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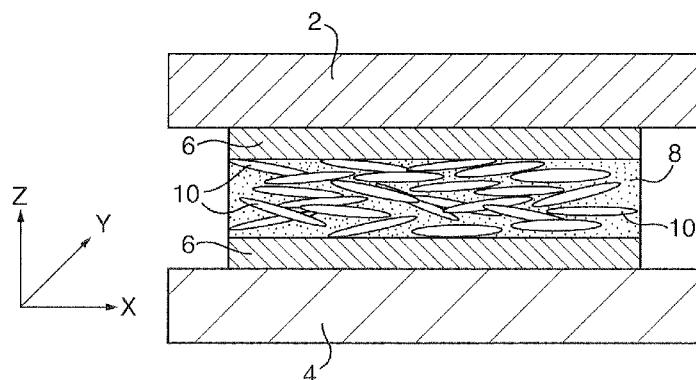
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Fig. 1



(57) Abstract: An isotropic conductive adhesive comprises silver coated polymer beads 12 within an adhesive matrix 8, wherein the mean average diameter of the polymer cores of the beads 12 is 5  $\mu\text{m}$  or greater and less than 30  $\mu\text{m}$ , and wherein the silver coating comprises interlinked silver deposits grown from dispersed nucleation sites scattered across the surface of the beads.

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## ISOTROPIC CONDUCTIVE ADHESIVE

The invention relates to an isotropic conductive adhesive and a method of manufacture thereof.

5 Isotropic conductive adhesives (ICAs) have been commercially available as an alternative to solder interconnects in electronic packaging for many years. An ICA typically consists of a non-conductive adhesive matrix filled with conductive particles. The mechanical strength of the ICA comes from the adhesive matrix, while the conductive fillers provide electrical conductivity.

10 The most common ICAs in the electronics industry consist of epoxy filled with silver flakes or particles. Figure 1 is a schematic drawing showing an ICA of this type used to connect a component 2 to a substrate 4. Both of the component 2 and substrate 4 have an electrical contact 6. The ICA, which comprises a polymer resin matrix 8 and silver flakes 10 is used to electrically connect the two contacts 6. The silver flakes 10 form a conductive network that allows for conduction of electricity in all directions. Before the adhesive is cured, the silver flakes 15 (in the adhesives) have a tendency to be oriented both during application and under the influence of gravity. This results in a better conductivity in the plane of the substrate compared to conductivity normal to this plane and hence the conductive properties of the adhesive are not truly isotropic. Traditionally, ICA compounds have been heavily loaded with silver particles, typically in the range of 25 – 30 volume% (up to 80 wt%), to ensure sufficient electrical 20 conductivity also in the z-direction. This leads to a high metal content for the adhesive. Such a high metal particle loading causes significant changes in the mechanical properties of the adhesives, including increased bulk modulus, reduced flexibility (a more brittle response) and an excessive use of precious metal.

25 Metal coated glass beads have also been proposed as the filler in ICAs. However the use of glass beads creates a mismatch in thermal coefficient of the bead with the epoxy matrix and this results in degradation and loss of conductivity when the adhesive undergoes thermal cycling. In addition, the rigidity of the glass beads and difficulties in generating tightly controlled size distribution for the particles results in limited contact areas with the surfaces that are adhered together, further limiting conductivity.

30 US 6942824 discloses an electrically conductive adhesive including a resin component, a photoinitiator, and metal-coated polymer beads. The resin is UV cured. The metal coating of the beads provides electrical conductivity. The use of polymer beads avoids some of the disadvantages associated with glass beads. The polymer beads are between 15 and 30  $\mu\text{m}$  in diameter and are coated with gold or silver having a thickness of between 20 and 100 nm. The 35 metal layer is a uniform coating formed by 'polymer bead shell metal plating', which is disclosed as comprising the formation of a uniform copper layer followed by plating with an additional layer, or by electroplating, which typically involves the use of a continuous nickel seed layer followed by

a gold or silver layer. The use of nickel is undesirable as it is classified as Carcinogenic 2B (possible carcinogen for humans) and is related to skin sensitisation and allergies.

Viewed from a first aspect, the invention provides an isotropic conductive adhesive comprising silver coated polymer beads within an adhesive matrix, wherein the mean average 5 diameter of the polymer cores of the beads is 5  $\mu\text{m}$  or greater and less than 30  $\mu\text{m}$ , and wherein the silver coating comprises interlinked silver deposits grown from dispersed nucleation sites scattered across the surface of the beads.

The polymer beads are spherical or close to spherical balls of polymer. Polymer beads of the sizes used herein are often referred to as micro-beads or micro-spheres. The use of silver 10 coated polymer beads offers improvements over silver particles and metal coated glass beads. Less metal and fewer processes may be required to provide the required conductivity and compared to glass beads the polymer beads can be more closely matched in terms of mechanical properties to the properties of the surrounding adhesive matrix, including thermal expansion coefficient and elastic deformation. This minimises degradation in the adhesive that 15 would otherwise occur under cycling thermal or mechanical loads.

As noted above, US 6942824 discloses the use of polymer beads. However, the silver or gold coating for the polymer beads of US 6942824 is created as a uniform layer. In order to deposit this uniform layer a continuous seed layer of copper or nickel is used. Growing a conductive layer of silver using nucleation sites on the surface of the beads advantageously uses 20 less metal and fewer manufacturing steps than the processes disclosed in US 6942824.

