

CONDUCTIVE ADHESIVE PRECURSOR, METHOD OF USING THE SAME, AND ARTICLE

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BACKGROUND

There are many applications in electronic assemblies that require electrically conductive interconnects. Integrated circuit dies and stiffeners often need to be grounded, and are commonly bonded to substrates using conductive adhesives. Conductive adhesive pastes are often used for these applications. However, these pastes do not provide sufficient green strength to hold substrates in place without mechanical fixturing. Also, the pastes can squeeze out during placement or cure, leading to undesirably large adhesive footprints.

Conductive film adhesives have also been used for forming conductive bonds, but typically require die cutting, which is not well-suited for short run applications, and which also typically generates substantial quantities of expensive scrap.

SUMMARY

The present disclosure describes a flowable conductive adhesive (typically printable) that can be B-staged using actinic radiation, and then thermally cured to securely bond two substrates. The conductive adhesive provides electrical conductivity between the two substrates.

In one aspect, the present disclosure provides a conductive adhesive precursor comprising:

- a) from 20 to 50 percent by weight of at least one polycarbonate,
- b) from 20 to 50 percent by weight of at least one free-radically polymerizable (meth)acrylate,
- c) from 20 to 40 percent by weight of conductive fibers, and
- d) from 2 to 10 percent by weight of conductive substantially spherical particles, wherein the percent by weight of components a) to d) is based on the total weight of components a) to d);

- e) an effective amount of at least one thixotrope;
- f) an effective amount of photoinitiator for the at least one free-radically polymerizable (meth)acrylate; and
- g) an effective amount of thermal curative for the at least one polyepoxide.

5 In another aspect, the present disclosure provides a method of conductively bonding a first substrate to a second substrate comprising:

applying a conductive adhesive precursor to the first substrate, the conductive adhesive precursor comprising:

- a) from 20 to 50 percent by weight of at least one polyepoxide,
- 10 b) from 20 to 50 percent by weight of at least one free-radically polymerizable (meth)acrylate,
- c) from 20 to 40 percent by weight of conductive fibers, and
- d) from 2 to 10 percent by weight of conductive substantially spherical particles, wherein the percent by weight of each of components a) to d) is
- 15 based on the total weight of components a) to d),
- e) an effective amount of at least one thixotrope,
- f) an effective amount of initiator for the at least one free-radically polymerizable (meth)acrylate, and
- g) an effective amount of thermal curative for the at least one
- 20 polyepoxide;

free-radically polymerizing at least a portion of the at least one free-radically polymerizable (meth)acrylate to convert the conductive adhesive precursor into a B-staged conductive adhesive precursor;

25 contacting the second substrate with the B-staged conductive adhesive precursor;
and
curing at least a portion of the at least one polyepoxide.

In yet another aspect, the present disclosure provides an article comprising a first substrate bonded to a second substrate by a conductive adhesive, the conductive adhesive comprising a reaction product of a conductive adhesive precursor comprising:

30 the conductive adhesive comprising a reaction product of a conductive adhesive precursor comprising:

- a) from 20 to 50 percent by weight of at least one polyepoxide,

- b) from 20 to 50 percent by weight of at least one free-radically polymerizable (meth)acrylate,
- c) from 20 to 40 percent by weight of conductive fibers, and
- d) from 2 to 10 percent by weight of substantially spherical conductive particles, wherein the percent by weight of components a) to d) is based on the total weight of components a) to d);
- e) an effective amount of at least one thixotrope;
- f) an effective amount of initiator for the at least one free-radically polymerizable (meth)acrylate; and
- g) an effective amount of thermal curative for the at least one polyepoxide.

In certain embodiments, the at least one free-radically polymerizable (meth)acrylate comprises at least one mono(meth)acrylate and at least one poly(meth)acrylate. In certain embodiments, the conductive adhesive precursor is essentially solvent-free. In certain embodiments, the B-staged conductive adhesive precursor is tacky. In certain embodiments, the first substrate and the second substrate comprise electronic device components.

Materials and methods according to the present disclosure overcome the aforementioned shortcomings of conductive adhesive pastes and films. For example, the conductive adhesive precursor can be dispensed, stenciled, or screen printed onto a substrate, then B-staged to convert the flowable conductive adhesive precursor to a, typically conductive, tacky or non-tacky adhesive decal on the printed substrate. This conversion reduces squeeze out and flow of the adhesive during the attachment of the second conductive substrate, which is attached with applied pressure and, optionally, heat. Moreover since it is possible to apply the conductive adhesive precursor only where needed, scrap can be reduced or even essentially eliminated.

