

THERMOCURABLE ELECTROCONDUCTIVE ADHESIVE SHEET, CONNECTION STRUCTURE AND CONNECTION METHOD USING THE SAME

FIELD OF THE INVENTION

The present invention relates to a thermocurable electroconductive adhesive sheet and more particularly to a thermocurable electroconductive adhesive sheet useful for connecting wiring patterns of an electrical circuit.

BACKGROUND OF THE INVENTION

Connections that are mechanically, thermally, and electrically stable are required when electrically connecting a large circuit, grounding a printed wiring board, or electrically connecting a microwave printed circuit board to a heat releasing plate, a housing, or the like.

In recent years, decreases in weight and the miniaturization of electronic apparatus have resulted in electrical circuits that are densely integrated with electronic parts. Generally, the electrical circuit controls the electrical apparatus through the use of high frequency signals. These high frequency signals however, are easily affected by external noise which may result in erroneous operation of the electrical apparatus. In order to eliminate the effects of such noise, shielding or grounding of the electrical circuit is required which usually includes an easily and reliably formed electrical connection of low resistance.

Conductive adhesives and metal foil tapes are typical electroconductive materials suitable for use in connecting wiring patterns of an electrical circuit when the size and weight of an electronic apparatus must be considered.

Japanese Patent Laid-Open Publication No. Hei 1-113480 and Japanese Patent Laid-Open Publication No. Hei 1-309206 disclose an electroconductive adhesive agent comprising thermocurable resin in which conductive particles are dispersed. The electroconductive adhesive agent is provided with conductivity by thermally curing the thermocurable resin under pressure so as to bring the conductive particles into contact with one another. The conductive particles are generally connected through point-contact.

That is, the conductive particles are electrically connected with one another with extremely narrow contact surface areas.

In such a case, conductivity of the electroconductive adhesive is adversely affected by changes in environment and poor instability. Additionally, it is difficult to thermally
5 cure the resin under pressure using standard equipment such as an oven. Furthermore, in order to apply pressure to the contact points at the time of thermal curing a specific jig is required. These factors complicate manufacturing processes.

Electrical apparatus, including such an electroconductive adhesive agent, suffer from problems associated with increases in contact resistance at the contact points, as well
10 as subsequent increases in heat generation, when a large electric current is applied. Conductive particles prepared from polymer particles plated with metal can provide an increase in the contact surface area up to a certain extent, however, the thickness of the conductive layer is extremely thin and can generate excess heat. For example, if 100
15 watts of power or higher is continuously applied to the electric connection formed by such an electroconductive adhesive, Joule heat is generated to the extent that the electrical parts therearound are adversely affected.

A metal foil tape is a conductive pressure-sensitive adhesive sheet basically composed of a metal foil and a pressure-sensitive adhesive layer. In the case of an embossed metal foil tape where the metal foil layer is embossed to have hollow convex
20 parts, the hollow convex parts need to push and tear the pressure-sensitive adhesive layer in order to form electric contact directly with a conductive adherend. Additionally, the hollow convex parts are malleable and thus easily deformed, so that relatively wide contact surface area can be reliably obtained. As a result, conductivity of the metal foil tape is more stable as compared with that of the above described conductive adhesive.

25 However, in the case of a metal foil tape, the pressure-sensitive adhesive layer generally contains an acrylic type pressure-sensitive adhesive agent and is inferior in thermal stability and mechanical strength. Thus, the Joule heat produced when large electric currents are applied cause the metal foils to separate from the adherend.

Due to the limitations of conductive adhesives and metal foil tapes as discussed
30 above, electrical connections that are required to carry large electric currents are typically formed by welding or mechanical caulking, as disclosed in Japanese Patent Examined Publication No. Hei 7-16090 (1995), which involves complicated processes.

The present invention aims to solve the above-described problems and provides a simple process for producing a thermocurable electroconductive adhesive sheet capable of forming electrical connections with low resistance and mechanical, thermal, and electrical stability.

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SUMMARY OF THE INVENTION

The present invention provides a thermocurable electroconductive adhesive sheet which includes a sheet form of an electroconductive layer having a front surface and a back surface, and an adhesive layer applied on the front surface of the electroconductive layer where a convex part raised toward the front surface direction is formed on the electroconductive layer. The adhesive layer is composed of a thermocurable adhesive agent. The convex part of the electroconductive layer passes through the adhesive layer and contacts with an adherend when the adhesive layer is adhered to the adherend by pressing and heating.

Furthermore, the present invention is to provide a thermocurable electroconductive adhesive sheet which includes a sheet form of an electroconductive layer having a front surface and a back surface, an adhesive layer applied on the front surface of the electroconductive layer, and an adhesive layer applied on the back surface of the electroconductive layer where a convex part raised toward the front surface direction and a convex part raised toward the back surface direction are formed on the electroconductive layer. The adhesive layer is composed of a thermocurable adhesive agent. The convex parts of the electroconductive layer pass through the adhesive layer and contacts with an adherend when the adhesive layer is adhered to the adherend by pressing and heating.

