of the multifunctional cycloaliphatic epoxy resin (2 g). In this case, the amount of quinoline was 0.87 mole based on one mole of the thermal cationic polymerization initiator.

Comparative Example 2

Example 2 was repeated to prepare a cationically polymerizable composition, except that no quinoline was added.

The cationically polymerizable compositions prepared in Example 2 and Comparative Example 2 were subjected to thermal analysis and gelling time-measurement in the same manners as in Example 1.

In this regard, the thermal analysis using a DSC was conducted under the following conditions 4) to 6) instead of the conditions 1) to 3) so as to measure a) the reaction-starting temperature (T_{onset} (°C)); b) the temperature of an exothermic peak (T_{peak} (°C); and c) a value of integration (ΔH (J/g)) of the exothermic peak.

Conditions for Thermal Analysis:

- 4) Immediately after the mixing of a monomer solution containing a quinoline stabilizer and a bisphenol A epoxy resin with a polymerization initiator solution.
- 5) After the solution mixture was left to stand alone at 25°C in the dark for 30 minutes after the mixing of the monomer solution with the polymerization initiator solution.
- 6) After the solution mixture was left to stand alone at 150°C in the dark for 10 minutes after the mixing of the monomer solution with the polymerization initiator solution.

Regarding the gelling time-measurement, in case where no increase in the viscosity of the composition was found after one hour had passed at 40°C, the hot plate was heated to 150° instead of 100°C so as to measure the gelling time at this temperature.

5 The results are shown in Table 3.

Table 3

Example 2	Condition	T _{onset} (°C)	T _{peak} (°C)	ΔH(J/g)
	4)	104	147	525
	5)	104	156	521
	6)	No exothermic peak		
Comparative Example 2	Condition	T _{onset} (°C)	T _{peak} (°C)	ΔH(J/g)
	4)	98	148	530
	5)	104	146	469
	6)	No exothermic peak		

It was found from the results of Table 3 that the cationically polymerizable composition of Example 2 maintained substantially the initial calorific value even
 10 after the composition had been left to stand alone at 25°C for 20 minutes after the activation of the heat-activated cationic polymerization initiator. Therefore, it was revealed that the cationially polymerizable composition of Example 2 was inhibited from being polymerized and was kept stably. In addition, no exothermic peak was observed in this composition by the DSC measurement after the
 15 composition had been left to stand alone at 150°C for 10 minutes. Therefore, it was confirmed that the cationically polymerizable composition had been sufficiently cured at 150°C.

On the other hand, it was revealed that the cationically polymerizable composition of Comparative Example 2 showed a decrease in the calorific value
 20 after left to stand alone at 25°C for 30 minutes after the activation of the heat-activated cationic polymerization initiator, as compared with that found immediately after the mixing. Therefore, it was known that, when no quinoline was added, the polymerization proceeded without any inhibition, and that the shelf stability of the composition became poor.

The gelling time of the cationically polymerizable compositions of Example 2 and Comparative Example 2 was measured in the same manner as in Example 1. The results are shown in Table 4.

Table 4

	Gelling time	
	40°C	100°C
Example 2	one hour or more	Immediately after the mixing
Comparative Example 2	Immediately after the mixing	--

It was found from the results of Table 4 that the cationically polymerizable composition of Comparative Example 2 started to form gel at 40°C and that the cationically polymerizable composition of Example 2 did not form gel at 40°C but started to form gel at 150°C.

Therefore, it was revealed that the addition of an adequate amount of a quinoline contributes to the stabilization of the cationically polymerizable composition, and also that the quinoline did not inhibit the polymerization while the composition was being thermally cured by heat treatment.

Next, the effects of an anisotropic conductive adhesive film of the present invention which contains an UV-activated cationic polymerization initiator will be described.

Construction of Anisotropic Conductive Adhesive Film

Example 3

An anisotropic conductive adhesive film was constructed using the components shown in the formulation of Table 5, as follows.

First, an epoxy resin having an epoxy equivalent of 219, an epoxy resin having an epoxy equivalent of 178, two kinds of thermoplastic elastomers each having an epoxy group in the molecule, and bisphenoxyethanolfulorene were homogeneously dissolved in tetrahydrofuran (THF). Then, conductive particles were added to this solution and stirred and dispersed therein to prepare a monomer solution.

On the other hand, two kinds of UV-activated cationic polymerization initiators, namely, cyclopentadienyl iron (II) (xylene) hexafluoroantimonate (CpFeXySbF_6) and cyclopentadienyl iron (II) (qumene) hexafluorophosphate (CpFeCmPF_6), a quinoline (stabilizer), di-*t*-butyloxalate (reaction accelerator), a
5 silane coupling agent and THF were homogeneously mixed in a light-screening bottle to prepare a polymerization initiator solution.

Next, the polymerization initiator solution and the monomer solution were homogeneously mixed to prepare a solution mixture. The solution mixture was applied to a silicone-treated polyester film substrate to coat it, using a knife coater.
10 Then, the coating of the solution mixture together with the polyester film was dried by heating at 55°C for 13 minutes to obtain an anisotropic conductive adhesive film with a thickness of 38 μm .