The joined conductive substrates can then be exposed to a thermal post-cure cycle that completes the cure. The resulting construction is two substrates with conductive surfaces strongly adhered and showing good electrical interconnection. Conductive adhesives according to the present disclosure are typically isotropic, although this is not a requirement.

Advantageously, conductive adhesive precursors according to the present disclosure contain specific conductive fillers (for example, fibers and substantially

spherical particles) that allow for high conductivity at low enough filler levels to still allow penetration of actinic (for example, ultraviolet (UV)) radiation through the entire thickness of the printed or dispensed conductive adhesive precursor. This enables photocuring, if desired, of the free-radically polymerizable components (for example, (meth)acrylates).

As used herein, unless otherwise specified:

"conductive" means electrically conductive;

"tacky" means slightly adhesive or gummy to the touch;

"thixotrope" means an additive used to impart thixotropy to a coating material; and

"thixotropy" refers to the property of a material which enables it to reversibly stiffen or thicken upon standing a relatively short time, but upon agitation or manipulation to change to a flowable consistency.

The details of one or more embodiments are set forth in the accompanying drawing and description below. Other features, objects, and advantages will be apparent from the description and drawings, and from the claims.

BRIEF DESCRIPTION OF THE DRAWING

Fig. 1 is a schematic cross-sectional side view of an exemplary article according to one aspect of the present disclosure.

DETAILED DESCRIPTION

Conductive adhesive precursors according to the present disclosure include curable components and conductive components. The curable components comprise at least one polyepoxide and at least one free-radically polymerizable (meth)acrylate.

As used herein, the term "polyepoxide" means a compound that has more than one epoxy group. Useful polyepoxides include, for example, alicyclic and aromatic polyepoxides.

Examples of useful alicyclic polyepoxides include monomeric alicyclic polyepoxides, oligomeric alicyclic polyepoxides, and polymeric alicyclic polyepoxides.

Exemplary useful alicyclic polyepoxides monomers include epoxycyclohexanecarboxylates such as, for example, 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate (for example, as "ERL-4221" from Dow Chemical Co.,

Midland, MI) and 3,4-epoxy-2-methylcyclohexylmethyl 3,4-epoxy-2-methylcyclohexanecarboxylate; diglycidyl ether of cyclohexanedimethanol (for example, as "HELOXY 107" from Hexion Specialty Chemicals, Columbus, OH); and hydrogenated bisphenol A diglycidyl ether (for example, as "EPONEX 1510" from
5 Hexion Specialty Chemicals).

Useful aromatic polyepoxides include, for example, monomeric aromatic polyepoxides, oligomeric aromatic polyepoxides, and polymeric aromatic polyepoxides. Exemplary aromatic polyepoxides include the polyglycidyl ethers of polyhydric phenols such as bisphenol A-type resins and their derivatives; epoxy cresol-novolac resins;
10 Bisphenol-F resins and their derivatives; epoxy phenol-novolac resins; and glycidyl esters of aromatic carboxylic acids (for example, phthalic acid diglycidyl ester, isophthalic acid diglycidyl ester, trimellitic acid triglycidyl ester, and pyromellitic acid tetraglycidyl ester), and mixtures thereof. Commercially available aromatic polyepoxides include, for example, those aromatic polyepoxides having the trade designation "EPON" (for example,
15 "EPON 828", "EPON 862", "EPON 1001F", "EPON DPL-862" and "EPON HPT-1079"), available, for example, from Hexion Specialty Chemicals; and aromatic polyepoxides having the trade designations "DER", "DEN" (for example, "DEN 438", and DEN 439"), and "QUATREX", available, for example, from Dow Chemical Co.

