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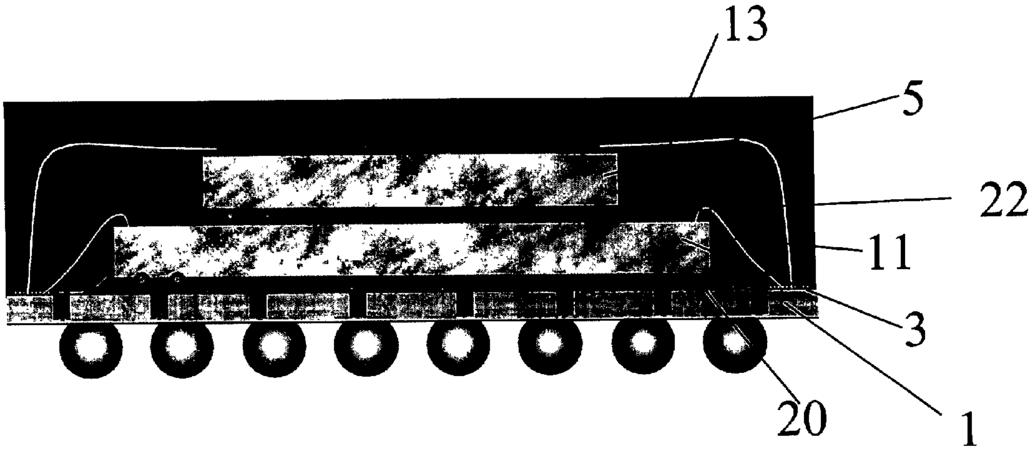
(54) **Title:** ADHESIVE COMPOSITIONS CONTAINING ORGANIC SPACERS AND METHODS FOR USE THEREOF



(57) **Abstract:** In accordance with the present invention, there are provided adhesive compositions and methods for use thereof, comprising at least one thermosetting monomer, at least one cure initiator, and a plurality of spacer elements constructed from one or more organic polymers. Invention adhesive compositions are useful for controlling bond line thickness and planarity between a device and a substrate. Bond line thickness and planarity is largely determined by the size of the spacer elements in the adhesive composition. Invention adhesive compositions are also useful for preparing stacked die structures comprising a plurality of semiconductor dice in a stacked arrangement.

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ADHESIVE COMPOSITIONS CONTAINING ORGANIC SPACERS AND METHODS FOR USE THEREOF

RELATED APPLICATIONS

[0001] This application is a continuation-in-part of Application No. 10/087,191, filed February 28, 2002, now pending, the entire contents of which are hereby incorporated by reference herein.

FIELD OF THE INVENTION

[0002] The present invention relates to adhesive bonding, and more particularly, to the bonding of surfaces where the control of bond line thickness and uniformity is desirable, as for example, in the packaging of semiconductor devices.

BACKGROUND OF THE INVENTION

[0003] Reliable performance of electronic devices depends primarily on the integrity of the microelectronic components contained therein. Most electronic devices contain several microchips which are housed in a variety of protective packages. These protective packages often contain a variety of adhesive pastes which play an important role in maintaining the integrity of the package and thereby the performance of the microchip housed therein.

[0004] The recent production of electronic components containing microchips which are stacked one on top of another (commonly referred to as "stacked die") presents challenges to the microelectronic packaging industry. For example, spacing between each die must be effectively controlled to allow for reliable wire bonding between die. Moreover, the recent trend toward thinner dies increases the propensity of the die to warp, resulting in non-planarity across the surface of the die (also a contributing factor to unreliable wire bonding). Thus, an adhesive used in a stacked die application ideally provides reproducible bond line thickness in addition to uniform planarity across the entire bondline.

[0005] Numerous structures, and methods for preparation thereof have been described in the art. For example, U.S. Patent No. 5,140,404, describes a semiconductor integrated circuit device in which a semiconductor die is mounted to a lead frame having no paddle die. The device of the '404 patent is manufactured by the steps of:

(a) applying a thermoplastic to a first side of a carrier material, the thermoplastic having a physical property such that as it is heated to about 100°C, it softens and flows, and as it cools to its preheated temperature, it returns to its preheated state;

(b) applying an adhesive to a second side of the carrier material;

(c) contacting the second side of the carrier material to leads of the lead frame;

(d) placing the semiconductor die on the first side of the carrier material;

(e) heating the thermoplastic to its soft state; and

(f) cooling the thermoplastic to its preheated state, thereby bonding the die and the leads to the carrier material supporting the die and the leads.

Epoxy pastes and films are disclosed as the thermoplastic material.

[0006] U.S. Patent No. 5,286,679, describes a method of attaching a semiconductor die formed of a plurality of bonding pads to a leadframe having a plurality of continuous metal lead fingers adapted to extend across a surface of the die for attachment to the bonding pads using fine bond wires. The method of the '679 patent involves:

depositing an adhesive selected from the group consisting of thermoplastic adhesives or thermosetting adhesives on the die and patterning the adhesive to form a pre-applied patterned adhesive layer on a surface of the die with the bonding pads of the die free of adhesive;

heating the adhesive layer during a packaging process; and

pressing the die, heated adhesive layer and lead fingers of the leadframe together during the packaging process to bond the adhesive layer and lead fingers and attach the lead fingers to the die.