Surprisingly, it has been found that silver deposits will readily grow on the surface of the beads using nucleation sites and that when the individual deposits become large enough to interlink then the conductive properties of an adhesive utilising the beads are comparable to conventional isotropic conductive adhesives. The absence of the seed layer also results in a metal layer that 25 is thinner (for a comparable thickness of silver). This can have advantages in terms of the mechanical properties of the beads, in particular when the seed layer is made of nickel which is a very hard and little compliant metal. The mechanical properties of the polymer core will be more dominant in a bead having a thinner coating allowing the properties of the beads to be more closely matched with the properties of the surrounding adhesive matrix. The absence of the 30 continuous seed layer also has advantages related to the density of the filler. A conductive filler with only a single metal layer can have a density closer to that of the resin and as such have a reduced tendency to sedimentation/separation.

A mean average diameter of the polymer cores of the beads of less than 30  $\mu\text{m}$  (excluding 35 30  $\mu\text{m}$ ) is set since the use of beads with larger diameters creates various disadvantages. The disadvantages include reduced conductivity, the need for a thicker bond line and reduced strength of the bonded adhesive. The reduced conductivity is as a consequence of the increased proportion of polymer in the adhesive compared to the amount of silver. The bond

line thickness is the thickness of adhesive required between the two parts that are joined together. For a conductive adhesive the required thickness needs to take the need for conductivity into account as well as the bond strength. When larger beads are used the bond line thickness is increased, which is a disadvantage. Also, the use of larger beads leads to 5 reduced shear strength for the bonded adhesive. It should be understood that the use of larger beads is possible, but it is not preferred and it is currently considered to give rise to significant disadvantages.

Preferably the mean average diameter of the polymer cores of the beads is 25  $\mu\text{m}$  or lower, more preferably 20  $\mu\text{m}$  or lower. Reducing the mean average diameter provides 10 increased conductivity and strength for the adhesive, and permits a thinner bond line.

The mean average diameter of the polymer cores of the beads is 5  $\mu\text{m}$  or more since smaller diameters will also create disadvantages. Preferably the mean average diameter of the polymer cores of the beads is more than 5  $\mu\text{m}$  and more preferably it is 6  $\mu\text{m}$  or above, optionally the mean average diameter is 10  $\mu\text{m}$  or above. As the cores are made smaller the relative 15 amount of silver for a given coating thickness increases since the surface area of the beads increases comparative to the volume of the beads. An adhesive product using smaller sized beads will include a higher proportion of silver than the equivalent product using larger sized beads and the same silver thickness. Whilst smaller sized beads will have advantages in relation to conductivity when the size of the beads is too small these advantages are not sufficient to 20 outweigh the disadvantage of increased silver use and the consequent increased manufacturing cost. Hence a minimum average diameter is a preferred feature.

In a particularly preferred embodiment the polymer cores of the beads have a mean average diameter of between 6  $\mu\text{m}$  and less than 30  $\mu\text{m}$ , optionally excluding 6  $\mu\text{m}$ , more preferably between 10  $\mu\text{m}$  and 25  $\mu\text{m}$ , optionally excluding the end points of this range and yet 25 more preferably between 10  $\mu\text{m}$  and 20  $\mu\text{m}$ , optionally excluding the end points of this range. These ranges of average sizes are considered to provide the best compromise between the amount of silver required to create the necessary interlinked deposits whilst also keeping the beads small enough to provide the capability for a thinner bond line, higher conductivity and good mechanical properties for the cured adhesive. It will be understood that when selecting the mean 30 average diameter for the polymer beads there are compromises between conductivity, mechanical properties and the amount of silver used. It has been found that good combinations of conductive and mechanical properties can be achieved with the use of beads having the preferred average diameters set out above.

The references to mean average diameter herein are references to a mean diameter of 35 the polymer cores of the beads prior to coating with silver as measured by an instrument such as a Coulter Counter, by microscopy or by an equivalent technique.

In preferred embodiments the polymer cores of the beads all have a coefficient of variation (CV) in diameter of less than 10%, preferably less than 5%, preferably less than 4%, and most preferably less than 3%. The CV value is defined by: CV = Standard deviation in diameter/Mean average diameter. It is also preferred to avoid "off size" particles with a diameter far from the average. Hence, preferably the incidence of polymer cores of the beads with a diameter less than two thirds of the mean diameter or with a diameter greater than 1.5 times the mean diameter should be less than 1 in 1000 and more preferably less than 1 in 10 000. It is known that a broad size distribution of spherical particles increases the percolation threshold. (See, for example, R. Yazici et. al, "Particulate based conductive composites exploiting percolation-range microstructure", <http://www.hfmi.stevens.edu/publications/147.PDF>). Again, a broad size distribution will increase the consumption of silver to provide the same conductivity.

A smaller CV of the beads, in particular an absence of "off size" particles has been found to be particularly advantageous for an isotropic conductive adhesive since the beads in the isotropic adhesive can pack together with contact in several directions through the adhesive. 15 This advantageous close packing is promoted when the diameters of the beads are within the preferred ranges set out above.

Appropriate polymer particles for the polymer cores of the beads can be obtained from various companies including Conpart AS of Norway.

The thickness of the silver layer can also be important. Larger thicknesses will use a greater amount of silver and will also have a more significant effect on the mechanical properties of the sphere. However the larger thickness will improve electrical conductivity and can also have advantages for thermal conductivity. Conversely, when the silver layer is thinner than the silver usage and conductivity is reduced, but the mechanical properties of the coated polymer bead are influenced more by the polymer core. It is advantageous for the mechanical properties to be influenced by the polymer core rather than by the silver coating since the mechanical properties of the polymer core can more closely match the mechanical properties of the adhesive matrix. In order for the adhesive to operate as intended, the amount of silver and the extent of the silver coating should be sufficient to produce a low resistance metal layer around the polymer core. In addition, the volume fraction of the beads must be sufficient to form an interconnected 30 conductive network in the adhesive matrix.