The at least one polyepoxide is present in an amount of from 20 to 50 percent by weight, typically in an amount of from 20 to 40 percent by weight, and more typically in an amount of from 25 to 35 percent by weight, based on the combined total weight of the at least one polyepoxide, at least one free-radically polymerizable (meth)acrylate, conductive fibers, and conductive substantially spherical particles.
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An effective amount of thermal curative for the at least one polyepoxide is included in the conductive adhesive precursor such that it can be sufficiently cured to develop a strong bond between the two substrates. Hence, the term "effective amount of thermal curative" refers to at least a minimum quantity. The precise amount will necessarily vary due to formulation and curing variables, but it is typically 10 percent by weight or less based on the total weight of the conductive adhesive precursor.
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Useful thermal curatives for the polyepoxide(s) include acid curatives and base curatives. Examples of useful curing agents include boron trifluoride complexes such as, for example, $\text{BF}_3 \cdot \text{Et}_2\text{O}$ and $\text{BF}_3 \cdot \text{H}_2\text{NC}_2\text{H}_4\text{OH}$; polyamines such as, for example, bis(4-
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aminophenyl)sulfone, bis(4-aminophenyl) ether, and 2,2-bis(4-aminophenyl)propane; aliphatic and aromatic tertiary amines such as, for example, dimethylaminopropylamine; fluorenediamines; and modified amine curing agents such as those commercially available from Air Products and Chemicals, Allentown, PA, under the trade designations

5 "ANCAMINE" (for example, "ANCAMINE 2337S", "ANCAMINE 2014", and "ANCAMINE 2441") and from Ajinomoto, Japan under the trade designation "AJICURE" (for example, "AJICURE PN23" and "AJICURE M353"); imidazoles such as, for example, methylimidazole and 2,4-diamino-6-(2'-methylimidazolyl-(1'))-ethyl-s-triazine hexakis(imidazole)nickel phthalate); hydrazines such as, for example, adipohydrazine;

10 guanidines, such as, for example, tetramethylguanidine and dicyandiamide (cyanoguanidine, also commonly known as DiCy); and combinations thereof.

The at least one free-radically polymerizable (meth)acrylate comprises one or more mono(meth)acrylate(s) and/or poly(meth)acrylate(s). As used herein, the term "(meth)acryl" encompasses both methacryl and/or acryl. For example, a

15 poly(meth)acrylate may have only acrylate groups, only methacrylate groups, or a combination of acrylate and methacrylate groups.

Useful free-radically polymerizable mono(meth)acrylates include, for example, phenoxyethyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, and (meth)acrylic esters of non-tertiary alcohols having from about 4 to about 12 carbon atoms in the alcohol moiety, and combinations thereof. Included in this latter class of (meth)acrylic esters are butyl

20 (meth)acrylate, hexyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, octyl (meth)acrylate, isooctyl (meth)acrylate, decyl (meth)acrylate, and dodecyl (meth)acrylate.

Useful free-radically polymerizable poly(meth)acrylates include, for example, 1,6-hexanediol di(meth)acrylate, trimethylolpropane tri(meth)acrylate, 1,2-ethylene glycol di(meth)acrylate, pentaerythritol tetra(meth)acrylate, and urethane and epoxy

25 di(meth)acrylate oligomers available under trade designation "EBECRYL" (for example, "EBECRYL 230", "EBECRYL 3605", and "EBECRYL 8804") from UCB Radcure, Smyrna, GA, and "CN" (for example, "CN 104") from Sartomer Co., Exton, PA, and combinations thereof.

Typically, a combination of free-radically polymerizable mono(meth)acrylate(s) and poly(meth)acrylate(s) is used. In some embodiments, the free-radically polymerizable (meth)acrylate(s) are selected such that polymerization results in a tacky B-staged

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conductive adhesive precursor (for example, a pressure-sensitive adhesive), although this is not a requirement.

The at least one free-radically polymerizable (meth)acrylate is present in an amount of from 20 to 50 percent by weight, typically in an amount of from 20 to 40 percent by weight, and more typically in an amount of from 25 to 35 percent by weight, based on the combined total weight of the at least one polyepoxide, at least one free-radically polymerizable (meth)acrylate, conductive fibers, and conductive substantially spherical particles.

An effective amount of photoinitiator for the at least one free-radically curable (meth)acrylate is included in the conductive adhesive precursor such that it can be sufficiently cured to B-stage (that is, sufficiently cured that it will soften but not melt if heated) the conductive adhesive precursor upon photopolymerization. Hence, the term "effective amount of photoinitiator" refers to at least a minimum quantity. The precise amount will necessarily vary due to formulation and curing variables, but it is typically 10 percent by weight or less based on the total weight of the conductive adhesive precursor. Typically, lower molecular weight photoinitiators are used in total amounts of about 0.001 to about 4 percent by weight based on the total weight of the conductive adhesive precursor, while higher molecular weight photoinitiators are used in total amounts of about 0.1 percent to about 8 percent by weight based on the total weight of the conductive adhesive precursor.