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BRIEF DESCRIPTION OF THE DRAWINGS

The invention may be more completely understood in consideration of the following detailed description of various embodiments of the invention in connection with the accompanying drawings, in which:

Fig. 1 is a cross-sectional view of one example of a thermocurable electroconductive adhesive sheet of the present invention.

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Fig. 2 shows the plan view of one example of a thermocurable electroconductive adhesive sheet of the present invention.

Fig. 3 is a flow diagram schematically showing the attachment to an adherend of a thermocurable electroconductive adhesive sheet of the present invention where the convex parts and the adhesive layer are formed on only one side of the conductive layer.

Fig. 4 is a cross-sectional view of a connection structure formed using a thermocurable electroconductive adhesive sheet of the present invention.

Fig. 5 is a flow diagram schematically showing the method for forming the electric connection by a thermocurable electroconductive adhesive sheet of the present invention.

Explanation of Numbering

- 1 Electroconductive layer,
- 2,2' Adhesive layer,
- 3 Thermocurable electroconductive adhesive sheet,
- 4,4' Projected part,
- 5,5' Adherend.

While the invention is amenable to various modifications and alternative forms, specifics thereof have been shown by way of example in the drawings and will be described in detail. It should be understood, however, that the intention is not to limit the invention to the particular embodiments described. On the contrary, the intention is to cover all modifications, equivalents, and alternatives falling within the spirit and scope of the invention.

DETAILED DESCRIPTION OF THE INVENTION

Throughout the Figures, similar or equivalent elements are assigned the same reference number.

With respect to Figure 1, which is a cross-sectional view of an example of a thermocurable electroconductive adhesive sheet of the present invention, the thermocurable electroconductive adhesive sheet includes an electroconductive layer 3, an adhesive layer 2 formed on the front surface of the electroconductive layer, and an adhesive layer 2' formed on the back surface of the electroconductive layer. The electroconductive layer 1 is a sheet form of a conductive material and has a front surface and a back surface.

The thickness of the electroconductive layer may vary, however it is generally from 1 to 2,000 μm , preferably from 30 to 1,000 μm , and more preferably 50 to 500 μm . If the electroconductive layer has a thickness thinner than about 1 μm , the rigidity of the electroconductive layer declines and the amount of stress which can be effectively applied to the contact points is limited. In contrast, if the electroconductive layer has a thickness thicker than about 2,000 μm , the rigidity becomes too high and intense pressure is required to closely adhere the adhesive layer to the adherend.

The thickness of the adhesive layers on both the back and front surfaces of the electroconductive layer depends on their ability to attain a sufficient adhesion strength and their ease in forming contact between the electroconductive layer 1 and the adherend (not shown in Fig.) Generally, the adhesive layers 2, 2' have a thickness of 1 to 100 μm , preferably 5 to 50 μm , and more preferably 10 to 30 μm , and are formed on both surfaces of the electroconductive layer 1.

A convex part 4 raised toward the front surface direction and a convex part 4' raised toward the back surface direction are formed on the conductive layer 1. The plan shape of the convex parts is not particularly restricted and may be round, polygonal, or lattice shape. The typical convex parts are projections with a round plan shape.

The size of the convex parts may vary depending on a variety of factors. For example, the useful minimum and maximum heights of the convex parts are generally related to the surface roughness of the adherend. The height of the convex part should generally exceed the maximum surface roughness of the adherend. If the height of the convex part is less than the surface roughness of the adherend then contact between the adherend and the thermocurable electroconductive adhesive sheet tends to be unstable. Additionally, however, the height of the convex part should generally not exceed the maximum surface roughness of the adherend by such a great degree that great pressures are required in order to make the desired connection. If the height of the convex part greatly exceeds the maximum surface roughness of the adherend then excess pressures may be required to deform the convex part in order to create the desired connection with an appropriate contact surface area. The size of convex parts 4, 4' are generally from 1 to 2,000 μm in height and from 10 to 20,000 μm in average diameter. In the case of using a 1-ton or less press machine and a usual adherend, the proper height and the average diameter are from 10 to 200 μm and from 100 to 2,000 μm .

The convex parts 4, 4' are preferably hollow. If the convex parts are hollow, they can be deformed relatively easily. As a result, when hollow convex parts are brought into direct contact with the adherend and receive pressure, the contact surface area with the adherend can increase due to such deformation and resistance of the electric connection can further be lowered. Furthermore, since the hollow convex parts are easily deformed, like a spring, the connection stability can be increased.

Although the convex parts 4, 4' and the electroconductive layer 1 are integrally formed in Fig. 1, the convex parts are not restricted to such forms as long as they can be brought into contact directly with the electroconductive member. Furthermore, the convex parts are not limited to one for each surface side. A plurality of convex parts may be formed in one surface or both surface sides of the electroconductive layer at intervals from one another so as to have as many contacts as possible with an adherend.

