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(71) Applicant (for all designated States except US): **AGUILA TECHNOLOGIES, INC.** [US/US]; 310 Via Vera Cruz, Suite 107, San Marcos, CA 92069 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **CAPOTE, Miguel, Albert** [US/US]; 4362 Point Reyes Court, Carlsbad, CA 92008 (US). **GRIEVE, Alan** [US/US]; 4465 Felton St., San Diego, CA 92116 (US).

(74) Agent: **NATH, Gary, M.**; Nath & Associates PLLC, 1030 15th Street NW, 6th Floor, Washington, DC 20005-1503 (US).

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(54) Title: THERMALLY CONDUCTIVE ADHESIVE COMPOSITION AND PROCESS FOR DEVICE ATTACHMENT

(57) Abstract: Thermally conductive, sinterable, adhesive compositions, free of fugitive solvents, that include a powder of a relatively high melting point metal or metal alloy, a powder of a relatively low melting point metal or metal alloy powder and a thermally curable adhesive flux composition that comprises (i) a polymerizable fluxing agent; (ii) an inerting agent to react with the fluxing agent at elevated temperature, rendering it inert. The fluxing agent preferably comprises a compound with formula RCOOH, wherein R comprises a moiety having one or more polymerizable carbon-carbon double bonds. Optionally, the inventive compositions also include (a) a diluent that is capable of polymerizing with the fluxing agent's polymerizable carbon-carbon double bonds; (b) free radical initiators; (c) a curable resin; and (d) crosslinking agents and accelerators. The compositions can be applied directly onto the surfaces of devices to be joined mechanically and/or electrically and are ideally suited for semiconductor die attachment. During heating, the fluxing agent promotes wetting of the high melting point powder by the molten low melting point powder, causing liquid phase sintering of the powders. The fluxing agent also promotes wetting of the metallizations on the die and substrate by the molten low melting point alloy, providing improved thermal conductivity. Simultaneously, the fluxing agent itself crosslinks to further mechanically bond the adherent surfaces. The absence of fugitive solvents creates a void-free bond.



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Thermally Conductive Adhesive Composition and Process for Device Attachment

Technical Field of the Invention

The present invention relates to the use of conductive adhesives for fabrication of electronic assemblies. More specifically it relates to materials, methods and assemblies for the fabrication of electronics containing devices requiring thermal dissipation for cooling. The present invention also relates to adhesives for semiconductor die attachment that provide improved thermal dissipation.

Background of the Invention

For a thermally conductive adhesive composition to be useful in the manufacture of semiconductor devices, it must meet certain performance, reliability and manufacturing requirements dictated by the particular application. Such performance properties include strength of adhesion, coefficient of thermal expansion, flexibility, temperature stability, moisture resistance, electrical and thermal conductivity and the like. Thermal conductivity is of particular importance in the electronics industry. With the trend towards miniaturization coupled with higher operating frequencies, there are ever-increasing demands on engineers to remove heat from circuitry. The extraction of heat generated by components within a package is necessary to prevent those components from overheating. This is a larger problem for electronics containing high-power devices that can dissipate many watts of energy during normal operation.

In the prior art, die attachment adhesives generally comprised a silver flake or powder dispersed in a curable resin, such as an epoxy. However, such prior-art adhesives have thermal conductivities unsuitable for devices that dissipate large amounts of heat. Additionally, the prior art adhesives often have poor mechanical properties. Another disadvantage is that some prior art adhesives contain solvents to maintain low viscosity. During cure, such solvents have a propensity to form voids, requiring a long bake-out operation to drive off the solvent prior to cure. This adds time and cost to the overall cure process. Another shortcoming is that adhesives generally have unstable contact resistance after environmental aging. Heat and humidity also tends to reduce adhesion of conductive adhesives. Moisture absorption of conductive adhesives can lead to delamination failures during printed circuit assembly.

Few prior-art die attachment adhesives have the thermal conductivity suitable for use with high power devices. As a result, solder bonding is often the preferred method. Solders have the advantage of having many times the thermal conductivity of most die attachment adhesives. Solders also have the advantage of the solder forming intimate metallurgical bonds with the devices being soldered. A metallurgical interface provides superior heat transfer compared to the typical adhesive interface.