Useful photoinitiators include, for example, substituted acetophenones such as 2,2-dimethoxy-2-phenylacetophenone; benzoin ethers such as benzoin methyl ether and substituted benzoin ethers such as anisoin methyl ether; substituted alpha-ketols such as 2-methyl-2-hydroxypropiophenone; benzophenone and its derivatives; phosphine oxides; polymeric photoinitiators; and combinations thereof. Many useful photoinitiators are commercially available from sources such as, for example, Ciba Geigy Corp., Tarrytown, NY, under the trade designations "IRGACURE" (for example, "IRGACURE 184", "IRGACURE 651", "IRGACURE 369", and "IRGACURE 907") and "DAROCUR" (for example, "DAROCUR 1173", "DAROCUR MBF", "DAROCUR TPO", and "DAROCUR 4265"), and under the trade designation "ESCACURE" from Sartomer Co., Exton, PA.

The conductive components include conductive fibers and conductive substantially spherical particles.

The conductive fibers are present in an amount of from 20 to 40 percent by weight, typically in an amount of from 20 to 35 percent by weight, and more typically in an amount of from 24 to 28 percent by weight, based on the combined total weight of the at least one polyepoxide, at least one free-radically polymerizable (meth)acrylate, conductive
5 fibers, and conductive substantially spherical particles.

Suitable conductive fibers include virtually any fiber material having a bulk resistivity below about 50 microohm-centimeters ($\mu\Omega$ -cm), typically below about 4 $\mu\Omega$ -cm. Examples of conductive fibers include fibers of conductive metals such as, for example, copper, aluminum, silver, and gold, and alloys thereof. Conductive fibers can
10 also be prepared by modifying electrically insulating fibers, such as by introducing a conductivity-imparting agent to a natural or synthetic polymer, for example, by incorporating metal particles into the fiber. Conductive fibers may also be formed by metal plating, or otherwise coating, onto a metal fiber or metal plating onto a non-metal fiber core. Metal plating for fiber includes copper, nickel, cobalt, silver, gold, palladium,
15 platinum, ruthenium, and rhodium, and alloys of thereof. Non-metal fiber cores include carbon, graphite, glass, polyester, and other synthetic materials. Exemplary metal-plated fibers include nickel-plated carbon fibers, polyethylene fiber coated with gold, acrylic fibers plated with gold, nylon fibers coated with rhodium, and silver coated glass fibers (for example, as "CONDUCT-O-FIL SILVER COATED E-GLASS FIBER SF82TF20"
20 from Potters Industries, Valley Forge, PA). Exemplary metal fibers include stainless steel fiber, copper fiber, silver fiber, aluminum fiber, and combinations thereof. Combinations of conductive fibers may also be used.

As used herein the term "substantially spherical particles" refers to regularly shaped, rounded particles that resemble spheres. The conductive substantially spherical
25 particles are present in an amount of from 2 to 10 percent by weight, typically in an amount of from 2 to 8 percent by weight, and more typically in an amount of from 2 to 5 percent by weight, based on the combined total weight of the at least one polyepoxide, at least one free-radically polymerizable (meth)acrylate, conductive fibers, and conductive substantially spherical particles.

30 Examples of conductive substantially spherical particles include metal spheres such as aluminum, nickel, gold, copper, or silver, and coated copper, nickel, polymeric, or glass spheres coated with conductive coatings such as aluminum, gold, silver, copper, or

nickel. Also useful are substantially spherical solder particles such as lead/tin alloys in varying amounts of each metal, for example, as available from Sherritt Gordon Limited, Canada. Examples of commercially available electrically conductive particles include conductive nickel spheres available from Novamet, Wykoff, NJ and silver coated glass spheres (for example, as "CONDUCT-O-FIL S-3000-S3MM" from Potters Industries).

Combinations of conductive substantially spherical particles may also be used.

