

Adhesive Composition and Precursor Thereof

BACKGROUND OF THE INVENTION

Technical Field of Invention

5 The present invention relates to an adhesive composition having improved non-combustibility. The present invention also relates to an adhesive precursor composition useful as a starting material for the adhesive composition.

Description of the Related Art

10 It is known that a film formed of an adhesive composition comprising a combination of various thermoplastic resins with an epoxy resin as a thermosetting resin is used as an adhesive film for protecting FPC (flexible printed circuit wiring board) (see, for example, Japanese Unexamined Patent Publication (Kokai) Nos. 9-132710, 9-125037, 5-5085, 3-6280, 2-145676, 62274690, 60-130666, 1-135844, and 61-43550).

15 Among various adhesive films disclosed in the above publications, an adhesive film formed of a composition comprising a phenoxy resin, an epoxy resin, and a curing agent possesses heat resistance, adhesion to metallic parts and other properties and hence has been regarded as useful in the art. A dicyandiamide has been used as the curing agent because of its potential for curability. Further, polyester resins and various elastomers are disclosed to be usable as the thermoplastic resin.

20 The adhesive composition according to the above formulation (the adhesive composition composed mainly of a phenoxy resin, an epoxy resin, and a dicyandiamide curing agent), however, has low non-combustibility and, in particular, cannot satisfy the non-combustibility requirement (VO) specified in UL standards. Regarding the adhesive film for protection of FPC, a further reduction in a change in dimension caused by stress
25 created in the course of heat curing, that is, a further improvement in dimensional stability, has been required in the art. The above-described conventional adhesive compositions, however, cannot meet this requirement without great difficulty.

30 On the other hand, in a general field of resin compositions, addition of brominated epoxy resin in combination with antimony pentaoxide to improve the noncombustibility of the resin compositions is a method known in the art. This method comprises mixing an antimony pentaoxide powder with the resin component to form a non-combustible

composition. An antimony pentaoxide powder is relatively inexpensive and can contribute to a lowering in product price in addition to an improvement in non-combustibility. Due to the size of the powder, however, it has a problem. Specifically, since the average particle diameter of the antimony pentaoxide powder is generally not less than 0.5 μ m, the antimony pentaoxide powder is likely to settle by gravity in a mixed liquid composed of an effective amount of the antimony pentaoxide powder, a resin component, and a solvent, making it difficult to prepare a composition wherein the components are intimately mixed with one another. Heterogeneous dispersion of the components in the adhesive composition leads to deteriorated adhesive strength and dimensional stability and unfavorably results in remarkably deteriorated properties as an adhesive for the adhesive film for protection of FPC. In other words, in the field of the adhesive composition, an adhesive composition, which contains antimony pentaoxide, in a dispersed state, in an amount necessary for satisfying the VO requirement (in general, not less than 3 % by weight based on the whole composition) while enjoying excellent adhesive properties (such as adhesive properties and dimensional stability) and further contains a phenoxy resin, an epoxy resin, and a curing agent, has never been known in the art.

Problems to be Solved by Invention

Accordingly, the present invention provides an adhesive composition, comprising a phenoxy resin, an epoxy resin, and a curing agent, which possesses non-combustibility good enough to pass the VO requirement and excellent adhesive performance (such as adhesive properties and dimensional stability) as an adhesive for an adhesive film for an FPC protection film.

The present invention also provides an adhesive composition precursor useful as a starting material for such an excellent adhesive composition.

Means for Solving the Problems

According to one aspect of the present invention, there is provided an adhesive composition containing a resin component, the resin component comprising a phenoxy resin, an epoxy resin, and a dicyandiamide, the epoxy resin comprising a brominated epoxy resin, the resin component containing colloidal particles of antimony pentaoxide

dispersed therein, the total amount of the brominated epoxy resin and the colloidal particles of antimony pentaoxide being in the range of 13 to 60% by weight based on the total amount of the adhesive composition.

According to another aspect of the present invention, there is provided an adhesive composition precursor which, after drying, provides the above adhesive composition, the adhesive composition precursor comprising a mixture of (i) the resin component, (ii) an antimony pentaoxide sol comprising a dispersing medium, containing methyl ethyl ketone, and dispersed in the dispersing medium, the colloidal particles of antimony pentaoxide, and (iii) a solvent containing methanol, the weight ratio of methanol (MEOH) to methyl ethyl ketone (MEK) in the mixture, MeOH/MEK, being in the range of 0.005 to 0.4.