Fig. 2 shows the plan view of one example of a thermocurable electroconductive adhesive sheet of the present invention. A plurality of projected parts 6, 6' and a plurality of recessed parts 7, 7' are regularly formed at prescribed intervals corresponding to the convex parts in an electroconductive layer. In this embodiment, the convex parts nearest to one another form the projected and recessed relations.

In the case that a plurality of convex parts are formed in the electroconductive layer, the intervals between the convex parts may vary, however they are generally from 0.01 to 20 mm. If the intervals between convex parts are less than the minimum limit, the force applied to the contact points decreases and it tends to become difficult to eliminate and pierce the adhesive layer, whereas if the intervals between convex parts are greater than the maximum limit, efficiency of the electric (or thermal) conduction tends to decrease.

In the case where the adherend is a high frequency wave printed wiring board such as a microwave printed circuit board, the intervals between convex parts should be half the wavelength of the high frequency wave, or shorter. If the intervals between convex parts are longer than half the wavelength of the high frequency wave, the conductive regions surrounding the non-contact parts work as antennae resulting in problematic noise production.

The materials for the above described electroconductive layer and convex parts may vary. However, when electric conductivity and thermal conductivity is considered, a

preferable electroconductive layer and convex parts are made of metal such as iron, stainless steel, silver, aluminum, tin, copper or any other metal that makes excellent electric and/or thermal connection possible between a high frequency wave printed wiring board and a heat releasing plate or box. The metal generally possesses elongation and ductility characteristics and is easily processed into a sheet such as a foil. Furthermore, in the case that the convex parts are hollow, plastic deformation of the embossed metal is easily accomplished. This allows for increased, almost permanent contact, with the adherend.

Copper, iron, and aluminum are preferred metals for use in producing the electroconductive layer of the present invention. They are considerably advantageous for the thermocurable electroconductive adhesive sheet of the present invention in terms their economic cost. Foils of the above-described metals may be plated with gold, tin, solder, silver, zinc, nickel or the like.

The adhesive layer is made of a thermocurable adhesive agent. Preferred thermocurable adhesives are, for example, a thermocurable resin composition containing the following components and having substantially no tack; (1) epoxy resin, (2) a curing agent for the epoxy resin, and (3) phenoxy resin.

Reaction of the epoxy resin with the curing agent is caused by heating but may take place at ambient temperature to form a cured product with a three-dimensional net structure. In this case, the cured epoxy resin possesses excellent heat resistance and cohesive strength when force is applied to the adhesive layer in order to adhere adherends to each other. As a result, unlike the metal foil tape previously described, the adhesive layer is rarely separated from adherends even if Joule heat is generated by electric connection between the adherends.

The epoxy resin may vary as long as it can provide an adhesive layer with high heat resistance and agglomeration force. Such an epoxy resin includes, for example, bisphenol A type epoxy resin, bisphenol F type epoxy resin, phenol novolak type epoxy resin, cresol novolak type epoxy resin, fluorene epoxy resin, glycidylamine resin, aliphatic epoxy resin, brominated epoxy resin, fluorinated epoxy resin, and the like.

The above described epoxy resin is generally present in the composition in an amount of 5 weight % to 80 weight %. Weight % as used herein is based on the total weight of the composition. If the amount of the epoxy resin is lower than about 5 weight

%, heat resistance of the composition tends to decrease, whereas if the amount of the epoxy resin is higher than about 80%, the cohesive force of the composition tends to decrease and the composition tends to be fluid. Preferably, 10 weight % to 50 weight % of the epoxy resin is present in the composition.

5 A curing agent is further added to the composition to thermally cure the composition by reaction with the epoxy resin at ambient or elevated temperatures. The curing agent may vary as long as it can thermally cure the composition as described above. Suitable curing agents include, for example, an amine type curing agent, acid anhydride, dicyanoamide, imidazol, a cation polymerization catalyst, a hydrazine compound and the
10 like. Dicyanodiamide is preferable since it has thermal stability at room temperature (30°C).

The curing agent is generally present in the composition at a level from 0.1 weight % to 30 weight %. If less than about 0.1 weight % of the curing agent is present in the composition, the resulting composition tends to possess insufficient hardness, whereas if
15 more than about 30 weight % of the curing agent is present in the composition, the desired properties of the cured composition tend to deteriorate. Preferably, 0.5 weight % to 10 weight % of the curing agent is present.

The phenoxy resin is typically a thermoplastic resin having a chain structure, generally has a weight average molecular weight of 2,000 to 2,000,000 or a number
20 average molecular weight of 1,000 to 1,000,000, and an epoxy equivalent weight of 500 to 500,000, and can provide the composition with a proper shape (for example a film). Furthermore, the phenoxy resin has a structure similar to the above described epoxy resin both of which are compatible with each other. The composition can be formed into an adhesive film. It is preferred that the phenoxy resin is used with a bisphenol A type epoxy
25 resin or a fluorene epoxy resin since these resins are extremely compatible with the phenoxy resin..