[0007] U.S. Patent No. 5,323,060 describes a multichip module, which includes:

a multichip module substrate;

a first chip, the first chip having opposed base and bonding faces, the base face being adhered to the multichip module substrate, the first chip bonding face including a central area and a plurality of bonding pads laterally peripheral to the central area;

a second chip, the second chip having opposed base and bonding faces, the second chip bonding face including a central area and a plurality of peripheral bonding pads;

an adhesive layer interposed between and connecting the first chip bonding face and the second chip base face, the adhesive layer having a thickness and a lateral perimeter, the lateral perimeter being positioned entirely within the central area inside of the peripheral bonding pads;

a plurality of first loop bonding wires bonded to and between the respective first chip bonding pads and the multichip module substrate, the respective first loop bonding wires having outwardly projecting loops of a defined loop height, the loop height being defined by the distance between the first chip bonding face and the vertexes of the outwardly projecting loops of the first loop bonding wires, the thickness of the adhesive layer being greater than the loop height to displace the second chip base face in a non-contacting relationship and with respect to the first wires; and

a plurality of second loop bonding wires bonded to and between the respective second chip bonding pads and the multichip module substrate.

[0008] U.S. Patent No. 6,465,893 describes a semiconductor chip assembly, which includes:

(a) a first semiconductor chip having a front surface, a rear surface and contacts on the front surface;

(b) a second semiconductor chip having a front surface, a rear surface and contacts on the front surface, the rear surface of the second semiconductor chip being juxtaposed with the front surface of the first semiconductor chip;

(c) a first backing element having electrically conductive first terminals, the first backing element being juxtaposed with the rear surface of the first semiconductor chip so that at least some of the terminals overlie the rear surface of the first semiconductor chip, at least some of the contacts on the first and the second semiconductor chips being electrically connected to at least some of the terminals; and

(d) a substrate having contact pads thereon, the first terminals being connected to the contact pads of the substrate, the substrate being adapted to connect the assembly with other elements of a circuit, at least some of the first terminals overlying the rear surface of the first semiconductor chip.

[0009] In addition, interfacial stress that arises from a thermal mismatch between the die and substrate is directly proportional to both the area of attachment and the modulus of elasticity of the bonding adhesive. This stress is also inversely proportional to the bond line thickness. Since the modulus of elasticity for a given die attach adhesive is substantially fixed, alternative methods to reduce interfacial stress must be employed, e.g., via bond line control between a given set of components. If the bond line thickness is sufficient, the resultant bond will exhibit good resistance to differential thermal expansion rates between each semiconductor die and substrate and will produce a bond having a high tensile strength.

[0010] The use of spacer elements has been described in the context of silver-glass adhesive materials (see U.S. Patent No. 5,232,962). The use of spacer elements has not, however, been described in the context of thermoset adhesives.

[0011] Accordingly, there is a need for effective methods to control bond line and planarity in the packaging of semiconductor devices.

SUMMARY OF THE INVENTION

[0012] In accordance with the present invention, there are provided adhesive compositions useful for effectively controlling bondline thickness and planarity. Invention adhesive compositions comprise at least one thermosetting monomer, optionally at least one cure initiator, and a plurality of spacers constructed from one or more organic polymers. Invention adhesive compositions are particularly useful for controlling bond line thickness and planarity between a device and a substrate, or between semiconductor dies in a stacked die package. Bond line thickness and planarity are largely determined by the size of the spacers in the adhesive composition.

[0013] In further aspects of the invention, there are provided methods for creating a substantially uniform bond line between a device and a substrate, for controlling adhesive gap thickness between a device and a substrate, for controlling planarity across an adhesive bond line, for creating substantially uniform bond lines between at least one semiconductor die attached to a substrate in a stacked arrangement, and for adhesively attaching at least two semiconductor dies to substrate in a stacked arrangement without the need for a spacer die.

[0014] In an additional aspect of the invention, there are provided assemblies comprising a first article adhered to a second article by a cured aliquot of invention adhesive composition.

BRIEF DESCRIPTION OF THE FIGURES

[0015] Figure 1 is a cross-sectional view of one embodiment of a stacked die assembly prepared employing invention adhesives.

[0016] Figure 2 is a cross-sectional view of another embodiment of a stacked die assembly prepared employing invention adhesives.

[0017] Figure 3 is a cross-sectional view of yet another embodiment of a stacked die assembly prepared employing invention adhesives.

DETAILED DESCRIPTION OF THE INVENTION

[0018] In accordance with the present invention, there are provided adhesive compositions comprising at least one thermosetting monomer, optionally at least one cure initiator, and a plurality of spacers constructed from one or more organic polymers.