Embodiments in the Practice of the Invention

The function and preferred embodiments of the present invention will be described.

The adhesive composition of the present invention is a composition comprising a resin component, the resin component comprising a phenoxy resin, an epoxy resin, and a dicyandiamide as a curing agent, wherein the brominated epoxy resin and the colloidal particles of antimony pentaoxide (hereinafter often referred to as "antimony pentaoxide particles") are contained in the above specific proportion, that is, so that the total amount of the brominated epoxy resin and the colloidal particles of antimony pentaoxide is in the range of 13 to 60% by weight based on the total amount of the adhesive composition. When the total amount of the brominated epoxy resin and the antimony pentaoxide particles is less than 13% by weight based on the whole adhesive composition, the adhesive composition generally does not satisfy the V0 requirement. On the other hand, when it exceeds 60% by weight, the adhesive strength may be lowered. For example, when use of the adhesive composition as an adhesive for an adhesive film for protection of FPC is contemplated, the strength of bonding particularly to copper should be enhanced. Incorporation of the brominated epoxy resin and the antimony pentaoxide particles in excess amount results in lowered adhesive strength.

The term "resin component" used herein refers to a mixture composed of a phenoxy resin, an epoxy resin, a dicyandiamide, and optionally an additional components and containing neither a solvent nor inorganic particles. Suitable additional components

include (i) thermoplastic polymers, such as polyesters and acrylic elastomers, (ii) curing agents, other than the dicyandiamide, and curing accelerators, and (iii) additives, such as tackifiers and plasticizers. Further, the epoxy resin may comprise either a brominated epoxy resin alone or a mixture of a brominated epoxy resin with a non-brominated epoxy resin. The term "brominated epoxy resin" used herein refers to an epoxy resin with a bromine atom introduced into the molecule, for example, one having such a structure that one or more hydrogen atoms on a benzene ring within the molecule of a bisphenol type epoxy resin has been substituted by a bromine atom. In the present specification, an epoxy resin other than the "brominated epoxy resin" is expressly defined as "non-brominated epoxy resin."

As described above, since the antimony pentaoxide particles are contained in the form of colloidal particles, the antimony pentaoxide particles do not settle by gravity in the dispersion containing the antimony pentaoxide particles and can be stably dispersed. Therefore, in the adhesive composition of the present invention prepared by drying this type of a dispersion can realize such a state that the components have been intimately mixed with one another, enabling the adhesive strength and the dimensional stability to be effectively improved.

The "colloidal particles of antimony pentaoxide" are generally fine particles of antimony pentaoxide having an average particle diameter in the range of 1 to 100 nm. In practicing the present invention, preferably, an antimony pentaoxide sol is mixed with the resin component so that the colloidal particles are contained in a dispersed state in the resin component.

As described above, in order to further effectively improve the non-combustibility, the adhesive properties, and the dimensional stability of the resultant adhesive composition, the content of the antimony pentaoxide is generally not less than 3% by weight, preferably not less than 4% by weight, particularly preferably not less than 5% by weight based on the whole adhesive composition.

On the other hand, an adhesive composition precursor, comprising a mixture of: a resin component comprising a phenoxy resin, an epoxy resin, and a dicyandiamide as a curing agent; an antimony pentaoxide sol comprising colloidal particles of antimony pentaoxide; and optionally a solvent, is suitable as a starting material for the above

adhesive composition. Since this adhesive composition precursor contains antimony pentaoxide particles as the antimony pentaoxide sol, a stably dispersed state can be easily realized. Further, the content of the antimony pentaoxide particles can be easily increased, for example, to not less than about 5% by weight based on the whole adhesive composition with satisfactory results.

According to the present invention, a precursor suitable as the above adhesive composition precursor comprises a mixture of (i) the resin component, (ii) an antimony pentaoxide sol comprising a dispersing medium, containing methyl ethyl ketone, and dispersed in the dispersing medium, the colloidal particles of antimony pentaoxide, and (iii) a solvent containing methanol, the weight ratio of methanol (MeOH) to methyl ethyl ketone (MEK) in the mixture, MeOH/MEK, being in the range of 0.005 to 0.4.

In this adhesive composition precursor, intimate mixing of the components with one another can be particularly easily realized, and the amount of the residual solvent can be minimized. The reason for this will be described.