It will be understood that with the use of interlinked deposits grown from dispersed nucleation sites then the silver may grow outwardly from the surface of the polymer as well as growing along the surface starting from the nucleation site. This means that the thickness of the silver coating is not constant. When an average coating thickness is referenced herein it refers to a mean average thickness of the silver as determined, for example, by a density measurement using a pycnometer or similar device. A suitable instrument is the Multipycnometer 35 manufactured by Quantathrome Instruments of Boynton Beach, Florida, USA.

To determine the amount of silver for present and to hence allow calculation of an average coating thickness using a density measurement technique first the volume of a measured weighted sample of beads comprising the pure polymer core is measured and the density of the polymer core is calculated. The volume and density measurement is then 5 repeated for a measured weight sample of beads with the addition of the silver coating on the polymer core, with beads taken from the same polymer core batch as the pure polymer core sample. The volume of silver relative to the volume of the polymer core material can then calculated based on the differences in volume and density. An average silver thickness indicating a mean average thickness for the silver coating across the entire surface area of each 10 bead can be determined from this using the mean average diameter of the beads. For particles with a broad size distribution it is important that the value for the average diameter used in the calculation is defined as the square root of an average of the square of the diameter, as in the formula below:

$$\text{Area weighted average diameter} = \sqrt{\left( \frac{\sum_1^n d^2}{n} \right)^2}$$

15 where d represents the measured diameter of individual particles and n represents the number of particles measured. This gives an average based on the surface area of the particles – not an average diameter. If the particles are identical in size then the average diameter and area weighted average become the same.

20 The amount of silver in the silver coating derived from this measurement technique can be expressed as an absolute thickness or alternatively it can be expressed as a volume of silver relative to the volume of the coated particles. Defining the thickness based on a relative volume of silver, for example as a volume percentage (vol%), gives a measure of the silver thickness that is independent of the mean average diameter. The vol% of silver in the coated particles is of course directly related to the thickness when expressed as a percentage of the core diameter.

25 The average thickness of the silver measured in this way may be 350 nm or less and/or less than 5% of the core diameter, preferably less than 3.5% of the core diameter, most preferably less than 3% of the core diameter and optionally less than 1.7% of the core diameter. If expressed as a vol% of silver in the coated particles then a thickness of less than 3% of the core diameter equates to a maximum of about 16.9 vol% of silver in the coated particles. The 30 maximum permitted thickness may be the larger of 350 nm and the percentage values set out above. For smaller diameters an average thickness of more than the percentage values can be tolerated and it can be advantageous in terms of conductivity to permit a higher maximum. It has been found that the disadvantages of a coating with an average thickness above these values outweigh the advantages. With thicker silver coatings the mechanical properties of the coated

polymer beads can be dominated by the metal coating and as noted above it is preferred for the properties to be more heavily influenced by the polymer core. Also, as the coating becomes thicker the disadvantage of increased costs for the additional silver can outweigh any benefits from increased conductivity. However, it may be that for certain applications, where thermal 5 conductivity is a significant advantage, then larger thicknesses than those stated above could be useful. For applications requiring high levels of thermal conductivity the use of particles at the lower end of the size ranges set out above may also be preferred.

It is preferred for the average thickness of the silver coating to be more than 0.5% of the core diameter, preferably more than 0.7% of the core diameter and optionally more than 0.85% 10 of the core diameter. These levels of silver are expected to provide good conductivity whilst also minimising material costs and limiting the effect of the coating on the mechanical properties of the beads. Alternatively, the average thickness of the silver may be more than 25 nm, preferably more than 50 nm, more preferably more than 100 nm. The minimum average thickness for the coating may be set as the smaller out of one of these values and one of the percentage values 15 above. For larger diameters an average thickness of less than the preferred percentage values above can be tolerated and thicknesses over these values can provide sufficient conductivity even at the larger diameters. A value of 50 nm with core diameters of 20  $\mu\text{m}$  to 25  $\mu\text{m}$  gives a thickness of 0.25% to 0.2% of the diameter. Some preferred embodiments use a thickness of more than 120 nm for enhanced conductivity.

20 In some preferred embodiments the average diameter of the polymer cores of the beads is between 6  $\mu\text{m}$  and less than 30  $\mu\text{m}$ , optionally excluding 6  $\mu\text{m}$ , more preferably between 10  $\mu\text{m}$  and 20  $\mu\text{m}$ , optionally excluding the end points of this range; and the average thickness of the coating, measured as above, is above 50 nm and below 350 nm, preferably above 100 nm, preferably below 200 nm; and/or with an average thickness of between 0.7% and 3% of the core 25 diameter. These combinations of thickness and diameter values have been found to give particularly good results.

30 Full coverage of the particle with silver is not a prerequisite for the functionality of the product. It is however preferred that the coverage be more than 80% of the particle surface area and more preferred complete coverage. This leads to the best conductive properties for the adhesive.

Silver may be deposited on small polymer particles by a number of methods. The most applicable are the methods collectively called electroless-plating. Electro-plating is also theoretically possible but extremely difficult on such small particles. Electroless-plating of silver on a polymer requires activation of the surface. In an example coating process, catalytic 35 quantities of metals atoms illustrated by but not restricted to palladium, platinum or silver are distributed evenly over the surface of the polymer core. This may be achieved by methods including vapour deposition, impregnation with a salt of the metal followed by reduction to the

metallic state or by sensitisation by acidic tin chloride followed by a salt such as palladium chloride. The methods are numerous and well known to one skilled in the art. Silver may then be deposited by the reduction of silver ions from a soluble salt such as silver nitrate or silver sulphate. This reaction may be performed with a number of reducing agents illustrated by but

5 not restricted to hydrazine, dimethyl ammonium borane, sugars such as glucose and fructose or ascorbic acid. In this example process silver deposition is initially catalysed by the activating metal and then thereafter by the silver layer forming. The silver deposition becomes autocatalytic. Not to be restricted by any one model it is believed that clusters of metal atoms are required to catalyse the silver reduction. Single atoms are not believed to be adequate.