In addition to the foregoing components, conductive adhesive precursors according to the present disclosure include an effective amount of at least one thixatrop. As used herein, term "effective amount" means a sufficient quantity that the conductive adhesive precursor rapidly develops shape stability the essentially eliminates flow after application after application of the conductive adhesive precursor to a substrate. Thixotropes are well known in the art, and many are widely commercially available. Examples of suitable thixotropes include treated and untreated fumed silicas such as those available under the trade designation "CAB-O-SIL" from Cabot Corp. of Boston, MA, or under the trade designation "AEROSIL" from Evonik Industries, Essen, Germany.

While not required, the conductive adhesive precursors may further contain minor amounts (for example, less than about 20 percent by weight) of one or more additive(s) such as, for example, tackifiers (for example, to facilitate adhesion to non-polar substrates), dyes, pigments, thermoplastic polymers, non-conductive fillers, and /or coupling agents.

While solvent may be included in the conductive adhesive and/or its precursor, it is generally desirable to limit the amount to a minor amount (for example, less than about 20 percent by weight). Advantageously, the conductive adhesive and/or its precursor may be formulated as essentially solvent-free, or even totally free of solvent. As used herein, the term "essentially solvent-free" means containing less than about one percent by total weight of solvent. The term "solvent" refers collectively to any volatile organic compound(s) (not reactive with other components that are present) added for the purpose of solvating at least some of the remaining components of a composition. Examples include toluene, heptane, ethyl acetate, methyl ethyl ketone, acetone, and mixtures thereof.

In practice, the conductive adhesive precursor is typically prepared from its constituent parts using a conventional mixing technique, for example, gentle rolling, roller milling, or ball milling. In some cases, it may be useful to heat the polyepoxide and/or

free-radically polymerizable (meth)acrylates (for example, up to about 80° C) to facilitate mixing.

Conductive adhesive precursors according to the present disclosure can be used to conductively bond a first substrate to a second substrate. Typically, in such a process a
5 conductive adhesive precursor according to the present disclosure is applied (for example, dispensed, stenciled, or screen printed) to a typically conductive portion of the first substrate (for example, a portion of a circuit trace). The conductive adhesive precursor is then exposed to actinic radiation (for example, ultraviolet and/or visible light) that decomposes at least a portion of the photoinitiator and causes polymerization of the at
10 least one (meth)acrylate sufficient to result in a B-staged conductive adhesive precursor. Sources of actinic radiation include, for example, low, medium or high pressure mercury lamps, lasers, and xenon flash lamps. Next, the second substrate is brought into contact with the B-staged conductive adhesive precursor; and the combination is heated (for example, in an oven) under conditions (for example, time and temperature) to sufficiently
15 cure the polyepoxide to achieve a secure conductive bond between the first and second substrates.

An exemplary such a bonded article is shown in Fig. 1, wherein an article 100 has first substrate 110 having support 112 with conducting element 114 thereon and second substrate 120 having support 122 with conducting element 124 thereon. The first and
20 second substrates are bonded one to another by conductive adhesive 130 according to the present disclosure.

While any substrates may be used, typically at least a portion of the substrates will be conductive. Examples of useful substrates include components of electronic devices (for example, integrated circuits, LEDS, sockets), flex circuitry, and printed circuit boards.

25 Objects and advantages of this disclosure are further illustrated by the following non-limiting examples, but the particular materials and amounts thereof recited in these examples, as well as other conditions and, details, should not be construed to unduly limit this disclosure.

30 EXAMPLES

Unless otherwise noted, all parts, percentages, ratios, etc. in the Examples and the rest of the specification are by weight.