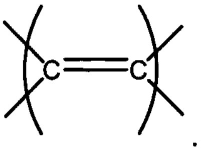
[0019] Spacers contemplated for use in the practice of the present invention can be any of a variety of shapes, e.g., spherical, imperfect spheres, non-spherical, solid, hollow, and the like. Presently preferred spacers contemplated for use in the practice of the present invention are substantially spherical, and typically have a particle size in the range of about 0.02 mils up to about 25 mils. Preferably, the spacers have a particle size in the range of about 0.1 mils up to about 15 mils. As employed herein, "mil" is a unit of measure equal to 1/1000 of an inch. Before, during, and after curing of invention adhesive formulations, the integrity of the spacers is maintained, i.e., the size and shape of the spacers remains substantially constant before, during, and after cure. For example, the spacers preferably do not swell, soften, or dissolve upon incorporation into the adhesive composition. Additionally, spacers contemplated for use in the practice of the present invention are preferably hydrophobic.

[0020] Spacers contemplated for use in the practice of the present invention include organic particulate materials, which may optionally contain reactive moieties which allow the spacers to crosslink with other components in the adhesive composition. As employed herein, "reactive moiety" refers to a functional group, which reacts with at least one other component in the composition.

[0021] Since it is well-established that many thermosetting compositions shrink upon cure (i.e., as the three-dimensional polymeric network is formed), spacers contemplated for use in the practice of the present invention may also have the ability to shrink to some degree during cure, so as not to damage the surface of the articles or substrates to be adhered. Indeed, the modulus of the spacer is preferably less than the modulus of the articles or substrates to be adhered, so as not to damage the surface of the articles. For example, the spacer is preferably softer than the passivation on a silicon die, so that spacers present in an adhesive composition dispensed on the surface of a die will not damage the surface of the die.

[0022] A variety of organic polymers can be employed in accordance with the present invention for construction of spacers suitable for use herein e.g., spacers contemplated for use herein can be substantially uncrosslinked polymers, partially crosslinked polymers, or substantially completely crosslinked polymers. Those of skill in the art readily recognize that “uncrosslinked polymers” refers to polymers which are substantially free of covalent bonds between individual polymer chains, whereas “substantially completely crosslinked polymers” refers to polymers which have extensive covalent bonding between individual polymer chains so as to render the resulting polymer relatively inflexible, while “partially crosslinked polymers” refer to polymers which have some, but not exhaustive, crosslinking between the individual polymer chains.

[0023] Polymers contemplated for use herein are typically the polymerization product of optionally substituted ethylenically unsaturated monomers. As employed herein, “ethylenically unsaturated monomers” refers to monomers having at least one localized (i.e., non-aromatic) carbon-carbon double bond, as shown below:



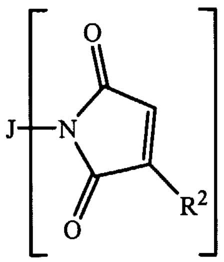
[0024] Polymers contemplated for use in the preparation of organic spacers useful in the practice of the present invention include, for example, polymerization products of α-olefins, (meth)acrylates, vinyl esters, acrylamides, acrylonitriles, and the like, as well as mixtures of any two or more thereof. Preferably, the organic polymers are the polymerization or copolymerization products of (meth)acrylates. Most preferably, the organic polymer is polymethylmethacrylate. The organic polymers contemplated for use as spacers typically have a molecular weight in the range of about 50,000 up to about 1,500,000. Preferably, the organic polymers have a molecular weight in the range of about 400,000 up to about 500,000.

[0025] Prior to incorporation into an adhesive formulation, the spacers are typically sieved to produce sets of particles where each set contains particle sizes which fall within a well-defined range. The particle size range chosen for incorporation into an adhesive composition will depend on the desired bond line thickness for a given package. For example, one may choose a sieve with a -120, +140 mesh, such that substantially no spacers of a particle size greater than about 5 mils will be present after sieving.

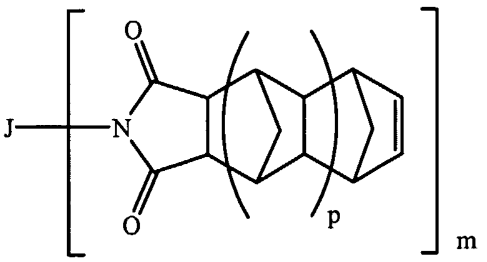
[0026] A particularly attractive benefit provided by invention compositions is the ability to control bond line thickness and planarity by appropriate choice of spacer as a component of the adhesive composition. Bond line thickness is thereby pre-determined by the appropriate choice of adhesive composition, which is a desirable alternative to the often laborious and uneconomical prior methods of controlling bond line thickness on a die-component placement machine.

[0027] Thermosetting monomers contemplated for use in the practice of the present invention include, for example, maleimide-, nadimide- or itaconamide-containing monomer(s), unsaturated anhydrides, (meth)acrylates, styrenes, cyanate esters, vinyl esters, divinyl compounds, acrylamides, acrylonitriles, allyl amides, epoxies, and the like. Presently preferred thermosetting monomers contemplated for use in the practice of the present invention are mixtures of one or more of the above-described maleimides, nadimides, or itaconimides, optionally in combination with one or more unsaturated anhydrides, (meth)acrylates, styrenes, cyanate esters, vinyl esters, divinyl compounds, acrylamides, acrylonitriles, allyl amides, epoxies, and the like.