10 The isotropic conductive adhesive preferably comprises a mixture of silver coated polymer beads and adhesive matrix with the polymer beads forming 20-60% of the mixture, by volume. Preferably the polymer beads form 25-55% and more preferably 45-50% of the volume of the mixture by volume. The percolation threshold for spheres is typically 30 – 40% by volume and hence it is preferred to exceed this threshold value. The percolation threshold in this context 15 is a mathematical value for the threshold above which, in a random system, a fully interconnected network will be formed, in this case a network of beads forming an isotropically conductive network. If the amount of polymer beads is too low then the conductivity of the adhesive will be reduced. Conversely, if too many beads are included then the mechanical properties of the cured adhesive can be adversely affected. For thin films of adhesive 20 conductivity will be obtained at lower volume fractions. At a volume fraction of about 17% one can say that conductivity in the X and Y directions essentially falls to zero and the adhesive becomes anisotropic. Discussion of the effect of volume fraction on conductivity can be found in US 2009/0288697.

25 The volume of beads in the mixture may be increased beyond 60% when multiple sizes of beads are used, for example a mixture of two diameters of beads selected so that the smaller beads will occupy the gaps left between the larger beads.

The adhesive matrix is typically based on a thermosetting resin such as, but not limited by, an epoxy resin, a crosslinkable polyurethane, a silicone, a cyano-acrylate or a thermoplastic material as exemplified by ethylene vinyl acetate or linear polyurethane. The adhesive matrix 30 may be a heat curing adhesive or an adhesive cured by UV or visible light. A heat curing adhesive matrix is preferred. It is preferred that an adhesive is used that can be processed at temperatures less than 180°C, typically around 150°C. Adhesives that can be processed at lower temperatures, even room temperature curing adhesive, may be used.

35 The polymer beads can comprise any suitable polymer material. Preferred materials are styrenics, acrylates and methacrylate, vinyl polymers and condensation polymers including polyesters, epoxy resins, phenol-aldehyde polymers and polyurethanes.

Particles may be produced by any method including emulsion polymerisation, suspension polymerisation, or dispersion polymerisation. Narrow size distributions may be obtained by using seeded polymerisations as described in US-A-4336173, US-A-4459378, US-A-6291553, DE 19634393, and US-A-6346592. Membrane, capillary techniques or any other method known to 5 one skilled in the art may also be used.

The polymer beads may, for example, be prepared from styrene, e.g. styrene crosslinked with divinylbenzene. Other styrene monomers of use in the invention include methylstyrene and vinyl toluene. Mixtures of styrene monomers may be used. Another option is polymer beads prepared from acrylic acid esters, methacrylic acid esters, acrylic acids, methacrylic acids, 10 acrylonitrile, methacrylonitrile, vinyl chloride, vinyl acetate and vinyl propionate. Mixtures of any of these monomers can also be used optionally together with the styrene monomers above. All monomers can be crosslinked with divinylbenzene or a diacrylic monomer such as ethane-dioldiacrylate. Some seeds may require treatment with base to hydrolyse ester groups to allow cross-linking. The use of a cross-linking agent and hence the formation of a cross-linked seed is 15 preferred.

Still another method for preparing polymer beads involves copolymerization of mixed anhydrides such as acrylic acid-acetic acid anhydride, or maleic and/or fumaric anhydride with styrene, and a small amount of divinylbenzene, and finally hydrolyzing the product. Some seed monomers may comprise epoxy groups such as glycidol methacrylate. The skilled man is able to 20 select the monomer combination and cross-linker he wants using his general knowledge.

Preferred polymer beads comprise a styrene, an acrylate or a methacrylate. Highly preferred monomers therefore include styrene, acrylic acid, butyl acrylate, 2-ethylhexyl acrylate, methyl acrylate, ethyl acrylate, acrylonitrile, divinylbenzene, methyl methacrylate, methacrylate, ethyleneglycol diacrylate hexanediol diacrylate and trimethylolpropane triacrylate (TMPTA).

25 The isotropic conductive adhesive may be used in any appropriate manner, for example by depositing or spreading the adhesive on surfaces of one or both of two parts in order to make a connection between the two parts. In some preferred embodiments the isotropic conductive adhesive takes the form of an isotropic conductive film and hence comprises a film substrate layer with a layer or coating of the mixture of conductive beads and adhesive matrix deposited on 30 the film substrate layer. The film substrate layer may be a plastic film, for example a polymer film such as a polypropylene film.

Viewed from a second aspect, the invention provides a method of manufacturing an isotropic conductive adhesive, the method comprising: combining silver coated polymer beads with an adhesive matrix, wherein the mean average diameter of the beads is 5  $\mu\text{m}$  or greater and 35 less than 30  $\mu\text{m}$ , and wherein the silver coating comprises interlinked silver deposits grown from dispersed nucleation sites scattered across the surface of the beads.

The polymer beads may have features as described above in relation to preferred features of the first aspect, for example in connection with the mean average diameter of the beads and the thickness of the silver coating.

5 The method may comprise the use of polymer beads sourced from an appropriate manufacturer. The beads may comprise a material or materials as described above.

In preferred embodiments the method includes a step of coating of polymer cores with silver to form the silver coated polymer beads. The coating step may comprise applying silver to coat the beads with at least 80% coverage of the surface, preferably complete coverage.