TABLE OF ABBREVIATIONS

ABBREVIATION	DESCRIPTION
ACR1	phenoxyethyl acrylate available as "AGEFLEX PEA" from Ciba Specialty Chemicals, Tarrytown, NY.
ACR2	Aliphatic urethane diacrylate, available as "EBECRYL 8804" from Cytec Surface Specialties, Smyrna, GA.
CFIB	SILVER COATED GLASS FIBER, powder resistivity 3.5 mohm-cm, mean particle size (length) = 130 micrometers, available as "CONDUCT-O-FIL SF8 2TF20" from Potters Industries, Valley Forge, PA.
CFIL	Silver coated solid glass spheres, average particle size = 41 micrometers, available as "CONDUCT-O-FIL S3000-S3M" from Potters Industries.
CUR	Cycloaliphatic amine curing agent available as "ANCAMINE 2441" from Air Products and Chemicals, Allentown, PA.
EP1	difunctional bisphenol A/epichlorohydrin derived liquid epoxy resin, epoxide equivalent weight = 185-192 g/eq, available as "EPON 828" from Hexion Specialty Chemicals, Houston, TX, purified.
EP2	bisphenol F/epichlorohydrin derived liquid epoxy resin, epoxide equivalent weight = 165-180 g/eq, available as "EPICLON 830" from Dainippon Ink and Chemicals, Tokyo, Japan.
EP3	bisphenol A/epichlorohydrin derived liquid epoxy resin, epoxide equivalent weight = 180-190 g/eq, available as "EPICLON 840" from Dainippon Ink and Chemicals.
EP4	liquid epoxy resin derived from epichlorohydrin and bisphenol F, epoxide equivalent weight = 165-173 g/eq, available as "EPON 862" from Hexion Specialty Chemicals, purified.
FUMSIL	hydrophobic fumed silica, available under the trade designation "AEROSIL R 202" from Evonik Industries AG, Essen, Germany.

PI	photoinitiator (CAS No. 119313-12-1; 2-benzyl-2-dimethylamino-4-morpholinobutyrophenone, available as "IRGACURE 369" from Ciba Specialty , Tarrytown, NY)
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EXAMPLE 1

ACR1 (27.6 parts), 1.4 parts of ACR2, 19 parts of EP1, 15 parts of EP2 were
 5 combined by mixing (rolling in a plastic bottle). To this mixture was added 4.6 parts of
 FUMSIL, 26.1 parts of CFIB, 3.3 parts of CFIL, 5.7 parts of CUR, and 0.3 parts of PI,
 with mixing in a centrifugal mixer marketed by Hauschild Engineering, Hamm, Germany
 as "DAC 600 FVZ SPEEDMIXER" operating at 2700 revolutions per minute (rpm) rpm
 resulting in Composition 1.

10 Composition 1 was stencil printed onto: a 2 mil (0.05 mm) thickness polyimide
 film with copper metallization plated with gold resulting in Sample (a), and the gold-
 plated side of a gold-plated PET polyester film (3 mil (80 micrometers) thickness),
 resulting in Sample (b), using a 3 mils (80 micrometers) thick metal stencil and an
 aluminum plate as a print blade. The films with the printed adhesives were passed two
 15 times through an ultraviolet (UV) lamp Fusion UV Systems lamp, model F300S, equipped
 with an "H bulb" available from Fusion UV Systems, Gaithersburg, MD, to obtain a total
 dose of 790 millijoules/centimeter² (mJ/cm²) in the UVA region of the spectrum.

After UV exposure, the printed Composition 1 had become tacky (that is, B-staged).
 For Samples (a) and (b) the B-staged adhesive was then bonded to an indium-tin-oxide
 20 (ITO)-coated side of an ITO-coated PET polyester film) (3 mils (0.08 mm) thickness) to
 test conductivity of the adhesive after cure. The ITO-coated film was pressed for 10
 seconds onto the adhesive in a Young Technology's precision thermal press set at 25
 pounds per square inch (0.2 MPa) and 55-65 °C. The samples were then placed between
 two sheets of stainless steel and cured by placing in an oven set at 120 °C for 30 minutes.

25 Conductivity was tested by probing the two substrate surfaces and measuring
 resistance through the adhesive using a model 73III multimeter marketed by Fluke
 Corporation, Everett, WA. Both laminated cured samples had an electrical resistance of
 1.7 ohms or less indicative of a good electrical interconnect.

EXAMPLE 2 and COMPARATIVE EXAMPLES A-C

A composition (Composition 2) was prepared by combining with mixing (rolling in a plastic bottle): 490 parts of ACR1, 10 parts of ACR2, 250 parts of EP2, 250 parts of EP3. To 243 parts of Composition 2 was added 19.5 parts of FUMSIL, and the combined ingredients were mixed for 2 minutes using a centrifugal mixer marketed by Hauschild Engineering as "DAC 600 FVZ SPEEDMIXER" operating at 2700 revolutions per minute rpm. CUR (24.2 parts) was added to the resultant mixture, which was then mixed for 2 minutes using a centrifugal mixer ("DAC 600 FVZ SPEEDMIXER") operating at 1900 rpm.