The dicyandiamide can be dissolved in only limited solvents, and, in many cases, resins, such as phenoxy resin and epoxy resin, are sparingly soluble in good solvents for the dicyandiamide. Therefore, in the adhesive composition prepared by drying the liquid containing the resin component and the antimony pentaoxide particles, the selection of the kind of the solvent is important for the formation of the above homogeneous dispersion structure.

For example, a mixed solvent composed of methyl ethyl ketone, dimethylformamide, and methyl cellosolve is useful as the above solvent. In this connection, the present inventors have actually confirmed that a solid composition prepared by drying a mixed liquid composed of the mixed solvent and the above resin component (comprising a phenoxy resin, an epoxy resin, and a dicyandiamide) can develop a homogeneous structure capable of realizing good adhesive properties and dimensional stability because the dicyandiamide, after it is once dissolved, is precipitated as a fine crystal.

In the above mixed solvent, however, dimethylformamide and methyl cellosolve have low evaporation rate, and drying at a relatively low temperature for a relatively short period of time causes dimethylformamide and methyl cellosolve to remain unremoved in a

relatively large amount in the composition after the drying. For example, it was confirmed that, when the above solid composition was dried at room temperature for 30 min and at 900C for 30 min, the residual amount of dimethylformamide and the residual amount of methyl cellosolve were respectively 33 μ g and 13 μ g per g of the composition after drying.

5 The resultant solvent, when the composition is used as an adhesive, creates foaming or soiling of the adherend. Therefore, preferably, the amount of the resultant solvent should be reduced as much as possible. Further, there is a possibility that the residual solvent is an obstacle to an improvement in adhesion and dimensional stability.

10 In the adhesive composition precursor of the present invention, only methyl ethyl ketone and methanol are used as the solvent, and the above solvent having low evaporation rate is not used. Therefore, even drying at a relatively low temperature for a relatively short period of time hardly causes the solvent to remain unremoved. The mixed solvent composed of methyl ethyl ketone and methanol has high evaporation rate and, at the same time, has excellent capability of dissolving the above resin component and offers excellent
15 dispersion stability of antimony pentaoxide particles.

In the adhesive composition precursor of the present invention, the weight ratio of methanol (MeOH) to methyl ethyl ketone (MEK), MeOH/MEK, is in the range of 0.005 to 0.4. The selection of the above mixing ratio in the mixed solvent is effective in enhancing the capability of dissolving the resin component and the dispersion stability of antimony
20 pentaoxide particles. Therefore, intimate mixing of the components with one another can be easily realized, and the amount of the residual solvent can be minimized. In general, methanol has a remarkably low capability of dissolving the phenoxy resin. However, addition of the brominated epoxy resin increases the compatibility region in the mixed solvent composed of methyl ethyl ketone and methanol. When the weight ratio
25 (MeOH/MEK) is less than 0.005, the solubility of the dicyandiamide is lowered. On the other hand, when it exceeds 0.4, the solubility of the phenoxy resin is lowered and, in addition, intimate mixing of the components with one another becomes difficult.

The adhesive composition and the precursor thereof according to the present invention and the adhesive film derived from the adhesive composition precursor will be
30 described.

Adhesive composition

The resin component contained in the adhesive composition of the present invention generally comprises the following components:

- (a) a phenoxy resin,
- 5 (b) a non-brominated epoxy resin,
- (c) a brominated epoxy resin, and
- (d) a dicyandiamide.

The contents of these components are not particularly limited so far as the effect of the present invention is not deteriorated. In general, the resin component comprises, based on the whole resin component, 40 to 90% by weight of the component (a), 4 to 30% by weight of the component (b), 4 to 50% by weight of the component (c), and 0.1 to 7% by weight of the component (d). Preferably, the resin component comprises, based on the whole resin component, 50 to 87% by weight of the component (a), 5 to 20% by weight of the component (b), 5 to 40% by weight of the component (c), and 0.5 to 5% by weight of the component (d). When the contents of the individual components in the resin component fall within the above respective ranges, intimate mixing of the components with one another in the adhesive composition (after drying) prepared using the precursor composition containing a mixed solvent composed of methyl ethyl ketone and methanol can be easily realized.