The adhesive layer preferably has a minimum storage shear elastic modulus (G') of 100,000 Pa or lower, or 10 to 100,000 Pa to limit flow out of the resin. Such an adhesive layer easily allows the convex parts to penetrate the layer itself and provide electric
30 connection with a low resistance between adherends. Such an adhesive layer provides these properties when a pressure of 60 to 260°C and 10^4 to 5×10^7 Pa is applied.

If the minimum storage shear elastic modulus exceeds about 100,000 Pa, high pressure is needed in order for the convex part to penetrate the adhesive layer. The storage shear elastic modulus (G') in this specification means the minimum value among the values measured using a dynamic viscosity measurement apparatus (for example, RDA II available from Rheometrics Co.) while the temperature is increased from 60°C to 260°C at 5°C/min under an angular velocity of 6.28 rad/sec (frequency of 1 Hz).

The adhesive layer may include bismaleimide resin in place of the epoxy resin or include bismaleimide resin in addition to the epoxy resin. Furthermore, a variety of super engineering plastics such as poly(hydroxy ether), obtained by a reaction of fluorenebisphenol and epoxy resin, or other thermoplastic resins may be used in place of the phenoxy resin or together with the phenoxy resin. The poly(hydroxy ether) into which the above described fluorene backbone structure is introduced not only improves the heat resistance of the adhesive layer but also provides the adhesive layer with water-proofness.

Unless the resulting composition does not fulfill the purposes or does not produce the desired effects of the present invention, a composition containing no such thermoplastic resin as described above but mainly containing epoxy resin, bismaleimide resin, or their mixture together with a curing agent may be used for forming the thermocurable adhesive layer. Furthermore, a thermocurable resin including ethylene-glycidyl methacrylate copolymer as a main component is suitable for use in high humidity conditions owing to its low water absorptivity.

In the above described thermocurable electroconductive adhesive sheet, the convex parts and the adhesive layer are formed on both surfaces of the conductive layer, however they may be formed on only one side. Fig. 3 shows the cross-sectional view of such a thermocurable electroconductive adhesive sheet.

The thermocurable electroconductive adhesive sheet of the present invention can be prepared by any conventional technique including that described below.

Adhesive layers suitable for use in the present invention include those produced as describe below. A thermocurable adhesive agent is prepared by mixing an epoxy resin, a phenoxy resin, and a curing agent together. The resulting thermocurable adhesive agent is dissolved in a solvent to obtain a coating solution. The solvent may vary as long as it can dissolve the thermocurable adhesive agent. Preferably, the solvent includes methyl ethyl ketone (MEK), is volatile at low temperatures, and possesses low toxicity.

After a prescribed amount of the coating solution is applied to one surface of a substrate, which is subjected to a release treatment as commonly known to one of skill in the art, it is dried at a prescribed temperature to form an adhesive layer. After the resulting adhesive layer is separated from the substrate, it is adhered to one or both surfaces of a
5 conductive layer to obtain a laminated body. The coating solution could also be directly applied to the conductive layer and dried.

Embossing treatment is carried out on the laminated body to form the convex parts in the conductive layer. At that time, since the adhesive layer has substantially no tack, the embossing treatment can be carried out relatively easily. An adhesive layer may also
10 be adhered to the conductive layer in which the convex parts were previously formed by embossing treatment. Furthermore, in the case of using solder to connect thermocurable electroconductive adhesive sheets to each other or an adhereand, a flux agent containing rosin may be applied to the surface of the conductive layer in order to facilitate connection.

The conductive layer may be separated into several regions having no
15 communication with one another by a means such as etching after adhesion of the adhesive layer.

A connection structure of the present invention, shown in Fig. 4, includes a thermocurable electroconductive adhesive sheet 3, adhesive layers 2, 2', and adherends 5, 5' formed thereon. The adhesive layers 2, 2' are adhered to the adherends 5, 5' and convex
20 parts 4, 4' of the conductive layer 1 penetrate the adhesive layers 2, 2' and are brought into contact with the adherends 5, 5'. As a result, if the adherends have conductivity, electric connection with low resistance among them can be formed by the thermocurable electroconductive adhesive sheet.

Fig. 5 is a flow diagram schematically showing the method for forming the electric
25 connection by a thermocurable electroconductive adhesive sheet of the present invention.

At first, as shown in Fig. 5(a), adherends 5, 5' are arranged on the adhesive layers of the thermocurable electroconductive adhesive sheet 3.

Next, as shown in Fig. 5(b), a prescribed degree of pressure is applied between the adherends while the adhesive layers of the thermocurable electroconductive adhesive sheet
30 3 are heated together with the adherends 5, 5'. The adhesive layers 2, 2' are softened and the convex parts 4, 4' of the conductive layer 1 eliminate and penetrate the adhesive layers 2, 2' and are brought into contact with the adherends 5, 5'.