10 Silver may be deposited on small polymer particles by a number of methods. The most applicable are the methods collectively called electroless-plating and the method hence may comprise applying the silver via electroless-plating. In an example coating process, catalytic quantities of metals atoms illustrated by but not restricted to palladium, platinum or silver are distributed evenly over the surface of the polymer core. This may be achieved by methods including vapour deposition, impregnation with a salt of the metal followed by reduction to the 15 metallic state or by sensitisation by acidic tin chloride followed by a salt such as palladium chloride. The methods are numerous and well known to one skilled in the art. Silver may then be deposited by the reduction of silver ions from a soluble salt such as silver nitrate or silver sulphate. This reaction may be performed with a number of reducing agents illustrated by but not restricted to hydrazine, dimethyl ammonium borane, sugars such as glucose and fructose or 20 ascorbic acid. In this example process silver deposition is initially catalysed by the activating metal and then thereafter by the silver layer forming. The silver deposition becomes autocatalytic. Not to be restricted by any one model it is believed that clusters of metal atoms are required to catalyse the silver reduction. Single atoms are not believed to be adequate.

25 The isotropic conductive adhesive preferably comprises a mixture of silver coated polymer beads and adhesive matrix with features as described above in connection with the first aspect. The method may comprise mixing of a two component epoxy to form the adhesive matrix, and then mixing the coated polymer beads into the matrix.

30 The method may include applying the combination of conductive beads and adhesive matrix to a film substrate layer in order to form an isotropic conductive film. The film substrate layer may be as described above.

In a further aspect the invention extends to use of an isotropic conductive adhesive for conductive and mechanical interconnection of two parts, the isotropic conductive adhesive being as described above in relation to the first aspect and preferred features thereof.

35 The isotropic conductive adhesive may be applied to one or both contact surfaces of the two parts, either in a continuous bead or discontinuously. There may be a curing step, for example heat curing or curing using UV and/or visible light. Preferably the curing step comprises heat curing. The isotropic conductive adhesive may be provided in the form of an isotropic

conductive film, which can be used in a similar fashion to existing conductive film adhesive products.

Certain preferred embodiments will now be described by way of example only and with reference to the accompanying drawings in which:

5 Figure 1 is a schematic drawing showing a conventional isotropic conductive adhesive using silver flakes; and

Figure 2 is a similar schematic drawing showing an isotropic conductive adhesive using silver coated polymer beads.

The invention concerns an isotropic conductive adhesive (ICA) of the type shown in 10 Figure 2. As with the ICA of Figure 1 the ICA of Figure 2 connects a component 2 to a substrate 4. Both of the component 2 and substrate 4 have an electrical contact 6. The ICA comprises an adhesive matrix 8 and silver coated polymer beads 12. In practice the beads 12 would generally not be aligned perfectly as shown in the Figure. Instead the beads 12 can be located almost 15 randomly during flow of the ICA onto the contact(s) 6. The volume fraction of beads 12 in the mixture of beads 12 and adhesive matrix is set so as to ensure that an isotropically conductive network of beads 12 is formed. Typically this will require in excess of 30% of beads and preferably more than 40% of beads, by volume. Examples are given below.

The silver coating provides the required conductivity for the ICA. The adhesive matrix, when cured, provides the strength for the joint between the two parts. The polymer cores of the 20 beads 12 provides a high and also controllable degree of flexibility of the adhesive by allowing the selection of suitable polymer compositions with adjusted mechanical properties that can be matched with the mechanical properties of the adhesive matrix. Since the silver layer on the polymer bead is relatively thin then the coated bead has mechanical properties highly influenced 25 by the polymer core. This allows, for instance, the coefficient of thermal expansion (CTE) and the elastic modulus of the conductive fillers to be much better matched to those of the epoxy resin in contrast to what is possible when loading the adhesive with the solid metal particles. Thereby the local stress concentrated at the interfaces between the conductive fillers and the resin can be reduced. Possible combinations of materials for the adhesive matrix and polymer beads are given in the examples below.

30 The polymer beads in the preferred embodiments are produced by emulsion, suspension or dispersion polymerisation, or more preferably, in order to produce smaller polydispersity, by a seeded polymerisation.

The silver coating is added by electroless-plating. An example process is described in 35 Example 1 below. Other suitable plating methods may be used in alternative embodiments. An example of a process for producing embodiments of isotropic conductive adhesives based on silver coated polymer particles is set out in Example 2. Examples 3.1 to 3.9 illustrate possible combinations of particle diameter and silver thickness for beads produced by routine adaptation

of the method of Example 1. The particle diameter is the mean average diameter of the polymer core and the silver thickness is the average thickness as measured using the technique described above. Measured conductivity values are also included for conductive adhesives using a selection of the coated beads of Examples 3.1 to 3.9, where the conductive adhesives 5 are produced using the process of Example 2.

Example 4 describes manufacturing of an isotropic conductive film. Example 5 relates to a use of the adhesives of the prior examples and Example 6 concerns poly-modal products with combinations of particle sizes.

Advantageously, as well as providing electrical conductivity the adhesives described 10 herein also provide improvements in thermal conductivity. In the discussion above the term 'conductive' is used to reference electrical conductivity, but it should be understood that the conductive adhesives may also be thermally conductive adhesives having a thermal conductance greater than that of the adhesive matrix. This has advantages in terms of spreading heat to dissipate heat from heat generating components into a substrate, or vice 15 versa, as well as avoiding stresses that may result from differential temperatures across an adhesively coupled joint.