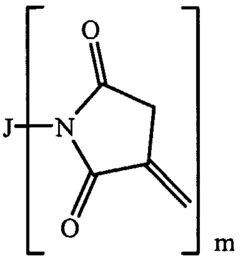
[0028] Maleimide-, nadimide-, and itaconimide-containing monomers contemplated for use in the practice of the present invention have, respectively, the structures I, II and III:



(I)



(II)



(III)

where:

m = 1-15,

p = 0-15,

each R^2 is independently selected from hydrogen or lower alkyl, and

J is a monovalent or a polyvalent moiety comprising organic or organosiloxane radicals, and combinations of any two or more thereof.

[0029] In one aspect of the invention, J is of sufficient length and branching to render the maleimide, nadimide, or itaconimide, respectively, in the liquid state at room temperature.

[0030] Monovalent moieties or polyvalent moieties are typically selected from hydrocarbyl, substituted hydrocarbyl, heteroatom-containing hydrocarbyl, substituted heteroatom-containing hydrocarbyl, hydrocarbylene, substituted hydrocarbylene, heteroatom-containing hydrocarbylene, substituted heteroatom-containing hydrocarbylene, polysiloxane, polysiloxane-polyurethane block copolymer, or combinations of two or more thereof, optionally containing one or more linkers selected from the group consisting of a covalent bond, -O-, -S-, -NR-, -O-C(O)-, -O-C(O)-O-, -O-C(O)-NR-, -NR-C(O)-, -NR-C(O)-O-, -NR-C(O)-NR-, -S-C(O)-, -S-C(O)-O-, -S-C(O)-NR-, -O-S(O)$_2$-, -O-S(O)$_2$-O-, -O-S(O)$_2$-NR-, -O-S(O)-, -O-S(O)-O-, -O-S(O)-NR-, -O-NR-C(O)-, -O-NR-C(O)-O-, -O-NR-C(O)-NR-, -NR-O-C(O)-, -NR-O-C(O)-O-, -NR-O-C(O)-NR-, -O-NR-C(S)-, -O-NR-C(S)-O-, -O-NR-C(S)-NR-, -NR-O-C(S)-, -NR-O-C(S)-O-, -NR-O-C(S)-NR-, -O-C(S)-, -O-C(S)-O-, -O-C(S)-NR-, -NR-C(S)-, -NR-C(S)-O-, -NR-C(S)-NR-, -S-S(O)$_2$-, -S-S(O)$_2$-O-, -S-S(O)$_2$-NR-, -NR-O-S(O)-, -NR-O-S(O)-O-, -NR-O-S(O)-NR-, -NR-O-S(O)$_2$-, -NR-O-S(O)$_2$-O-, -NR-O-S(O)$_2$-NR-, -O-NR-S(O)-, -O-NR-S(O)-O-, -O-NR-S(O)-NR-, -O-NR-S(O)$_2$-O-, -O-NR-S(O)$_2$-NR-, -O-NR-S(O)$_2$-, -O-P(O)R$_2$-, -S-P(O)R$_2$-, -NR-P(O)R$_2$-, where each R is independently hydrogen, alkyl or substituted alkyl, and combinations of any two or more thereof.

[0031] As employed herein, the term “substituted”, when used in conjunction with any of the species referred to herein, includes substituents such as hydroxy, alkyl, alkoxy (of a lower alkyl group), mercapto (of a lower alkyl group), cycloalkyl, substituted cycloalkyl, heterocyclic, substituted heterocyclic, aryl, substituted aryl, heteroaryl, substituted heteroaryl, aryloxy, substituted aryloxy, halogen, trifluoromethyl, cyano, nitro, nitrone, oxo, amino, amido, maleimido, succinimido, itaconimido, -C(O)H, acyl, oxyacyl, carboxyl, carbamate, sulfonyl, sulfonamide, sulfuryl, and the like.

[0032] As employed herein, “hydrocarbyl” comprises any organic radical where the backbone thereof comprises carbon and hydrogen only. Thus, hydrocarbyl embraces alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl, aryl, alkylaryl, arylalkyl, arylalkenyl, alkenylaryl, arylalkynyl, alkynylaryl, and the like. “Substituted hydrocarbyl” refers to hydrocarbyl groups further bearing one or more substituents as set forth above.

[0033] As employed herein, “alkyl” refers to saturated straight or branched chain hydrocarbon radical having in the range of 1 up to about 500 carbon atoms. “Lower alkyl” refers to straight or branched chain alkyl radicals having in the range of about 1 up to 4 carbon atoms. “Substituted alkyl” refers to alkyl groups further bearing one or more substituents as set forth above.

[0034] As employed herein, the term “cycloalkyl” refers to cyclic ring-containing groups containing in the range of 3 up to about 20 carbon atoms, and “substituted cycloalkyl” refers to cycloalkyl groups further bearing one or more substituents as set forth above.

[0035] As employed herein, “alkenyl” refers to straight or branched chain hydrocarbyl groups having at least one carbon—carbon double bond, and typically having in the range of about 2 up to 500 carbon atoms, and “substituted alkenyl” refers to alkenyl groups further bearing one or more substituents as set forth above.