A photoinitiator solution was separately prepared from a one-to-one blend of ACR1 and PI, heated at 95 °C for 20 minutes to partially liquefy it.

This photoinitiator solution (2.6 parts) was combined with 252.5 parts of Composition 2, which was then mixed at rpm for 2 minutes using a centrifugal mixer ("DAC 600 FVZ SPEEDMIXER") operating at 1900 rpm resulting in Composition 3.

Four formulations were prepared as shown in Table 1 (below).

TABLE 1

EXAMPLE	FORMULATION	COMPOSITION 3, parts	CFIL, parts	CFIB, parts
COMPARATIVE EXAMPLE A	A	71	0	29
COMPARATIVE EXAMPLE B	B	71	29	0
EXAMPLE 2	C	71	3	26
COMPARATIVE EXAMPLE D	D	23	77	0

Each of the above formulations at rpm for 2 minutes using a centrifugal mixer ("DAC 600 FVZ SPEEDMIXER") operating at 2200 rpm. Formulations A, B, and C were vacuum degassed while slowly stirring for about 10 min. Formulation D was vacuum degassed without stirring for one hour.

Each formulation was stencil printed onto an interdigitated comb-patterned printed circuit board using a surface insulation resistance test circuit defined by the solder mask qualification board IPC-B-25A (see IPC-9201 Surface Insulation Resistance Handbook, July 1996, IPC, Northbrook, IL) with nickel-gold top layer metallurgy having an area of 0.5 inch (2.5 cm) by 1.25 inches (3.18 cm) made from stamped openings in 5.5 mils (130 micrometers) thick polyester film. The circuit pattern having an 0.5 millimeter line spacing was tested. The dispensed patterns of each formulation were B-staged by exposure to UV light using a Fusion UV Systems lamp, model F300S, equipped with an "H bulb", and operated at a conveyor speed of 20 feet/minute (6.1 m/min). The ultraviolet light dosage was measured using an energy meter ("UV POWER PUCK" from EIT, Sterling, VA) at 485.4 mJ/cm² UV-A and 448.4 mJ/cm² UV-B. The connection resistance between the interdigitated patterns was measured with a model 73III multimeter from Fluke Corporation, Everett, WA. Four replicates were measured for each formulation. Results are reported in Table 2 (below).

Table 2

EXAMPLE	CONNECTION RESISTANCE, ohms			
	Replicate 1	Replicate 2	Replicate 3	Replicate 4
COMPARATIVE EXAMPLE A	1.88×10^7	1.27×10^7	2.1	7.00×10^4
COMPARATIVE EXAMPLE B	open	open	open	open
EXAMPLE 2	114.6	4.3	6.2	1.15×10^7
COMPARATIVE EXAMPLE C	8.4	5.2	1.75×10^6	19.5

As can be seen in Table 2, Example 2 and Comparative example C gave conductive B-staged compositions, thereby permitting testing (and potentially repair) of the electrical connection prior to subjecting them to thermal curing.

One set of B-stage printed boards (including two of the test patterns) were placed in an oven for 30 minutes at 150 °C to C-stage them. The connection resistance between the interdigitated patterns was measured again, and are reported in Table 3 (below).

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Table 2

EXAMPLE	Connection Resistance, ohms	
	Replicate 1	Replicate 2
COMPARATIVE EXAMPLE A	0.5	0.3
COMPARATIVE EXAMPLE B	open	open
EXAMPLE 2	0.5	0.7
COMPARATIVE EXAMPLE C	0.1	0.1

The same pattern of each of Example 2 and Comparative Examples A-C was stenciled onto bare polyester film. These patterns were also exposed to the abovementioned UV light source. A second polyester film was placed over each of the printed formulations and pressed together by applying pressure with a weighted roller (4.5 lbs, (2.2 kg)). The two polyester films were then peeled apart to demonstrate the integrity of the B-Staged film. In the case of Formulations Comparative Examples A and B, and Example 2 the pattern was separated from the top polyester layer as a complete film indicated sufficient UV treatment through the full thickness of the material. In the case of Comparative Example C, the material did not cleanly separate from the top polyester layer indicating incomplete UV treatment through the thickness of the material.