20 The components constituting the resin component will be further described. The phenoxy resin as the component (a) is one of the components which contribute to an improvement in adhesive strength of the composition. In the phenoxy resin, the intermolecular force, between the hydroxyl group of the polymer molecule constituting the phenoxy resin and the surface of the adherend, and the flexibility inherent in the resin
25 mainly contribute to an improvement in adhesive strength in terms of peel strength. Preferably, the kind and the amount of the phenoxy resin added are selected so that the glass transition temperature of the cured composition is not 70°C or below. This results in enhanced dynamic folding resistance of the cured composition and hence can effectively prevent breaking or separation of the adhesive layer during use.

30 The non-brominated epoxy resin as the component (b) functions to enhance the glass transition temperature of the cured composition through a reaction thereof with a

curing agent, such as a dicyandiamide, The high glass transition temperature is advantageous in enhancing the dimensional stability and the heat resistance. Preferably, the kind and the amount of the non-brominated epoxy resin added are selected so that the glass transition temperature of the cured composition is not 70°C or below. Non-brominated epoxy resins usable herein include, for example, bisphenol A type epoxy resin, bisphenol F type epoxy resin, cresol novolak type epoxy resin, phenol novolak type epoxy resin and the like. Although the non-brominated epoxy resin is not an indispensable component, incorporation thereof is preferred from the viewpoint of enhancing the adhesive strength.

As described above, the brominated epoxy resin as the component (c) functions to enhance the noncombustibility of the composition and to enhance the solubility of the phenoxy resin in the mixed solvent composed of methyl ethyl ketone and methanol. Further, the brominated epoxy resin exhibits the same function as the non-brominated epoxy resin through a reaction thereof with the dicyandiamide. Preferably, the kind and the amount of the brominated epoxy resin added are selected so that the non-combustibility of the composition, the solubility of the phenoxy resin, and the glass transition temperature (above 70°C) of the composition are balanced. Brominated epoxy resins usable herein include, for example, a bromination product of bisphenol A type epoxy resin.

The dicyandiamide as the component (d) is a curing agent for the components (b) and (c). The term "dicyandiamide" used herein embraces both dicyandiamide and a dicyandiamide derivative. Preferably, the kind and the amount of the dicyandiamide added also are selected in the same manner as described above in connection with the other components constituting the resin component.

As described above, the resin component may comprise, in addition to the components (a) to (d), other additional components. Preferably, the amount of the additional components is selected in the same manner as described above in connection with the above other components constituting the resin component.

Adhesive composition precursor

The adhesive composition precursor is a starting material, for an adhesive composition, which, after drying, provides the adhesive composition of the present invention. This precursor generally comprises the above resin component, colloidal
5 particles of antimony pentaoxide, and a solvent.

The antimony pentaoxide particles are generally mixed as a sol with the above other components.

Therefore, they can be homogeneously dispersed in a vehicle comprising the resin component and the solvent. The antimony pentaoxide sol generally comprises antimony
10 pentaoxide particles dispersed in an organic solvent. Preferably, the solvent for the sol is selected by taking into consideration the solubility of the resin component therein. Among others, methyl ethyl ketone is preferred as the solvent. This is because methyl ethyl ketone has a good capability of dissolving the resin component and, in addition, is not detrimental to the dispersion stability of the sol (particles) in the precursor. The concentration of the
15 antimony pentaoxide is generally in the range of 5 to 50% by weight.

As described above, a mixed solvent containing methyl ethyl ketone and methanol is suitably used as the solvent. In addition to methyl ethyl ketone and methanol, the solvent may contain other solvents, for example, alcohols such as ethanol, isopropyl alcohol, npropyl alcohol, n-butyl alcohol, sec-butyl alcohol, tbutyl alcohol and the like,
20 nitrogen-containing solvents such as acetonitrile and the like, and others. Among these solvents, ethanol exhibits a good solubility in dicyandiamide, shows a lower evaporation rate than that of methyl ethyl ketone, and does not remarkably reduce an evaporation rate of the mixed solvent. Accordingly, ethanol can effectively improve a uniformity of the coating without reducing a drying speed of the coating.

25 The adhesive composition precursor may be prepared, for example, by the following method.

The above resin component is first mixed with the above solvent to prepare a homogeneous solution. Examples of suitable mixing means include a high speed mixer, a planetary mixer, a homomixer, and a sand mill. The concentration of the resin solution is
30 generally in the range of 5 to 70% by weight.