However, solder bonding has a number of disadvantages. Solder preforms are usually employed to dispense solder between devices to be bonded, which are more expensive to apply during production than adhesive pastes. In addition, many die attachment solders contain lead, which is not desirable due to environmental concerns. The best lead-free solders require very high process temperatures that are often damaging to the assemblies themselves. Another difficulty is that solder remelts if heated to an elevated temperature, yet elevated temperatures are required during electronic fabrication, e.g. during assembly of components to printed circuit boards. Such remelting of solder between components in a circuit can cause the parts to separate and subsequently fail.

Prior art related to adhesives is found in U.S. Patent Nos. 6,613,123, 6,528,169, 6,238,599, 6,140,402, 6,132,646, 6,114,413, 6,017,634, 5,985,456, 5,985,043, 5,928,404, 5,830,389, 5,713,508, 5,488,082, 5,475,048, 5,376,403, 5,285,417, 5,136,365, 5,116,433, 5,062,896, and 5,043,102. Representative prior art directed to die attachment is found in U.S. Patent Nos. 4,811,081, 4,906,596, 5,006,575, 5,250,600, 5,386,000, 5,399,907, 5,489,637, 5,973,052, 6,147,141, 6,242,513, and 6,351,340, and published PCT application WO 98/33645. The entire contents of all listed documents is hereby incorporated by reference.

There is clearly a need for a new composition that provides the best advantages of both solder and conductive adhesive. There is a need for a conductive adhesive that forms metallurgical bonds with the devices being bonded. There is also a need for an adhesive with significantly more thermal conductivity than is currently possible with silver powder-resin compositions while retaining high mechanical strength. There is a need for a bonding material that hardens when used so that it does not remelt at elevated temperatures. There is also a need for a bonding material that has high thermal conductivity yet can be dispensed in paste form, without solvents, rather than preforms. There is also a need for a bonding material that is lead-free. There is, furthermore, a need for a conductive adhesive that does not suffer delamination, reduced adhesion, or conductivity after aging, humidity exposure, etc.

Brief Summary of the Invention

The present inventive subject matter relates to a thermally conductive adhesive composition devoid of fugitive solvents comprising:

- a) a powder of a high melting point metal or metal alloy;
- b) a powder of a low melting point metal or metal alloy; and
- c) a thermally curable adhesive flux composition that is comprised of:
 - (i) a polymerizable fluxing agent represented by the formula RCOOH wherein R comprises a moiety having one or more polymerizable carbon-carbon double bonds; and
 - (ii) an inerting agent to react with the polymerizable fluxing agent at elevated temperature, rendering the polymerizable fluxing agent inert.

The present inventive subject matter is also drawn to an electronic assembly comprising an electronic device and a substrate bonded by a sintered thermally conductive adhesive, said adhesive devoid of fugitive solvents and comprising:

- a) a powder of a high melting point metal or metal alloy;
- b) a powder of a low melting point metal or metal alloy; and
- c) a thermally curable adhesive flux composition that is comprised of:
 - (i) a polymerizable fluxing agent;
 - (ii) an inerting agent to react with the fluxing agent at elevated temperature, rendering the polymerizable fluxing agent inert.

In a preferred embodiment, the thermally conductive adhesive composition further comprises one or more components selected from the group consisting of: (a) a diluent that is capable of polymerizing with the fluxing agent's polymerizable carbon-carbon double bonds; (b) a source of free radical initiators; (c) a curable resin; (d) a crosslinking agent that improves crosslinking of the curable resins or fluxing agents; and (e) an accelerator to increase the rate of reaction.