Example 4

Example 3 was repeated to obtain an anisotropic conductive adhesive film
15 with a thickness of 38 μm , except that the amount of the quinoline was increased from 0.008 g to 0.0016 g as shown in Table 5.

Comparative Example 3

Example 3 was repeated to obtain an anisotropic conductive adhesive film with a thickness of 38 μm , except that no quinoline was added.

Table 5

	Example 3	Example 4	Comparative Example 3
Epoxy resin ¹⁾ (epoxy equivalent of 219)	4.0 g	4.0 g	4.0 g
Epoxy resin ²⁾ (epoxy equivalent of 178)	1.0 g	1.0 g	1.0 g
Styrene-based thermoplastic elastomer ³⁾ (epoxy equivalent of 1000)	3.0 g	3.0 g	3.0 g
Styrene-based thermoplastic elastomer ⁴⁾ (epoxy equivalent of 570)	2.0 g	2.0 g	2.0 g
Bisphenoxyethanolfluorene ⁵⁾	0.5 g	0.5 g	0.5 g
THF(for monomer solution)	12 g	12 g	12 g
Conductive paritcle ⁶⁾	1.5 g	1.5 g	1.5 g
CpFeXySbF ₆	0.010 g	0.010 g	0.010 g
CpFeCmPF ₆ ⁷⁾	0.048 g	0.048 g	0.048 g
Quinoline ⁸⁾ (equivalent to catalyst)	0.008 g (0.48)	0.016 g (0.96)	0 g (0)
Di-t-butyloxalate	0.060 g	0.060 g	0.060 g
Silane coupling agent ⁹⁾	0.20 g	0.20 g	0.20 g
THF (for initiator solution)	0.60 g	0.60 g	0.60 g

Notes:

- 1) Epoleat (trade name) GT401 (Disel Kagaku Kogyo Co., Ltd.)
- 2) Epicoat (trade name) 152 (Yuka Shell Epoxy Co., Ltd.)
- 3) Epofriend (trade name) A1010 (Disel Kagaku Kogyo Co., Ltd.)
- 4) Epofriend (trade name) CT128 (Disel Kagaku Kogyo Co., Ltd.)
- 5) BPEF (Osaka Gas Chemical Co., Ltd.)
- 6) 6GNM5-Ni (Nippon Kagaku Kogyo Co., Ltd.; gold plated nickel paritcles; average particle diameter of 6 μ m)
- 7) Ilgacure (trade name) 261 (Chiba Gaigy, Japan)
- 8) Wako Junyaku Kogyo Co., Ltd.
- 9) γ -Glysidoxypyltrimethoxysilane (Nippon Unica Co., Ltd., "A187")

Evaluation of Anisotropic Conductive Adhesive Film

Next, circuit connection test pieces having conductor circuits were constructed as follows, using the anisotropic conductive adhesive films of Examples 3 and 4 and Comparative Example 3. Then, the connection resistance between each of the circuit substrates through each anisotropic conductive adhesive film was measured so as to evaluate the performance of each circuit connection test piece.

Construction of Circuit Connection Test Piece

One hundred and ninety-six lead wires of copper conductors with width of 200 μm plated with gold with thickness of 35 μm were arranged at pitches of 400 μm on a glass epoxy substrate with thickness of 0.6 mm (FR4, Kyoden Co., Ltd.) to prepare a printed circuit board (PCB).

The anisotropic conductive adhesive film together with the polyester film substrate was cut into pieces of 3 mm (width) X 4 cm (length) and such a piece was applied to the above printed circuit board (PCB) with the anisotropic conductive adhesive film facing to the lead wires on the PCB.

The printed circuit board (PCB) with the anisotropic conductive adhesive film/the polyester film applied thereon was heated and subjected to thermocompression bonding for 4 secs. while the temperature being kept at 50°C. Then, the substrate was removed to expose the anisotropic conductive adhesive film.

Next, the exposed surface of the anisotropic conductive adhesive film was irradiated with UV for 10 secs., using the above UV-irradiating apparatus. During the irradiation, the anisotropic conductive adhesive film was air-cooled so that heat could not be applied thereto so as to inhibit the proceeding of thermal curing.

Separately, 196 lead wires of copper with a width of 200 μm plated with tin with a thickness of 18 μm were arranged on a polyimide film with a thickness of 75 μm at pitches of 400 μm to construct a flexible printed circuit board (FPC). The anisotropic conductive adhesive film applied on the above printed circuit board was applied and bonded to the lead wire-arranged surface of the FPC. In this stage, the lead wires of the PCB and those of the FPC were aligned with each other.

After that, while the anisotropic conductive adhesive film was being heated and kept at 85°C, a pressure of 1.2 MPa was applied to the anisotropic conductive adhesive film through the PCB and the FPC for 12 secs. for thermocompression bonding. Thus, a circuit connection test piece (conductor circuit) was completed.