The antimony pentaoxide sol is added to and mixed with the resin component solution by mixing means to prepare a dispersion, thereby preparing an adhesive composition precursor comprising the dispersion. According to the above method, a precursor containing antimony pentaoxide particles homogeneously stably dispersed in the above resin component can be easily prepared. Mixing of the resin component solution with the antimony pentaoxide sol may be carried out by the same means as described above.

The adhesive composition precursor may comprise various additives so far as these additives are not detrimental to the effect of the present invention. Suitable additives usable herein include, for example, surfactants and viscosity modifiers.

Adhesive film

The adhesive composition of the present invention can be advantageously used, for example, in the form of an adhesive film. Although the thickness of the adhesive film is not particularly limited, it is generally in the range of 5 to 1,000 μm .

The adhesive film may be produced by coating the adhesive composition precursor of the present invention on a suitable substrate and drying the coating. Coating means may be the same as that commonly used in the production of conventional adhesive films. Examples thereof include a knife coater, a bar coater, a die coater, and an extruder. Drying conditions are not particularly limited. In general, however, drying is carried out at a temperature of 60 to 100°C for several seconds to one hr from the viewpoint of preventing the solvent from remaining unremoved and, in addition, preventing excessive progress of the curing reaction of the composition at the time of drying.

Substrates on which the precursor may be coated include plastic films, such as polyimide and polyester films, metallic foils, such as copper and aluminum foils, and the like. In this case, the product may be utilized as an adhesive sheet or an adhesive tape comprising a layer of an adhesive film and a substrate.

Alternatively, the adhesive film as such may be used. In this case, the substrate may be a release film which, in use of the adhesive film, is entirely removed.

When the adhesive film, in use, is adhered to a suitable adherend, for example, stacking of the adhesive film onto the adherend followed by thermocompression bonding

under conditions of a temperature of 180°C, a bonding time of one min, and a pressure of 2 to 50 kg/cm² can complete the bonding. The application may be followed by heating at 150 to 170°C for 1 to 5 hr.

5 Preferably, the thickness of the adhesive film and the composition of the adhesive composition are suitably prepared so that any of the components constituting the composition does not flow out from the end face of the film during the thermocompression bonding.

10 Preferably, the formulation of the adhesive composition is determined so that the tensile storage modulus of the cured adhesive film was not less than 1010 dyne/cm² at 60°C. This adhesive composition is best suited as an adhesive for an FPC protection film which has high dynamic folding resistance at 60°C and can be repeatedly folded. The adhesive for an adhesive film for an FPC protection film is preferably such that the shrinkage of the adhesive film after the thermocompression bonding is not more than 0.1%. The "shrinkage of the film" refers to the percentage of a reduction in the dimension
15 of the adhesive film upon thermocompression bonding (after curing), relative to the dimension of film before thermocompression bonding (before curing).

Examples

20 The present invention will be described with reference to the following examples. It should be understood that the present invention is not limited to these examples.

Solubility test (Reference Example)

25 In this example, a solubility test was carried out according to the following procedure in order to evaluate the solubility of a phenoxy resin in a mixed solvent composed of methyl ethyl ketone (MEK) and methanol (MeOH).

Compatibility of three-component system of YP50S + MEK + MeOH:

30 A phenoxy resin "YP50S (tradename), manufactured by Tohto Kasei Co., Ltd., number average molecular weight: 1,180, weight average molecular weight: 58,600" and an MEK/MeOH mixed solvent were mixed together in proportions specified in Table 1 to prepare 30 phenoxy resin solutions. The resin solutions were visually inspected for the solubility of the phenoxy resin. For the resin solutions under test, the solubility was

evaluated as "PS" when phase separation occurred; as "Sol" when the phenoxy resin could be dissolved; and as "Op" when the solution was opaque. The results of the evaluation are summarized in Table 1 and, in addition, are shown in Fig. 1 as a correlation diagram (a triangular diagram) showing the compatibility of a three-component system of YP50S + MEK + MEOH. In Fig. 1, ○ represents "Sol" or "Op," and ● "Ps."