[0036] As employed herein, “cycloalkenyl” refers to cyclic ring-containing groups containing in the range of about 3 up to 20 carbon atoms and having at least one carbon-carbon double bond, and “substituted cycloalkenyl” refers to cycloalkenyl groups further bearing one or more substituents as set forth above.

[0037] As employed herein, “alkynyl” refers to straight or branched chain hydrocarbyl groups having at least one carbon—carbon triple bond, and typically having in the range of about 2 up to 500 carbon atoms, and “substituted alkynyl” refers to alkynyl groups further bearing one or more substituents as set forth above.

[0038] As employed herein, “aryl” refers to aromatic groups having in the range of 6 up to 14 carbon atoms and “substituted aryl” refers to aryl groups further bearing one or more substituents as set forth above.

[0039] As employed herein, “alkylaryl” refers to alkyl-substituted aryl groups and “substituted alkylaryl” refers to alkylaryl groups further bearing one or more substituents as set forth above.

[0040] As employed herein, “arylalkyl” refers to aryl-substituted alkyl groups and “substituted arylalkyl” refers to arylalkyl groups further bearing one or more substituents as set forth above.

[0041] As employed herein, “arylalkenyl” refers to aryl-substituted alkenyl groups and “substituted arylalkenyl” refers to arylalkenyl groups further bearing one or more substituents as set forth above.

[0042] As employed herein, “alkenylaryl” refers to alkenyl-substituted aryl groups and “substituted alkenylaryl” refers to alkenylaryl groups further bearing one or more substituents as set forth above.

[0043] As employed herein, “arylalkynyl” refers to aryl-substituted alkynyl groups and “substituted arylalkynyl” refers to arylalkynyl groups further bearing one or more substituents as set forth above.

[0044] As employed herein, “alkynylaryl” refers to alkynyl-substituted aryl groups and “substituted alkynylaryl” refers to alkynylaryl groups further bearing one or more substituents as set forth above.

[0045] As employed herein, “hydrocarbylene” refers to divalent straight or branched chain hydrocarbyl groups including alkylene groups, alkenylene groups, alkynylene groups, cycloalkylene groups, heterocycloalkylene groups, arylene groups, alkylarylene groups, arylalkylene groups, arylalkenylene groups, arylalkynylene groups, alkenylarylene groups, alkynylarylene groups, and the like; and “substituted hydrocarbylene” refers to hydrocarbylene groups further bearing one or more substituents as set forth above.

[0046] As employed herein, “alkylene” refers to saturated, divalent straight or branched chain hydrocarbyl groups typically having in the range of 1 up to about 500 carbon atoms, and “substituted alkylene” refers to alkylene groups further bearing one or more substituents as set forth above.

[0047] As employed herein, “alkenylene” refers to divalent straight or branched chain hydrocarbyl groups having at least one carbon—carbon double bond, and typically having in the range of about 2 up to 500 carbon atoms, and “substituted alkenylene” refers to alkenylene groups further bearing one or more substituents as set forth above.

[0048] As employed herein, “alkynylene” refers to divalent straight or branched chain hydrocarbyl groups having at least one carbon-carbon triple bond, and typically having in the range of about 2 up to 500 carbon atoms, and “substituted alkynylene” refers to alkynylene groups further bearing one or more substituents as set forth above.

[0049] As employed herein, “cycloalkylene” refers to divalent ring-containing groups containing in the range of 3 up to about 20 carbon atoms, and “substituted cycloalkylene” refers to cycloalkylene groups further bearing one or more substituents as set forth above.

[0050] As employed herein, "heterocycloalkylene" refers to divalent cyclic (i.e., ring-containing) groups containing one or more heteroatoms (e.g., N, O, S, or the like) as part of the ring structure, and having in the range of 1 up to about 14 carbon atoms and "substituted heterocycloalkylene" refers to heterocycloalkylene groups further bearing one or more substituents as set forth above.

[0051] As employed herein, "cycloalkenylene" refers to divalent ring-containing groups containing in the range of 3 up to about 20 carbon atoms and having at least one carbon-carbon double bond, and "substituted cycloalkenylene" refers to cycloalkenylene groups further bearing one or more substituents as set forth above.

[0052] As employed herein, "arylene" refers to divalent aromatic groups typically having in the range of 6 up to 14 carbon atoms and "substituted arylene" refers to arylene groups further bearing one or more substituents as set forth above.

[0053] As employed herein, "alkylarylene" refers to alkyl-substituted divalent aryl groups typically having in the range of about 7 up to 16 carbon atoms and "substituted alkylarylene" refers to alkylarylene groups further bearing one or more substituents as set forth above.

[0054] As employed herein, "arylalkylene" refers to aryl-substituted divalent alkyl groups typically having in the range of about 7 up to 16 carbon atoms and "substituted arylalkylene" refers to arylalkylene groups further bearing one or more substituents as set forth above.

[0055] As employed herein, "arylalkenylene" refers to aryl-substituted divalent alkenyl groups typically having in the range of about 8 up to 16 carbon atoms and "substituted arylalkenylene" refers to arylalkenylene groups further bearing one or more substituents as set forth above.