Pressure is further applied to completely adhere the adhesive layers to the adherents 5, 5' with no voids as shown in Fig. 5(c). At that time, in the case that the convex parts 4, 4' are hollow, the tip end parts are deformed by the applied pressure to increase the surface area contacting the adherends. As a result, the adhesive sheet can provide electric connection with low resistance and excellent stability between the adherends. If necessary, the adhesive layers may be further heated to completely cure the thermocurable adhesive.

The convex parts 4, 4' of the conductive layer, and the adherends 5, 5', may be melted and bonded by applying current as high as 10 to 100,000 Amps between the convex parts 4, 4' and the adherends 5, 5'. Furthermore, in the case that a brazing material such as solder, tin, zinc, aluminum, low melting point metal or the like exists between the convex parts of the conductive layer and the adherents, brazing (including soldering) of the convex parts 4, 4' of the conductive layer and the adherends 5, 5' may be carried out by either properly adjusting the temperature used for heating and bonding or applying a proper quantity of electric current between the convex parts 4, 4' and the adherends 5, 5'. The use of such means results in a firm connection between the convex parts 4, 4' and the adherends 5, 5'.

Examples

Hereinafter, the present invention will be described according to the following examples, however the present invention is not restricted to those examples. In the examples, the terms "parts" and "%" are by weight based on the total weight of the composition, unless otherwise stated.

Examples 1-4

Preparation of Adhesive Layer

As shown in Table 1, phenoxy resin (YP 50S available from Tohto Kasei K.K.), epoxy resin (DER 332 available from Dow Chemical Co.), and a dicyanodiamide-based curing agent (DICY) were blended to prepare thermocurable adhesive agents. These thermocurable adhesive agents were then dissolved in a solvent mixture of methyl ethyl ketone (MEK) and methanol (MeOH) to obtain coating solutions.

Table 1
Composition of Coating Solution (Parts)

	Example 1	Example 2	Example 3	Example 4
phenoxy resin ^a	95	90	80	70
Epoxy resin ^b	5	10	20	30
dicyanodiamide	0.49	0.97	1.94	2.91
MEK	100	100	100	100
MeOH	40	40	40	40

^a YP 50S available from Tohto Kasei K.K.; number average molecular weight of 11,800

^b DER 332 available from Dow Chemical Co.; epoxy equivalent weight of 174

Next, a prescribed amount of each coating solution was applied to one surface of a poly(ethylene terephthalate) (PET) film (50 μm thickness), that was pretreated with silicone for separation, and dried for 20 minutes at 100°C to obtain a 30 μm thick adhesive layer.

Measurement of Elasticity of Adhesive Layer

After the adhesive layer was separated from the PET film, the storage shear elastic modulus (G') was measured as described below. The storage shear elastic modulus (G') was measured using a dynamic viscoelasticity measurement apparatus (RDA II available from Rheometrics Co.) while increasing the temperature from 60°C to 260°C at 5°C/min under an angular velocity of 6.28 rad/sec. Table 2 shows the minimum value ($G'_{\min}$) of the storage shear elastic modulus from 60°C to 260°C for each adhesive layer and the storage shear elastic modulus ($G'_{\max 280^\circ\text{C}}$) at 260°C.

Preparation of Thermocurable Electroconductive Adhesive Sheet

Adhesive layers were formed on surfaces of both sides of a cold-rolled copper foil (SPCC-SB available from Nippon Seihaku K.K.), which was a conductive layer having a thickness of 35 μm . The two adhesive layers were then adhered to the cold-rolled copper foil by pressure applied by rollers heated at 100°C to obtain a laminated body. In order to obtain a thermocurable electroconductive adhesive sheet, the obtained laminated body was then embossed to form convex parts and concave parts (diameter of 1.5 mm, height of

0.2 mm, and distance of neighboring convex parts $d = 5$ mm), having a repetitive unit as shown in Fig. 2.

Formation of Connection Structure

Next, adherends made of the above described cold-rolled copper foil were further disposed to both surfaces of the thermocurable electroconductive adhesive sheet and the resulting body was sandwiched between a pair of aluminum sheets having a thickness of 1 mm. The thermocurable electroconductive adhesive sheet and the adherends were heated for 2 hours in an oven at 150°C while applying a pressure of 5×10^5 Pa to obtain a connection structure.

Measurement of Resistance and Adhesion Strength of Connection Structure

The above described connection structure was separated from the pair of the aluminum sheets and cooled to room temperature, 30°C. Once cooled to room temperature, resistance between the two adherends was measured and the measured value was defined as initial resistance. Successively, the resulting connection structure was floated on a treatment bath of melted solder at 260°C for 1 minute and then cooled to room temperature, 30°C. Upon cooling, the resistance between both adherends was measured in the same manner as described above and the measured value was defined as final resistance.

Furthermore, one of the adherends was peeled from the connection structure at 50 mm per minute to measure 180° peel adhesion strength.

Table 2 shows the initial resistance, the final resistance, and the 180° peel adhesion strength of the connection structure of each example.