Table 1

Compatibility of three component system, YP50S + MEK + methanol

No.	YP50S	MEK	MeOH	Evaluation Results
1	8.7	87	4.3	PS
2	8.3	83.3	8.3	PS
3	7.7	76.9	15.4	PS
4	7.1	71.4	21.4	PS
5	6.7	66.7	26.7	PS
6	15.4	76.9	7.7	Op
7	14.3	71.4	14.3	PS
8	13.3	66.3	20.0	PS
9	21.4	71.4	7.1	Sol
10	20.0	66.7	13.3	Sol
11	18.8	62.5	18.8	PS
12	26.7	66.7	6.7	Sol
13	25.0	62.5	12.5	Sol
14	23.5	58.8	17.6	PS
15	20.0	50.0	30.0	PS
16	38.9	55.6	5.6	Sol
17	47.6	47.6	4.8	Sol
18	35.0	50.0	15.0	Sol
19	45.0	40.0	15.0	Sol
20	35.0	35.0	30.0	PS
21	70.0	20.0	10.0	PS
22	20.0	55.0	25.0	PS
23	50.0	25.0	25.0	PS
24	5.0	95.0	0	PS
25	10.0	90.0	0	PS
26	20.0	80.0	0	PS
27	30.0	70.0	0	Sol
28	50.0	50.0	0	Sol
29	80.0	20.0	0	Sol
30	20.0	60.0	20.0	PS

Compatibility of four-component system of YP50S + MEK + MEOH + YDB400 (10 pbw):

The procedure of the solubility test described above was repeated, except that, in the preparation of the phenoxy resin solution, 10 parts by weight, based on 100 parts by weight of the resin solution, of a brominated epoxy resin "YDB400 (tradename), manufactured by Tohto Kasei Co., Ltd., epoxy equivalent = 380 to 420" was further added. The results of the evaluation are summarized in Table 2 and, in addition, are shown in Fig. 2 as a correlation diagram (a triangular diagram) showing the compatibility of a four-component system of YP50S + MEK + MEOH + YDB400 (10 pbw). In Fig. 2, ● represents "Sol" or "Op," and ● "PS."

Table 2

Compatibility of four component system, YP50S + MEK + methanol + YDB400 (10pbw)

No.	YP50S	MEK	MeOH	Evaluation Results
1	10.0	80.0	10.0	Sol
2	10.0	70.0	20.0	Op
3	10.0	60.0	30.0	Sol
4	20.0	70.0	10.0	Sol
5	20.0	60.0	20.0	Sol
6	20.0	50.0	30.0	PS
7	30.0	60.0	10.0	Sol
8	30.0	50.0	20.0	Sol
9	30.0	40.0	30.0	PS
10	40.0	50.0	10.0	Sol
11	40.0	40.0	20.0	Sol
12	40.0	30.0	30.0	PS
13	50.0	40.0	10.0	Sol
14	50.0	30.0	20.0	Sol
15	50.0	20.0	30.0	PS

As is apparent from the results shown in Table 2 and Fig. 2, addition of a brominated epoxy resin can broaden the region where the phenoxy resin is compatible with the MEK/MeOH mixed solvent. Further, from Fig. 1, it is apparent that the weight ratio of MEOH to MEK to, MeOH/MEK, suitable for providing a homogeneous phenoxy resin solution, is not more than 0.4.

In connection with the solubility test, use of the dicyandiamide (DICY) as the curing agent was studied.

The stoichiometric amount of the dicyandiamide (DICY) relative to 10 parts by weight of the brominated epoxy resin is 0.53 part by weight, and the maximum solubility of DICY in MEOH is 5% by weight. Therefore, at least 11 parts by weight of MEOH is necessary to dissolve DICY. That is, for preparing a homogeneous solution of YP50S + MEK + MEOH + YDB400 (10 pbw) + DICY in which a concentration of the solid content is at least 5% by weight, a weight ratio of MEOH to MEK, MeOH/MEK, should be of not less than 0.005. In this connection, it should be noted that the DICY content is generally determined based on the contents of the non-brominated epoxy resin, the brominated epoxy resin, and the phenoxy resin. The DICY content is preferably determined so that it amounts about 0.5 to 1.5 times of the epoxy equivalent of the total epoxy resin.