[0056] As employed herein, "arylalkynylene" refers to aryl-substituted divalent alkynyl groups typically having in the range of about 8 up to 16 carbon atoms and "substituted arylalkynylene" refers to arylalkynylene group further bearing one or more substituents as set forth above.

[0057] As employed herein, "alkenylarylene" refers to alkenyl-substituted divalent aryl groups typically having in the range of about 7 up to 16 carbon atoms and "substituted alkenylarylene" refers to alkenylarylene groups further bearing one or more substituents as set forth above.

[0058] As employed herein, "alkynylarylene" refers to alkynyl-substituted divalent aryl groups typically having in the range of about 7 up to 16 carbon atoms and "substituted alkynylarylene" refers to alkynylarylene groups further bearing one or more substituents as set forth above.

[0059] As employed herein, "polysiloxane-polyurethane block copolymers" refer to polymers containing both at least one polysiloxane (soft) block and at least one polyurethane (hard) block.

[0060] When one or more of the above described monovalent or polyvalent groups contain one or more of the above described linkers to form the "J" appendage of a maleimide, nadimide or itaconimide group, as readily recognized by those of skill in the art, a wide variety of organic chains can be produced, such as, for example, oxyalkyl, thioalkyl, aminoalkyl, carboxylalkyl, oxyalkenyl, thioalkenyl, aminoalkenyl, carboxyalkenyl, oxyalkynyl, thioalkynyl, aminoalkynyl, carboxyalkynyl, oxycycloalkyl, thiocycloalkyl, aminocycloalkyl, carboxycycloalkyl, oxycloalkenyl, thiocycloalkenyl, aminocycloalkenyl, carboxycycloalkenyl, heterocyclic, oxyheterocyclic, thioheterocyclic, aminoheterocyclic, carboxyheterocyclic, oxyaryl, thioaryl, aminoaryl, carboxyaryl, heteroaryl, oxyheteroaryl, thioheteroaryl, aminoheteroaryl, carboxyheteroaryl, oxyalkylaryl, thioalkylaryl, aminoalkylaryl, carboxyalkylaryl, oxyarylalkyl, thioarylalkyl, aminoarylalkyl, carboxyarylalkyl, oxyarylalkenyl, thioarylalkenyl, aminoarylalkenyl, carboxyarylalkenyl, oxyalkenylaryl, thioalkenylaryl, aminoalkenylaryl, carboxyalkenylaryl, oxyarylalkynyl, thioarylalkynyl, aminoarylalkynyl, carboxyarylalkynyl, oxyalkynylaryl, thioalkynylaryl, aminoalkynylaryl or carboxyalkynylaryl. oxyalkylene, thioalkylene, aminoalkylene, carboxyalkylene, oxyalkenylene, thioalkenylene, aminoalkenylene, allylamido, carboxyalkenylene, oxyalkynylene, thioalkynylene, aminoalkynylene, carboxyalkynylene, oxycycloalkylene, thiocycloalkylene, aminocycloalkylene, carboxycycloalkylene, oxycycloalkenylene, thiocycloalkenylene, aminocycloalkenylene, carboxycycloalkenylene, oxyarylene, thioarylene, aminoarylene, carboxyarylene, oxyalkylarylene, thioalkylarylene, aminoalkylarylene, carboxyalkylarylene, oxyarylalkylene, thioarylalkylene, aminoarylalkylene, carboxyarylalkylene, oxyarylalkenylene, thioarylalkenylene, aminoarylalkenylene, carboxyarylalkenylene, oxyalkenylarylene, thioalkenylarylene, aminoalkenylarylene, carboxyalkenylarylene, oxyarylalkynylene, thioarylalkynylene, aminoarylalkynylene, carboxy arylalkynylene, oxyalkynylarylene, thioalkynylarylene, aminoalkynylarylene, carboxyalkynylarylene, heteroarylene, oxyheteroarylene, thioheteroarylene, aminoheteroarylene, carboxyheteroarylene, heteroatom-containing di- or polyvalent cyclic moiety, oxyheteroatom-containing di- or polyvalent cyclic moiety, thioheteroatom-containing di- or polyvalent cyclic moiety, aminoheteroatom-containing di- or polyvalent cyclic moiety, carboxyheteroatom-containing di- or polyvalent cyclic moiety, and the like.

[0061] As employed herein, “heteroarylene” refers to divalent aromatic groups containing one or more heteroatoms (e.g., N, O, S or the like) as part of the aromatic ring, and typically having in the range of 3 up to about 14 carbon atoms and “substituted heteroarylene” refers to heteroarylene groups further bearing one or more substituents as set forth above.