These results show that the formulations with the fiber fillers can provide a consistent electrical connection after UV B-Stage while the formulations with only spherical particles require very high loading level for consistent electrical connection. Also, in the case of loading levels of 29 percent by weight the UV treatment allows for complete exposure and full film characteristic formation through the 5.5 mil thickness while in the case of the high spherical particle loading level (77 percent by weight), the material exhibited poor stencil printing characteristics and the UV light exposure did not allow for full film characteristic formation.

Various modifications and alterations to this disclosure will become apparent to those skilled in the art without departing from the scope and spirit of this disclosure. It should be understood that this disclosure is not intended to be unduly limited by the illustrative embodiments and examples set forth herein and that such examples and
5 embodiments are presented by way of example only with the scope of the disclosure intended to be limited only by the claims set forth herein as follows.

What is claimed is:

1. A conductive adhesive precursor comprising:
 - a) from 20 to 50 percent by weight of at least one polyepoxide,
 - 5 b) from 20 to 50 percent by weight of at least one free-radically polymerizable (meth)acrylate,
 - c) from 20 to 40 percent by weight of conductive fibers, and
 - d) from 2 to 10 percent by weight of conductive substantially spherical particles, wherein the percent by weight of components a) to d) is based on the
10 total weight of components a) to d);
 - e) an effective amount of at least one thixotrope;
 - f) an effective amount of photoinitiator for the at least one free-radically polymerizable (meth)acrylate; and
 - g) an effective amount of thermal curative for the at least one polyepoxide.
- 15 2. The conductive adhesive precursor of claim 1, wherein the at least one free-radically polymerizable (meth)acrylate comprises at least one mono(meth)acrylate and at least one poly(meth)acrylate.
- 20 3. The conductive adhesive precursor of claim 1 or 2, wherein the conductive adhesive precursor is essentially solvent-free.
4. A method of conductively bonding a first substrate to a second substrate comprising:
 - 25 applying a conductive adhesive precursor to the first substrate, the conductive adhesive precursor comprising:
 - a) from 20 to 50 percent by weight of at least one polyepoxide,
 - b) from 20 to 50 percent by weight of at least one free-radically polymerizable (meth)acrylate,
 - 30 c) from 20 to 40 percent by weight of conductive fibers, and

d) from 2 to 10 percent by weight of conductive substantially spherical particles, wherein the percent by weight of each of components a) to d) is based on the total weight of components a) to d),

e) an effective amount of at least one thixotrope,

5 f) an effective amount of initiator for the at least one free-radically polymerizable (meth)acrylate, and

g) an effective amount of thermal curative for the at least one polyepoxide;

10 free-radically polymerizing at least a portion of the at least one free-radically polymerizable (meth)acrylate to convert the conductive adhesive precursor into a B-staged conductive adhesive precursor;

contacting the second substrate with the B-staged conductive adhesive precursor; and

15 curing at least a portion of the at least one polyepoxide.

5. The method of claim 4, wherein the at least one free-radically polymerizable (meth)acrylate comprises at least one mono(meth)acrylate and at least one poly(meth)acrylate.

20 6. The method of claim 4 or 5, wherein the conductive adhesive precursor is essentially solvent-free.

7. The method of any one of claims 4 to 6, wherein the first substrate and the second substrate comprise electronic device components.

25 8. The method of any one of claims 4 to 7, wherein the B-staged conductive adhesive precursor is tacky.

9. An article comprising a first substrate bonded to a second substrate by a conductive adhesive, the conductive adhesive comprising a reaction product of a conductive adhesive precursor comprising:

a) from 20 to 50 percent by weight of at least one polyepoxide,

- b) from 20 to 50 percent by weight of at least one free-radically polymerizable (meth)acrylate,
- c) from 20 to 40 percent by weight of conductive fibers, and
- d) from 2 to 10 percent by weight of substantially spherical conductive particles, wherein the percent by weight of components a) to d) is based on the total weight of components a) to d);
- e) an effective amount of at least one thixotrope;
- f) an effective amount of initiator for the at least one free-radically polymerizable (meth)acrylate; and
- g) an effective amount of thermal curative for the at least one polyepoxide.

10. The article of claim 9, wherein the at least one free-radically polymerizable (meth)acrylate comprises at least one mono(meth)acrylate and at least one poly(meth)acrylate.

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11. The article of claim 9 or 10, wherein the conductive adhesive precursor is essentially solvent-free.

12. The article of any one of claims 9 to 11, wherein the first substrate and the second substrate comprise electronic device components.

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