Examples 1 to 5 and Comparative Examples 1 to 8

Preparation of adhesive solution (adhesive composition precursor)

A resin component composed of (a) a phenoxy resin "YP50S" (noted above), (b) a bisphenol A type nonbrominated epoxy resin "DER332 (tradename), manufactured by Dow Chemical Company, epoxy equivalent = 173", (c) a brominated epoxy resin "YDB400" (noted above) and (d) a dicyandiamide (DICY) "Amicure CG1200 (tradename), manufactured by ACR, amine equivalent = 21" was mixed with a mixed solvent composed of MEK and MEOH to prepare a homogeneous resin solution. In each example, the amounts of the components (a) to (c) (parts by weight) were as specified in Table 3, and the amount of the component (d) added was the stoichiometric amount determined by the following equation:

$$"DICY"(pts.wt.) = \left(\frac{"DER332"(pts.wt.)}{173} + \frac{"YDB400"(pts.wt.)}{400} \right) \times 21 \dots (1)$$

Further, as can be understood from the following Table 3, in each example, the composition of the resin solution was regulated so that the weight ratio of MEOH to MEK, MeOH/MEK, was in the range of 0.1 to 0.4 and the concentration of the resin component composed of the above components (a) to (d) was in the range of 10 to 50% by weight.

An antimony pentaoxide (Sb_2O_5) sol "Suncolloid AME130 (tradename), manufactured by Nissan Chemical Co., particle diameter = 5 to 50 nm, solid content = 30% by weight (solvent: MEK)" in an amount (parts by weight) specified in the following Table 3 was added to and mixed with the resin solutions, prepared above, to prepare homogeneous dispersions. Thus, adhesive composition precursors having respective compositions indicated in the following Table 3 were prepared.

Preparation of adhesive film

The adhesive composition precursor prepared in each example was coated on a polyimide film "KAPTON, (tradename), manufactured by Du Pont (E.I.) de Nemours Co., thickness = 25 μm ," and the coating was dried at 90°C for 30 min to prepare an adhesive film comprising a layer of an adhesive composition and a polyimide film. The thickness of the adhesive composition layer after drying was 30 μm .

Non-combustibility test (VO requirement)

The adhesive film prepared in each example was used before the thermosetting of the adhesive composition and subjected to a non-combustibility test according to the procedure set forth in UL94 to evaluate whether each adhesive film could satisfy the VO requirement. The results of the evaluation are summarized in the following Table 3. In this test, the non-combustibility was evaluated as "passed" when the VO requirement was satisfied; and as "failed" when the VO requirement was not satisfied.

Table 3

Evaluation of VO non-combustibility of phenoxy/epoxy/ DICY adhesive

Ex.	YP50S	DER332	YDB400	Sb_2O_5	VO
COMP.Ex.1	80	10	10	0	Failed
Comp.Ex.2	75	10	15	0	Failed
Comp.Ex.3	60	20	20	0	Failed
Comp.Ex.4	50	20	30	0	Failed
Comp.Ex.5	40	20	40	0	Failed
Comp.Ex.6	50	0	50	0	Failed
Ex.1	70	20	10	6	Passed
Ex. 2	60	20	20	6	Passed
Ex.3	50	20	30	6	Passed
Ex.4	50	20	40	20	Passed

Ex.	YP50S	DER332	YDB400	Sb ₂ O ₅	VO
Comp.Ex.7	75	20	5	6	Failed
Comp.Ex.8	70	20	10	3	Failed
Ex.5	90	0	10	6	Passed

Evaluation of dimensional stability

In this evaluation test, the adhesive films prepared in Examples 1 and 2 were used. A square cut having a size of about 35 mm x 35 mm was provided on the polyimide film in each of the adhesive films, and the length of one side of the square was accurately measured. Thereafter, a 25 μ m-thick film of "KAPTON V (tradename, noted above)" was stacked on the bonding face of each of the adhesive films, followed by thermocompression bonding under conditions of a temperature of 180°C, a bonding time of 1 min, and a pressure of 10 kg/cm². After one hour has passed from the completion of the thermocompression bonding at 180°C, the length of one side of the square was measured again and compared with the length of one side before the application to determine a percentage change (ΔL).

The ΔL values for the adhesive films prepared in Examples 1 and 2 were respectively -0.02% and -0.03%. "-" in the ΔL value indicates that the dimension after the application was smaller than the dimension before the application. For both the adhesive films, the percentage change in dimension was not more than 0.1%, indicating that the dimensional stability was good.

For comparison (Comparative Example 9), an adhesive film comprising 50 parts by weight of YP50S, 20 parts by weight of DER332, and DICY in an stoichiometric amount relative to the amount of these resins incorporated was prepared in the same manner as in Example 1, except that an adhesive composition precursor for Comparative Example 9 was used. The adhesive film this obtained was evaluated for the dimensional stability in the same manner as described above. Since the adhesive film prepared in Comparative Example 9 contained neither antimony pentaoxide and brominated epoxy resin, the ΔL value was -0.11%, indicating that the dimensional stability was poor.