[0062] In another embodiment of the present invention, maleimide-, nadimide-, and itaconimide-containing monomers contemplated for use in the practice of the present invention have the structures I, II, or III where,

$m = 1\text{-}6$,

$p = 0\text{-}6$, and

J is

(a) saturated straight chain alkyl or branched chain alkyl, optionally containing substituents selected from hydroxy, alkoxy, carboxy, nitrile, cycloalkyl cycloalkenyl, or optionally substituted aryl moieties as substituents on the alkyl chain or as part of the backbone of the alkyl chain, and where the alkyl chains have up to about 20 carbon atoms;

(b) alkylene, oxyalkylene, alkenyl, alkenylene, oxyalkenylene, ester, or polyester, optionally containing substituents selected from hydroxy, alkoxy, carboxy, nitrile, cycloalkyl or cycloalkenyl;

(c) a siloxane having the structure $-(C(R^3)_2)_d-[Si(R^4)_2-O]_f-Si(R^4)_2-(C(R^3)_2)_e-$, $-(C(R^3)_2)_d-C(R^3)-C(O)O-(C(R^3)_2)_d-[Si(R^4)_2-O]_f-Si(R^4)_2-(C(R^3)_2)_e-O(O)C-(C(R^3)_2)_e-$, or $-(C(R^3)_2)_d-C(R^3)-O(O)C-(C(R^3)_2)_d-[Si(R^4)_2-O]_f-Si(R^4)_2-(C(R^3)_2)_e-C(O)O-(C(R^3)_2)_e-$ where,

each R^3 is independently hydrogen, alkyl or substituted alkyl,
each R^4 is independently hydrogen, lower alkyl or aryl,
$d = 1\text{-}10$,
$e = 1\text{-}10$, and
$f = 1\text{-}50$;

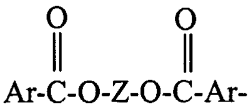
(d) a polyalkylene oxide having the structure:

$[(CR_2)_r-O-]_f-(CR_2)_s-$

where:

each R is independently hydrogen, alkyl or substituted alkyl,
$r = 1\text{-}10$,
$s = 1\text{-}10$, and
f is as defined above;

(e) aromatic groups having the structure:



$$Ar-\overset{\displaystyle O}{\overset{\|}{C}}-O-Z-O-\overset{\displaystyle O}{\overset{\|}{C}}-Ar-$$

where each Ar is a monosubstituted, disubstituted or trisubstituted aromatic or heteroaromatic ring having in the range of 3 up to 10 carbon atoms, and Z is:

(i) saturated straight chain alkylene or branched chain alkylene, optionally containing saturated cyclic moieties as substituents on the alkylene chain or as part of the backbone of the alkylene chain, or

(ii) polyalkylene oxides having the structure:

$$-[(CR_2)_r-O-]_q-(CR_2)_s-$$

where:

each R is independently defined as above,
$r = 1\text{-}10$,
$s = 1\text{-}10$, and
$q = 1\text{-}50$;

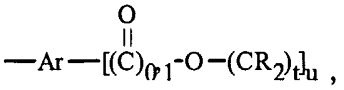
(f) di- or tri-substituted aromatic moieties having the structure:

$$(CR_2)_t-O-(C{=}O)-Ar-[(C{=}O)-O-(CR_2)_a]_{1,2}—$$

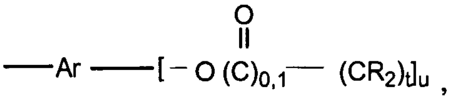
where:

each R is independently defined as above,
$t = 2\text{-}10$,
$a = 2\text{-}10$, and
Ar is as defined above;

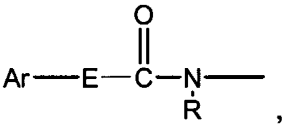
(g) aromatic groups having the structure:



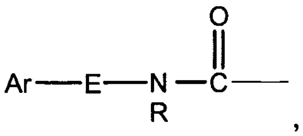
$—Ar—[(\overset{\overset{O}{\|}}{C})_{0,1}-O-(CR_2)_t]_u$,



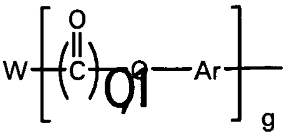
$—Ar—[-O\,(\overset{\overset{O}{\|}}{C})_{0,1}—(CR_2)_t]_u$,



$Ar—E—\overset{\overset{O}{\|}}{C}—\underset{R}{N}—$,

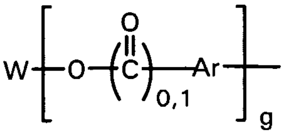


$Ar—E—\underset{R}{N}—\overset{\overset{O}{\|}}{C}—$,



$W\!-\!\left[\left(\overset{O}{\overset{\|}{C}}\right)_{0,1}\!-O-Ar\right]_g$

or



$W\!-\!\left[O-\left(\overset{O}{\overset{\|}{C}}\right)_{0,1}\!-Ar\right]_g$

where:

t = is as defined above,

u = 1, 2 or 3,

g = 1 up to about 50,

each R is independently defined as above,

each Ar is as defined above,

E is –O- or $-NR^5-$, where R^5 is hydrogen or lower alkyl;

and

W is

(i) straight or branched chain alkyl, alkylene, oxyalkylene, alkenyl, alkenylene, oxyalkenylene, ester, or polyester, optionally containing substituents selected from hydroxy, alkoxy, carboxy, nitrile, cycloalkyl or cycloalkenyl,