Example 1: In a first example 50g polymer particles comprised of a copolymer of methylmethacrylate and ethyleneglycol dimethacrylate with average diameter of 15 microns were soaked in 150ml a solution of  $\text{SnCl}_2$  (20g/l  $\text{SnCl}_2$  30g/l Concentrated HCl) at room temperature 20 for 30 minutes. The particles were washed and then soaked in 150ml Palladium Chloride solution (0.2g/l  $\text{PdCl}_2$  for 30 minutes). The particles were then coated with silver from a solution of silver nitrate and triethylene tetramine ( $\text{AgNO}_3$  44.9g TETA 83g) reduced by ascorbic acid (90g) at 40°C. The product was washed and dried. The product was a free flowing grey powder with a theoretical average silver thickness of 150nm.

Example 2: One production method used to make isotropic conductive adhesives based 25 on silver coated polymer particles is as below. In this example the adhesive is applied to a test board. The application process can be adapted using routine techniques to apply the adhesive to fix any desired component(s).

- i. Mix the selected epoxy system by mixing part A and part B in accordance with the 30 technical data sheet. EPO-TEK 353ND from Epoxy Technology is used for the adhesives of Example 3.
- ii. Add a predetermined weight particles to the mixed epoxy system. The weight of particles is selected to achieve the required volume % of filler in final isotropic adhesive system.
- iii. Speed mix the adhesive in 20 ml containers at 2000 rpm for 2 min
- iv. Apply the adhesive to a PCB board designed to test four point resistance, using a stencil 35 with width of openings equal to 2 mm and thickness equal to 150 um, and using a razor blade to fill the openings in the stencil.

- v. Cure the samples for 15 min at 150 degrees Celsius.
- vi. Cool the sample to Room Temperature.
- vii. Measure the four point resistance with a Keithley 3706 Multimeter to test the conductivity.

Examples 3.1 to 3.9: With different diameters for the starting particles and using a scaled

- 5 version of method 1 compensating for surface area and desired metal thickness then various combinations of diameter and silver thickness can be produced. The combinations of values in the table below are examples of appropriate combinations for isotropic adhesive products.

|             | <b>Particle diameter</b> | <b>Silver thickness</b> |
|-------------|--------------------------|-------------------------|
| Example 3.1 | 6 $\mu\text{m}$          | 100 nm                  |
| Example 3.2 | 6 $\mu\text{m}$          | 150 nm                  |
| Example 3.3 | 10 $\mu\text{m}$         | 100 nm                  |
| Example 3.4 | 10 $\mu\text{m}$         | 150 nm                  |
| Example 3.5 | 15 $\mu\text{m}$         | 100 nm                  |
| Example 3.6 | 15 $\mu\text{m}$         | 150 nm                  |
| Example 3.7 | 20 $\mu\text{m}$         | 150 nm                  |
| Example 3.8 | 20 $\mu\text{m}$         | 200 nm                  |
| Example 3.9 | 10 $\mu\text{m}$         | 220nm                   |

10

Certain coated particles from the examples above were incorporated into an adhesive product using the process of Example 2 with volumes of particles as set out in the table below, which also provides measurements for the conductivity of the adhesive. It should be noted that for Examples 3.5 and 3.9 the measured values relate to the use of a different epoxy mix, with the

- 15 EPO-TEK 353ND referenced above being replaced by Araldite PY302-2 mixed with JEFFAMINE D-230 at weight ratio 100:35 (both available from HUNTSMAN)

| <b>Particle from;</b> | <b>Vol% in EPO-TEK 353ND</b> | <b>Bulk Conductivity</b>       |
|-----------------------|------------------------------|--------------------------------|
| Example 3.1           | 40 Vol%                      | 400 ( $\Omega\text{cm}$ ) ^-1  |
| Example 3.2           | 50 Vol%                      | 1300 ( $\Omega\text{cm}$ ) ^-1 |
| Example 3.4           | 35 Vol%                      | 10 ( $\Omega\text{cm}$ ) ^-1   |
| Example 3.4           | 45 Vol%                      | 550 ( $\Omega\text{cm}$ ) ^-1  |
| Example 3.4           | 50 Vol%                      | 700 ( $\Omega\text{cm}$ ) ^-1  |
| Example 3.5           | 48 Vol%                      | 1350 ( $\Omega\text{cm}$ ) ^-1 |
| Example 3.9           | 51 Vol%                      | 1750 ( $\Omega\text{cm}$ ) ^-1 |
| Example 3.9           | 42 Vol%                      | 1050 ( $\Omega\text{cm}$ ) ^-1 |
| Example 3.9           | 40 Vol%                      | 450 ( $\Omega\text{cm}$ ) ^-1  |

In an alternative to the method of Example 2 the polymer particles could be introduced prior to or simultaneously with the step of mixing of the epoxy system. For example, the particles could be mixed in the separate epoxy components (or one of the two components) followed by mixing the epoxy compounds together.

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Example 4: One production method used to make a film of the isotropic conductive adhesive based on silver coated polymer particles is as below. In this example the adhesive is applied to a test slide. The application process can be adapted using routine techniques to apply the adhesive to fix any desired component (s).

- 10 i. Mix the components of selected resin system into a resin mix. Resin mix used in this example contained 70 weight parts EPIKOTE 1002 and 30 weight parts NIPOLE 1072. (EPIKOTE 1002 is available from Momentive Specialty Chemical Inc., and NIPOLE 1072 is available from Zeon Chemicals), made into a 40% solution in toluene.
  - 15 ii. Add 20% by volume NOVACURE, a latent curing agent for epoxy resin (NOVACURE is available from Asahi Kasei E-Materials)
  - iii. Speed mix the mixture at 1500 rpm for 5 minutes
  - iv. Add a predetermined weight of particles to the mixed adhesive for the film system. The weight of particles is selected to achieve the required volume % of filler in final isotropic adhesive film. The particles may, for example, have sizes and coating thicknesses as in Examples 3.1 to 3.9.
  - 20 v. Speed mix the mixture at 1500 rpm for 5 minutes
  - vi. Coat a biaxial stretched polypropylene film using a 50  $\mu\text{m}$  blade applicator with the above mentioned adhesive film mixture.
- Drying at 90 degrees Celsius for 15 minutes results in an isotropic conductive adhesive film material having a thickness of approximately 25  $\mu\text{m}$ .