Evaluation of adhesive strength

In this evaluation test, the adhesive films prepared in Example 1 and Comparative Example 9 were used. For the adhesive films, the adhesive composition face and a 30 μm -thick rolled copper foil were stacked on top of the other. Thermocompression bonding was first performed under conditions of a temperature of 180°C, a bonding time of one min, and a pressure of 20 kg/cm^2 and then under conditions of a bonding time of four hr, a temperature of 150°C, and a pressure of 30 kg/cm^2 to complete the bonding (curing) between the copper foil and each of the adhesive films.

The bonded copper foil was peeled at a peel angle of 180° and a peel rate of 50 mm/min to determine the peel strength as the adhesive strength. As a result, the adhesive strength of the adhesive film prepared in Example 1 was 0.57 kg/cm , while the adhesive strength of the adhesive film prepared in Comparative Example 9 was 0.45 kg/cm .

Examples 6 and 7 and Comparative Example 10

An adhesive film of Example 6 was prepared in the same manner as in Example 1, except that a 50 μm -thick aluminum foil was used instead of the polyimide film. Further, adhesive films of Example 7 and Comparative Example 10 were prepared in the same manner as in Example 6, except that the same adhesive composition precursors as prepared in Example 2 and the same adhesive composition precursors as prepared in Comparative Example 9 were used respectively in Example 7 and Comparative Example 10.

Each of the adhesive films was put on a hot plate kept at 180°C so that the whole surface of the aluminum foil in each of the adhesive films came into contact with the surface of the hot plate. In this state, heating was performed for one min. Thereafter, the warpage (radius of curvature) of each of the adhesive films was measured, and the created stress was calculated based on the warpage. The stress (kg/cm^2) was determined by the following equation (2):

$$\text{Stress}(\text{kg}/\text{cm}^2) = \frac{E \times (h_1)^3 \times \left\{ 1 + (h_2/H)^2 / 3 \right\}}{6 \times h_1 \times H \times R} \dots (2)$$

In the above equation, E represents the modulus of elasticity, h_1 , h_2 and H respectively represent the thickness of the adhesive layer, the thickness of the aluminum

foil, and the thickness of the whole adhesive film (the total thickness of the adhesive layer and the aluminum foil), and R represents the radius of curvature of the adhesive film as measured on the surface of the aluminum foil.

The stress determined by the above calculation for the adhesive films was
5 0.4 kg/cm² for Example 6, 0.5 kg/cm² for Example 7, and 1.4 kg/cm² for Comparative Example 10. The lower this stress, the better dimensional stability.

Effect of the Invention

As described above, the present invention can provide an adhesive which
10 comprises a phenoxy resin, an epoxy resin, and a curing agent and possesses noncombustibility satisfying the VO requirement and, in addition, excellent performance (such as adhesive properties and dimensional stability) as an adhesive film for an FPC protection film. Further, according to the present invention, an adhesive composition precursor is provided which can be advantageously used as a starting material for the
15 preparation of the above adhesive composition.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a triangular diagram showing the compatibility of a three-component system of YP50S + MEK + MEOH.

20 Fig. 2 is a triangular diagram showing the compatibility of a four-component system of YP50S + MEK + MEOH + YDB400 (10 pbw).



CLAIMS

1. An adhesive composition containing a resin component, the resin component comprising a phenoxy resin, an epoxy resin, and a dicyandiamide, the epoxy resin comprising a brominated epoxy resin, the resin component
5 containing colloidal particles of antimony pentaoxide dispersed therein, the total amount of the brominated epoxy resin and the colloidal particles of antimony pentaoxide being in the range of 13 to 60% by weight based on the total amount of the adhesive composition.
- 10 2. An adhesive composition precursor which, after drying, provides the adhesive composition according to claim 1, the adhesive composition precursor comprising a mixture of (i) the resin component, (ii) an antimony pentaoxide sol comprising a dispersing medium, containing methyl ethyl ketone, and dispersed in the dispersing medium, the colloidal particles of
15 antimony pentaoxide, and (iii) a solvent containing methanol, the weight ratio of methanol (MeOH) to methyl ethyl ketone in the mixture, MeOH/MEK, being in the range of 0.005 to 0.4.