Table 2

	Example 1	Example 2	Example 3	Example 4
$G'_{\min}$ (Pa)	1.48×10^3	3.00×10^3	3.26×10^3	7.00×10^2
$G'_{\max 260^\circ\text{C}}$ (Pa)	1.47×10^4	1.60×10^5	1.60×10^6	2.54×10^6
Adhesion strength (kgf/cm ²)	1.084	0.649	0.541	0.491
Initial resistance (ohm)	<0.1	<0.1	<0.1	<0.1
Resistance after treatment with solder (ohm)	5.4	10.5	<0.1	<0.1

Example 5Preparation of Adhesive Layer and Elastic Modulus

In this example, an adhesive layer having a thickness of 30 μm was prepared in the same manner as Examples 1 to 4 except that the coating solution was prepared according to Table 3.

Table 3

Component	Composition (part)
phenoxy resin ^a	55
phenoxy resin ^b	15
epoxy resin ^c	15
Brominated epoxy resin ^d	15
30% ethyl acetate solution of poly(nBA/PEA) ^e	10
30% MEK sol of antimony pentoxide ^f	10
dicyanidiamide	1.5
TDI-Urea ^g	0.1
MEK	80
MeOH	35
EtOH	15

^a YP 55 available from Tohto Kasei K.K.

^b PKHM 30 available from Phenoxy Associate Co.

^c YD 128 available from Tohto Kasei K.K.; epoxy equivalentweight of 180

^d YDB 400 available from Tohto Kasei K.K.

^e 30% ethyl acetate solution of n-butyl acrylate/phenoxyethyl acrylate = 50/50 (weight ratio) copolymer

^f AME 130 available from Nissan Chemical Industries, Ltd

^g Amicure UR 2T available from Amicron Chem. Co.

Measurement of Elastic Modulus of Adhesive Layer

Elastic modulus of the adhesive layer was measured in the same manner as Examples 1 to 4, the G'_{min} and $G'_{\text{max}260^\circ\text{C}}$ were found to be 2400 Pa and 160,000 Pa, respectively.

Preparation of Thermocurable Electroconductive Adhesive Sheet

The thermocurable electroconductive adhesive sheet of this example was prepared as described below.

5 A copper foil (a conductive layer), available under the trade name of TCu-0-35 from Fukuda Kinzoku Hakufun K.K., was embossed with a square lattice pattern each side having a length of 1.8 mm, and composed of convex parts having a line width of 0.3 mm and a height of 0.075 mm (hereinafter, referred to as an embossed surface). The copper foil was exposed to a 5% MEK solution of rosin (KE 604 available from Arakawa Kagaku K.K.). The embossed surface was then dried to remove MEK.

10 After the above described adhesive layer was separated from the PET film, The copper foil was then laminated on an adhesive layer, prepared on a PET film as described above, so that the embossed surface was adhered to the adhesive layer. The adhesive layer and the copper foil were then laminated by pressing them with rollers heated at 120°C to obtain a thermocurable electroconductive adhesive sheet as shown in Fig. 3.

Formation of Connection Structure

15 After the above described thermocurable electroconductive adhesive sheet was cut into a rectangular shape having a width of 10 mm and a length of 70 mm an adherend was laminated onto the adhesive layer. The adherend, a tin plated-copper foil (width of 20 13 mm, length of 30 mm, and thickness of 2 mm), was laminated onto the adhesive layer with a 60% tin/40% lead solder foil (width of 5 mm, length of 10 mm, and thickness of 0.1 mm). The tin-plated copper is available under the trade name of C 1110P from Test Piece Co. and was standardized according to JIS (the Japanese Industrial Standards) H 3100.

25 A pressure of 5×10^6 Pa was applied to the thermocurable electroconductive adhesive sheet and the tin-plated copper foil at 210°C for 60 seconds. The solder foil melted, and was sealed between the thermocurable electroconductive adhesive sheet and the tin-plated copper foil. The thermocurable electroconductive adhesive sheet was thermally bonded to the tin-plated copper foil through a contact surface area measured as 30 $10 \times 20 \text{ mm}^2$.

The adhesive layer was cured to obtain a connection structure when the thermocurable electroconductive adhesive sheet, together with the solder foil and the

tin-plated copper foil, was heated in an oven at 150°C for 2 hours without applying external force.

Measurement of Resistance and Adhesion Strength of Connection Structure

Resistance between the conductive layer and the adherend of the connection structure was measured. As described above, the adherend was peeled from the connection structure at 50 mm per minute in order to measure 180° peel adhesion strength. The resistance of the connection structure of this example and the 180° peel adhesion strength are shown in Table 4.

Table 4

Sample No.	Resistance value (mΩ)	Adhesion strength (kgf/cm)
1	1.87	0.93
2	1.94	0.97
3	2.26	1.32
Average	2.02	1.07

Electrification of Connection Structure

Next, the connection structure of this example was connected in series to an AC power source of 100 V and an incandescent electric bulb (375 W RH) through an electric lead wire to form an electric circuit. Electric current was applied between the conductive layer and the adherend for 30 minutes. The conductive layer and the adherend did not undergo a significant temperature increase (5°C or higher) at the contact point with the electric lead wire.