Furthermore, the present inventive subject matter is directed to a method of attaching an electronic device to a substrate comprising the steps of:

- (a) obtaining an electronic device with at least one bondable surface;
- (b) obtaining a substrate with a corresponding bondable surface;
- (c) dispensing a thermally conductive adhesive on one or both of the bondable surfaces of the substrate or electronic device, said adhesive devoid of fugitive solvents and comprising:
 - (i) a powder of a high melting point metal or metal alloy;
 - (ii) a powder of a low melting point metal or metal alloy; and
 - (iii) a thermally curable adhesive flux composition that is comprised of:
 - (A) a polymerizable fluxing agent;
 - (B) an inerting agent to react with the fluxing agent at elevated temperature, rendering the polymerizable fluxing agent inert;
- (d) placing the electronic device on the substrate so the bondable surface of the electronic device is mated with the bonding surface of the substrate, thereby forming a combined assembly;
- (e) heating the combined assembly to an elevated temperature, thereby causing the powder of the low melting point metal or metal alloy to liquefy;
- (f) allowing the liquefied low melting point metal or metal alloy to sinter with the high melting point metal or metal alloy and the inerting agent to react with the fluxing agent, rendering the fluxing agent inert;
- (g) polymerizing the fluxing agent; and
- (h) allowing the assembly to cool.

Detailed Description of the Invention

Unlike the prior art, the adhesives of the present invention form metallurgical bonds to devices and substrates. In this sense, the adhesives bond similarly to prior-art solders used in die-attachment. However, unlike the solders of the prior art, the inventive adhesives comprise pastes that, when heated, first melt, then harden. Thereafter the adhesives do not remelt if they are elevated to the temperature at which they first melted. The invention addresses many of the shortcomings of prior art solders and adhesives, providing an easily-processed, solvent-free adhesive capable of forming metallurgical joints similar to solder. The inventive compositions have the further advantage they may be used as a replacement for solder paste during surface mount (SMT) manufacturing. The invention further comprises an electronic assembly employing inventive adhesive compositions for improved thermal dissipation.

The compositions of the present invention are free of fugitive solvents and comprise

- a) a powder of a relatively high melting point metal or metal alloy;
- b) a powder of a relatively low melting point metal or metal alloy; and
- c) a thermally curable adhesive flux composition that comprises:
 - (i) a polymerizable fluxing agent;
 - (ii) an inerting agent to react with the fluxing agent at elevated temperature, rendering the polymerizable fluxing agent inert.

The thermally curable adhesive flux composition optionally comprises these additional components:

- (i) a fluxing agent represented by the formula RCOOH wherein R comprises a moiety having one or more polymerizable carbon-carbon double bonds;
- (ii) a diluent that is capable of polymerizing with the fluxing agent's polymerizable carbon-carbon double bonds;
- (iii) a source of free radical initiators;

- (iv) a curable resin;
- (v) crosslinking agents that improve crosslinking of the curable resins or fluxing agents;
- (vi) an accelerator to increase the rate of these reactions.

Sintering and curing of the inventive compositions is achieved by heating. When compositions are heated to the liquidus or melting point of the low melting point component, the composition forms a transient liquid phase. Unlike the prior art taught by U.S. Patent 6,613,123, the included thermally curable adhesive flux composition serves initially as a fluxing agent, facilitating the removal of oxides from the surfaces of the metal powders and also facilitating wetting of metallic surfaces by the molten metals. As the heating process is continued, the liquid phase and the high melting point metals react and isothermally solidify through a process known in the art as liquid-phase sintering. The heating process also serves to neutralize the fluxing components in the resin so that the components become non-corrosive and chemically stable. Unlike prior art compositions, such as described in US Patent 5,376,403, this may occur before, during or after the sintering of the metals. After the sintering process occurs, the heat causes the thermally curable adhesive flux composition to polymerize, forming a hard intractable binder. Heating is done by either continuous reflow processes commonly used in soldering or by using simple isothermal processing methods.

Preferably, the primary inventive fluxing agent in these compositions integrate within a single molecule carboxylic acid groups that provide the fluxing action for the soldering process without need of corrosive ions or halogens, and polymerizable carbon-carbon double bonds that can polymerize upon application of heat, to form a high-strength solid adhesive polymer. This is accomplished without generating gases, water, or other harmful by-products. An inerting or neutralizing agent is included to react during heating with the flux acid groups and any flux residues. As a consequence, after the thermally curable adhesive composition is cured, the flux residues do not need to be washed away or removed since they are inert and non-corrosive.

Solvents are not required as the thermally curable adhesive flux composition itself can comprise a relatively low-viscosity liquid. By incorporating low-viscosity fluxing agents,