25 Example 5: The isotropic conductive adhesive, as described in any of Examples 1- 4, being used as electrical interconnection in solar module manufacturing. In this example the conductive adhesive replaces solder in silicon based solar modules, and offers an affordable alternative to silver flake adhesives for thin film solar modules.

30 Example 6: A poly-modal isotropic conductive adhesive, can be obtained by the use of two or more particle sizes, for example by combinations of two or more particle sizes as described in any of examples 3.1 to 3.9. An example of a poly-modal product comprises 40 vol% particles mixed with 60 vol% adhesive matrix, which may for example be EPO-TEK 353ND. The 40 vol% of particles is, for example, divided into 10% of 6  $\mu\text{m}$  diameter (4% of the isotropic

conductive adhesive) 30% of 10  $\mu\text{m}$  diameter (12% of the isotropic conductive adhesive) and 60% of 15  $\mu\text{m}$  diameter (24% of the isotropic conductive adhesive).

CLAIMS:

1. An isotropic conductive adhesive comprising silver coated polymer beads within an adhesive matrix, wherein the mean average diameter of the polymer cores of the beads is 5  $\mu\text{m}$  or greater and less than 30  $\mu\text{m}$ , and wherein the silver coating comprises interlinked silver deposits grown from dispersed nucleation sites scattered across the surface of the beads.

2. An isotropic conductive adhesive as claimed in claim 1, wherein the mean average diameter of the polymer cores of the beads is 25  $\mu\text{m}$  or lower.

10 3. An isotropic conductive adhesive as claimed in claim 1, wherein the mean average diameter of the polymer cores of the beads is 20  $\mu\text{m}$  or lower.

15 4. An isotropic conductive adhesive as claimed in claim 1, 2 or 3, wherein the mean average diameter of the polymer cores of the beads is 6  $\mu\text{m}$  or above.

5. An isotropic conductive adhesive as claimed in any preceding claim, wherein the mean average diameter of the polymer cores of the beads is 10  $\mu\text{m}$  or above

20 6. An isotropic conductive adhesive as claimed in any preceding claim, wherein the polymer cores of the beads have a coefficient of variation (CV) in diameter of less than 10%,

25 7. An isotropic conductive adhesive as claimed in any preceding claim, wherein the polymer cores of the beads have a coefficient of variation (CV) in diameter of less than 5%.

8. An isotropic conductive adhesive as claimed in any preceding claim, wherein the polymer cores of the beads have a coefficient of variation (CV) of less than 3%.

30 9. An isotropic conductive adhesive as claimed in any preceding claim, wherein the incidence of polymer cores of the beads with a diameter less than two thirds of the mean diameter or with a diameter greater than 1.5 times the mean diameter is less than 1 in 1000.

35 10. An isotropic conductive adhesive as claimed in any preceding claim, wherein the average thickness of the silver is 350 nm or less.

11. An isotropic conductive adhesive as claimed in any preceding claim, wherein the average thickness of the silver is less than 5% of the diameter of the polymer core of the bead

12. An isotropic conductive adhesive as claimed in any preceding claim, wherein the average thickness of the silver is less than 3% of the diameter of the polymer core of the bead.

5 13. An isotropic conductive adhesive as claimed in any preceding claim, wherein the average thickness of the silver is less than 1.7% of the diameter of the polymer core of the bead.

14 An isotropic conductive adhesive as claimed in any preceding claim, wherein the average thickness of the silver is more than 0.7% of diameter of the polymer core of the bead.

10 15. An isotropic conductive adhesive as claimed in any preceding claim, wherein the average thickness of the silver is more than 0.85% of the diameter of the polymer core of the bead.

15 16. An isotropic conductive adhesive as claimed in any preceding claim, wherein coverage of the polymer core of the bead with silver is more than 80% of the surface area of the polymer core.

20 17. An isotropic conductive adhesive as claimed in any preceding claim, comprising a mixture of silver coated polymer beads and adhesive matrix with the polymer beads forming 20-60% of the mixture, by volume.

25 18. An isotropic conductive adhesive as claimed in any preceding claim, comprising a mixture of silver coated polymer beads and adhesive matrix with the polymer beads forming 25-50% of the mixture, by volume.

19. An isotropic conductive adhesive as defined in any preceding clause, comprising a film substrate layer upon which the mixture of the silver coated polymer beads within the adhesive matrix is deposited.

30 20. A method of manufacturing an isotropic conductive adhesive, the method comprising: combining silver coated polymer beads with an adhesive matrix, wherein the mean average diameter of the beads is 5  $\mu\text{m}$  or greater and less than 30  $\mu\text{m}$ , and wherein the silver coating comprises interlinked silver deposits grown from dispersed nucleation sites scattered across the surface of the beads.

21. A method as claimed in claim 20, wherein the silver coated polymer beads are as claimed in any of claims 2 to 16.

22. A method as claimed in claim 20 or 21, including a step of applying silver to coat 5 the beads with at least 80% coverage of the surface.