Example 6

Formation of Adhesive Layer and Measurement of Elastic Modulus

In this example, an adhesive layer having a thickness of 30 μm was prepared in the same manner as Examples 1 to 4 except that the coating solution was prepared according to Table 5.

The elastic modulus of the adhesive layer was measured also in the same manner as Examples 1 to 4, and $G'_{\min}$ and $G'_{\max 260^{\circ}\text{C}}$ was measured as 85 Pa and 1.03×10^7 Pa, respectively.

Table 5

Component	Composition (parts)
phenoxy resin ^a	40
epoxy resin ^b	30
epoxy resin modified with polycaprolactone ^c	30
30% ethyl acetate solution of poly(nBA/PEA) ^d	20
Dicyanodiamide	2.91
MEK	100
MeOH	40

^a YP 50S available from Tohto Kasei K.K.; number average molecular weight of 11,800

^b DER 332 available from Dow Chemical Japan Co.

^c PLACCEL G402 available from Daicel Kagaku K.K.; epoxy equivalent weight of 1,350

^d 30% ethyl acetate solution of n-butyl acrylate/phenoxyethyl acrylate = 50/50 (weight ratio) copolymer

Preparation of Thermocurable Electroconductive Adhesive Sheet and Formation of Connection Structure

The thermocurable electroconductive adhesive sheet of this example was prepared in the same manner as Examples 5 except that the above described adhesive layer was used.

After the thermocurable electroconductive adhesive sheet of this example was cut into a rectangular shape having a width of 25 mm and a length of 70 mm, a galvanized iron sheet was directly adhered to the copper foil of the sheet. After that, a pressure of 5×10^6 Pa was applied between the thermocurable electroconductive adhesive sheet and the galvanized iron sheet at 150°C. The adhesive layer was cured to obtain a connection structure.

Measurement of Resistance and Adhesion Strength of Connection Structure

Next, resistance between the conductive layer and the adherend of the connection structure of this example was measured. Also, as described above, the adherend was

peeled from the connection structure at 50 mm per minute to measure 180° peel adhesion strength. The resistance of the connection structure of this example and the 180° peel adhesion strength are shown in Table 6.

5

Table 6

Sample No.	Resistance value (milliohm)	Adhesion strength (kgf/cm)
1	1.5	0.42
2	1.0	0.61
3	0.8	0.51
Average	1.1	0.51

Electrification of Connection Structure

An electric current was applied to the connection structure of this example in the same manner as Example 5. The conductive layer and the adherend did not undergo a significant temperature increase (5°C or higher) at the contact point with the electric lead wire.

10

Comparative Example 1

Preparation of Thermocurable Electroconductive Adhesive Sheet

15

In this comparative example, 5% of gold-plated polymer conductive particles (Bright 20 GNR 4,6-EH available from Nippon Kagaku Kogyo K.K.) were dispersed in the coating solution. An adhesive layer having a thickness of 35 μm was prepared in the same manner as Example 5 except using the resulting coating solution, which was then used to prepare a thermocurable electroconductive adhesive sheet.

20

Formation of Connection Structure

25

Adherends, which are respectively a rolled copper foil and a tin-plated copper foil having a thickness of 35 μm , were disposed respectively on both side surfaces of the thermocurable electroconductive adhesive sheet. Then, a pressure of 2×10^7 Pa was applied between the rolled copper foil and the tin-plated copper foil at 150°C for 2 hours to form a connection structure. In this case, the thermocurable electroconductive adhesive

sheet was bonded and pressed to the tin-plated copper foil and to the rolled copper foil through a contact surface area measured as $10 \times 20 \text{ mm}^2$.

Measurement of Resistance and Adhesion Strength of Connection Structure

5 The, resistance between the rolled copper foil and the tin-plated copper foil of the connection structure of this comparative example was measured. Also, the tin-plated rolled copper foil was peeled from the connection structure at 50 mm per minute to measure 180° peel adhesion strength. The resistance of the connection structure of this comparative example and the 180° peel adhesion strength are shown in Table 7.

10 Substantially the same experiment was conducted except that curing was carried out at 150°C for 2 hours without applying external force after it was pressed for 1 minute at 150°C . The connection resistance was measured as 1 ohm or higher.

Comparative Example 2

15 Formation of Connection Structure

 In this comparative example, an electroconductive pressure sensitive adhesive sheet (#1245 available from Sumitomo 3M Co.) which bears a copper foil having a square lattice pattern on a front surface, formed by embossing treatment, was closely adhered to a rolled copper foil having a thickness of $35 \mu\text{m}$. In this case, the electroconductive pressure-sensitive adhesive sheet was closely adhered to the rolled copper foil through a contact surface area measured as $25 \times 25 \text{ mm}^2$ and formed a connection structure.