Measurement of Connection Resistance

Next, the connection resistance between the FPC and the PCB of the circuit connection test piece was measured under the following conditions 7) and 8), using MILLIOHMMETER (HEWLETT PACKERD Co., Ltd.). The maximal values of the connection resistances measured are shown in Table 6.

7) The FPC and the PCB were subjected to thermocompression bonding immediately after the irradiation with UV.

8) The FPC and the PCB were subjected to thermocompression bonding after the anisotropic conductive adhesive film was left to stand alone at 30°C under a 70% RH atmosphere for 30 mins. after the irradiation with UV.

Table 6

	Example 3	Example 4	Comparative Example 3
Stabilizer	Quinoline	Quinoline	None
Amount(mol) of stabilizer to one mol of initiator	0.48	0.96	--
Maximal value of connection resistance (mΩ)			
Immediately after UV irradiation	0.335	0.398	0.351
After 30 mins. under atmosphere of 70% RH at 30°C	0.336	0.335	0.676

It was found from the results of Table 6 that the anisotropic conductive adhesive films of Examples 3 and 4 according to the present invention showed substantially no change in the maximal values of connection resistance even after left to stand alone at 30°C under the atmosphere of 70% RH for 30 mins. after the irradiation with UV.

In contrast, it was found that the anisotropic conductive adhesive film of Comparative Example 3 showed a large change in the maximal value of connection resistance.

Effect of the Invention

The cationically polymerizable composition of the present invention has excellent stability because of containing a quinoline as a stabilizer, and therefore, this composition can be prepared as one-pack type curable composition, and also
5 does not inhibit the polymerization of the cationically polymerizable monomer while being cured. Further, the cationically polymerizable composition of the present invention can be bonded to an adherent under thermocompression at a relatively low temperature and in relatively short time, and further, this composition exhibits an excellent thermocompression bonding property even after
10 long time has passed since the start of curing. Therefore, this composition is suitable for use in thermocompression bonding of an adherent having a conductor on the surface, for example, a printed circuit board.

Brief Description of the Drawing

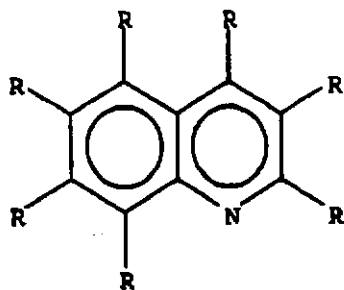
Fig. 1 is a schematic sectional view of a conductor circuit of the present
15 invention.

Description of Reference Numbers

- 10 or 14 = a conductor
- 12 or 18 = an electronic circuit substrate
- 20 = a conductor circuit
- 20 24 or 28 = a conductive substance

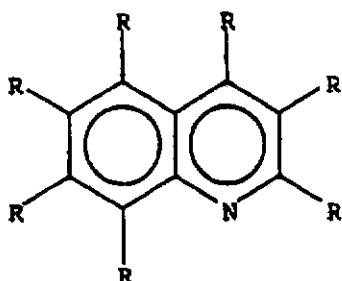
CLAIMS

1. A cationically polymerizable composition comprising
a cationically polymerizable monomer,
a cationic polymerization initiator,
a stabilizer comprising a quinoline,
characterized in that said quinoline is a compound of the formula:



wherein R is independently selected from a hydrogen atom or an alkyl group, and
an electrically conductive material dispersed therein.

2. A cationically polymerizable composition according to claim 1 wherein said alkyl group contains 1 to 10 carbon atoms.
3. A cationically polymerizable composition according to claim 1 wherein said cationically polymerizable monomer comprises at least one material selected from an epoxy resin and a material containing vinyl ether.
4. An adhesive film comprising
a thermoplastic material having an epoxy group in the molecule,
a cationically polymerizable monomer,
a cationic polymerization initiator,
a stabilizer comprising a quinoline,
characterized in that said quinoline is a compound of the formula:



wherein each R is independently selected from a hydrogen atom or an alkyl group, and an electrically conductive material dispersed therein.

5. The adhesive film according to claim 4 wherein said cationically polymerizable monomer comprises at least one material selected from an epoxy resin and a material containing vinyl ether.

6. A conductor circuit comprising two adherents carrying conductors on their surfaces, respectively, said adherents being bonded with an adhesive film according to claim 4, and being in electrically connection with each other by allowing said conductive materials to contact with each other between said conductors.

7. A cationically polymerizable composition according to claim 1 wherein the quinoline is selected from the group consisting of 2-methylquinoline, 3-methylquinoline, 4-methylquinoline, 6-methylquinoline, 7-methylquinoline and 8-methylquinoline.

8. An adhesive film according to claim 4 wherein the quinoline is selected from the group consisting of 2-methylquinoline, 3-methylquinoline, 4-methylquinoline, 6-methylquinoline, 7-methylquinoline and 8-methylquinoline.