23. A method as claimed in claim 20, 21 or 22, comprising applying the silver via electroless-plating.

10 24. A method as claimed in any of claims 20 to 23, comprising mixing a two component epoxy to form the adhesive matrix, and then mixing the coated polymer beads into the matrix.

15 25. A method as claimed in any of claims 20 to 24, wherein the silver coated polymer beads and adhesive matrix are combined with the silver coated polymer beads forming 20-60% of the mixture, by volume.

20 26. A method as claimed in any of claims 20 to 24, wherein the silver coated polymer beads and adhesive matrix are combined with the silver coated polymer beads forming 25-50% of the mixture, by volume.

25 27. A method as claimed in any of claims 20 to 26, comprising applying the combined silver coated polymer beads and adhesive matrix to a film substrate layer to thereby form an isotropic conductive film

28. Use of an isotropic conductive adhesive as claimed in any of claims 1 to 19 for conductive and mechanical interconnection of two parts.

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Fig. 1

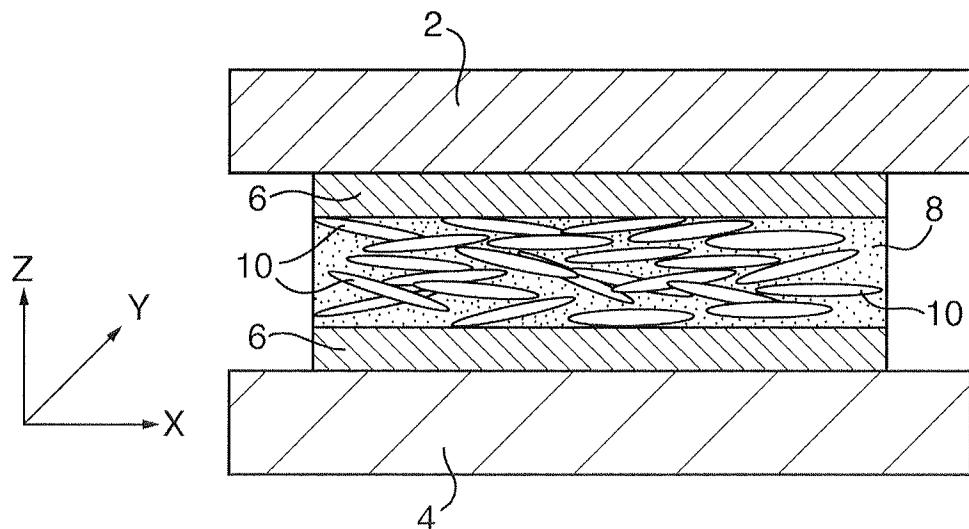
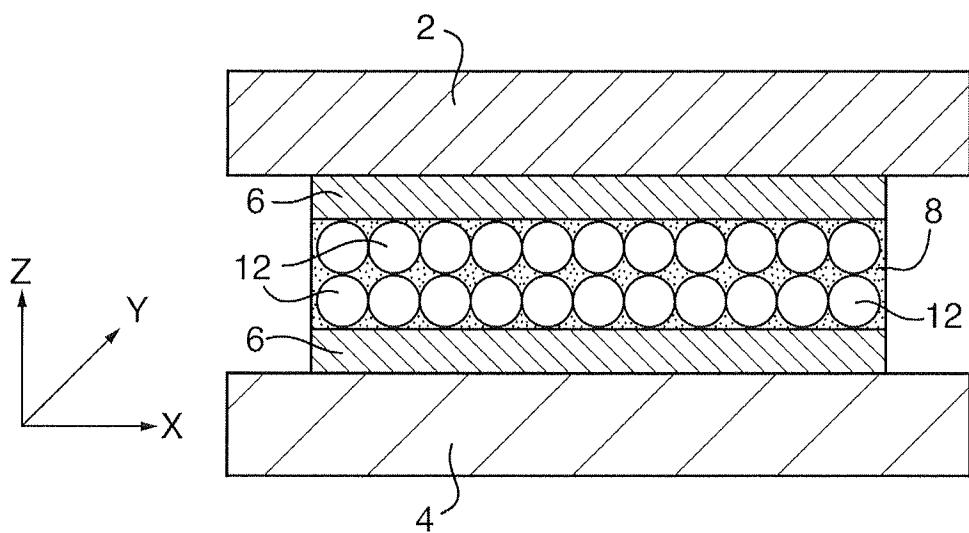


Fig. 2



# INTERNATIONAL SEARCH REPORT

International application No  
PCT/EP2013/061091

**A. CLASSIFICATION OF SUBJECT MATTER**  
INV. C09J9/02 H01B1/22 H01R4/04  
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
C09J H01B H01R

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages  | Relevant to claim No.    |
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| X         | EP 0 242 025 A1 (HITACHI CHEMICAL CO LTD [JP]) 21 October 1987 (1987-10-21)<br>page 2, line 19 - page 8, line 12; claims 1-10; examples 17-19, 33-35<br>-----   | 1-16,<br>19-24,<br>27,28 |
| X         | WO 2012/056244 A1 (CONPART AS [NO]; REDFORD KEITH [NO]; HALACIUGA IONEL [US]; GOIA DAN V) 3 May 2012 (2012-05-03)<br>claims 1-18; example C1<br>-----   | 1-16,<br>19-24,<br>27,28 |



Further documents are listed in the continuation of Box C.



See patent family annex.

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| Date of the actual completion of the international search  | Date of mailing of the international search report |
| 16 October 2013  | 24/10/2013   |
| Name and mailing address of the ISA/<br>European Patent Office, P.B. 5818 Patentlaan 2<br>NL - 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040,<br>Fax: (+31-70) 340-3016 | Authorized officer<br><br>Marsitzky, Dirk          |

**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International application No

PCT/EP2013/061091

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