Measurement of Resistance and Adhesion Strength of Connection Structure

25 Next, resistance between those two copper foils of the connection structure of this comparative example was measured. Also, the rolled copper foil was peeled from the connection structure at 50 mm per minute to measure 180° peel adhesion strength. The resistance of the connection structure of this example and the 180° peel adhesion strength are shown in Table 7.

Table 7

	Initial resistance (milliohm)	Resistance after 120°C/24 H (milliohm)	Adhesion strength (kgf/cm)
Comparative Example 1	5	10	1.0
Comparative Example 2	200	500	0.5

Example 7Electric Welding

5 The adhesive layer described in Example 5 was laminated on a thin layer of a tin-plated iron foil having a thickness of 100 μm by pressing them with a roll heated to 120°C. A molding die was pressed to form one convex part having a height of 30 μm and a diameter of 1.5 mm so that the convex part was formed on the tin plate surface. An electroconductive adhesive sheet having a size of 13 x 30 mm was obtained. The sheet
10 was put on a tin-plated copper sheet (C1110P) used in Example 5, so that the convex part contacted the sheet, and was bonded and pressed at 150°C for 20 seconds.

 The resulting connection body was sandwiched between electrodes of a National resistance welding apparatus (YR-080SRF-7) and electric current was applied between the tin-plated copper foil and the tin plating foil (set in a memory 65) to weld the convex part
15 and the tin-plated copper sheet.

 Without applying external force to the connection body, resin was cured by heating at 150°C for 2 hours.

 Resistance between the tin-plated copper and the tin-plated iron of the connection body was measured at 30°C, and measured as 1.6 milliohm.

Claims

1. A thermocurable electroconductive adhesive sheet comprising a sheet form electroconductive layer having a front surface and a back surface, and an adhesive layer applied on the front surface of the electroconductive layer, wherein:

a convex part raised toward the front surface direction is formed on the electroconductive layer, the adhesive layer is composed of a thermocurable adhesive containing an epoxy resin and a phenoxy resin, and the convex part of the electroconductive layer passes through the adhesive layer and contacts an adherend when the adhesive layer is adhered with pressing and heating to the adherend.

2. A thermocurable electroconductive adhesive sheet comprising a sheet form electroconductive layer having a front surface and a back surface, a first adhesive layer applied on the front surface of the electroconductive layer, and a second adhesive layer applied on the back surface of the electroconductive layer, wherein:

a first convex part raised toward the front surface direction, and a second convex part raised toward the back surface direction are formed on the electroconductive layer, the first and second adhesive layers are composed of a thermocurable adhesive containing an epoxy resin and a phenoxy resin, and the first and second convex part of the electroconductive layer pass through the first and second adhesive layers, respectively, and contact a first and second adherend, respectively, when the adhesive layers are adhered with pressing and heating to the adherends.

3. A connection structure comprising the thermocurable electroconductive adhesive sheet of claim 1 or claim 2, and an adherend placed on the adhesive layer of the thermocurable electroconductive adhesive sheet, wherein:

the adhesive layer adheres to the adherend, and the convex part of the electroconductive layer passes through the adhesive layer and contacts the adherend.

4. The connection structure according to claim 3, wherein the adherend and the convex part are bonded by welding or soldering.
5. A connecting process comprising the steps of placing an adherend on the adhesive layer of the thermocurable electroconductive adhesive sheet of claim 1 or claim 2; heating the adhesive layer of the thermocurable electroconductive adhesive sheet; and applying pressure between the thermocurable electroconductive adhesive sheet and the adherend, whereby the convex part is made to pass through the adhesive layer and contact the adherend.
6. A thermocurable electroconductive adhesive sheet of claim 1 or 2 having a plurality of convex parts on one or both sides of the electroconductive layer.
7. A thermocurable electroconductive adhesive sheet of claim 1 or 2 wherein the convex parts are hollow.
8. A thermocurable electroconductive adhesive sheet of claim 1 or 2 wherein the thermocurable adhesive further comprises a curing agent for the epoxy resin.
9. A thermocurable electroconductive adhesive sheet of claim 1 or 2 wherein the epoxy resin is present in an amount of 5 wt% to 80 wt%.
10. A thermocurable electroconductive adhesive sheet of claim 1 or 2 wherein the phenoxy resin has an epoxy equivalent weight of 500 to 500,000.
11. A thermocurable electroconductive adhesive sheet of claim 1 or 2 wherein the adhesive layer includes a bismaleimide resin in place of the epoxy resin.
12. A thermocurable electroconductive adhesive sheet of claim 1 or 2 wherein the adhesive layer includes a bismaleimide resin in addition to the epoxy resin.
13. A thermocurable electroconductive adhesive sheet of claim 1 or 2 wherein the adhesive layer includes a poly(hydroxy ether) resin in place of the phenoxy resin.

14. A thermocurable electroconductive adhesive sheet of claim 1 or 2 wherein the adhesive layer includes a poly(hydroxy ether) resin in addition to the pheoxy resin.

15. A thermocurable electroconductive adhesive sheet of claim 1 or 2 wherein the convex parts are formed by embossing.