(ii) a siloxane having the structure $-(C(R^3)_2)_d-[Si(R^4)_2-O]_f-Si(R^4)_2-(C(R^3)_2)_e-$, $-(C(R^3)_2)_d-C(R^3)-C(O)O-(C(R^3)_2)_d-[Si(R^4)_2-O]_f-Si(R^4)_2-(C(R^3)_2)_e-O(O)C-(C(R^3)_2)_e-$, or $-(C(R^3)_2)_d-C(R^3)-O(O)C-(C(R^3)_2)_d-[Si(R^4)_2-O]_f-Si(R^4)_2-(C(R^3)_2)_e-C(O)O-(C(R^3)_2)_e-$ where,

each R^3 is independently hydrogen, alkyl or substituted alkyl,

each R^4 is independently hydrogen, lower alkyl or aryl,

d = 1-10,

e = 1-10, and

f = 1-50; or

(iii) a polyalkylene oxide having the structure:

$-[(CR_2)_r-O-]_f-(CR_2)_s-$

where:

each R is independently defined as above,

$r = 1\text{-}10$,

$s = 1\text{-}10$, and

f is defined as above;

optionally containing substituents selected from hydroxy, alkoxy, carboxy, nitrile, cycloalkyl or cycloalkenyl;

(h) a urethane group having the structure:

$$R^7\text{-U-C(O)-NR}^6\text{-R}^8\text{-NR}^6\text{-C(O)-(O-R}^8\text{-O-C(O)-NR}^6\text{-R}^8\text{-NR}^6\text{-C(O))}_v\text{-U-R}^8\text{-}$$

where:

each R^6 is independently hydrogen or lower alkyl;

each R^7 is independently an alkyl, aryl, or arylalkyl group having 1 to 18 carbon atoms;

each R^8 is an alkyl or alkyloxy chain having up to about 100 atoms in the chain, optionally substituted with Ar;

U is -O-, -S-, -N(R)-, or $-P(L)_{1,2}$- where R as defined above, and where each L is independently =O, =S, -OR or -R; and

$v = 0\text{-}50$;

(i) polycyclic alkenyl; or

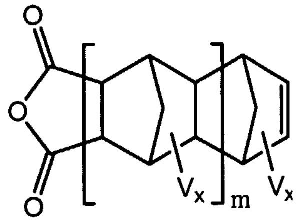
(j) mixtures of any two or more thereof.

[0063] The attachment point(s) of the J moiety to the maleimide(s), nadimide(s) or itaconimide(s) are understood to be at any atom(s) of the J moiety having sufficient valence to accommodate such attachment. Thus, for example, any C-H, N-H, O-H, or S-H bond may be replaced by a bond between the non-hydrogen atom and the maleimide, nadimide or itaconimide.

[0064] Preferred maleimide-, nadimide-, and itaconimide-containing monomers contemplated for use in the practice of the present invention are those which exist as liquids at ambient temperature, as noted above. Presently preferred maleimide-, nadimide-, and itaconimide-containing monomers include compounds where J contains 12-500 carbon atoms and sufficient branching to render the resulting monomer liquid at or about room temperature. Most preferred maleimide-, nadimide-, and itaconimide-containing monomers include compounds where J contains 20-100 carbon atoms and sufficient branching to render the resulting monomer liquid.

[0065] Adhesive compositions according to the invention optionally contain a plurality of comonomers, i.e., in some embodiments, the maleimide-, nadimide- and/or itaconamide-containing monomer(s) as described herein, in combination with one or more unsaturated anhydrides, (meth)acrylates, styrenes, cyanate esters, vinyl esters, divinyl compounds, epoxies, and the like.

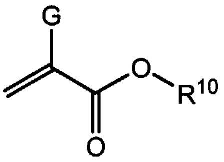
[0066] In preferred embodiments, anhydrides contemplated for use in the practice of the present invention include maleic anhydride, citraconic anhydride, itaconic anhydride, and the like, or Diels-Alder adducts of maleic anhydride, citraconic anhydride, itaconic anhydride, and the like, and cyclopentadiene. Diels-Alder adducts contemplated for use in the practice of the present invention have the following structure:



where each V is independently an alkyl or substituted alkyl, each x is independently 0, 1 or 2, and m = 0-9.

[0067] Exemplary (meth)acrylates contemplated for use in the practice of the present invention may be prepared from a host of different compounds. As used herein, the terms (meth)acrylic and (meth)acrylate are used synonymously with regard to the monomer and monomer-containing component. The terms (meth)acrylic and (meth)acrylate include acrylic, methacrylic, acrylate and methacrylate. The (meth)acrylates may comprise one or more members selected from a monomer represented by:

(a) the formula:

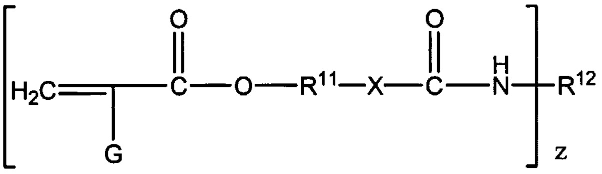


where:

G is hydrogen, halogen, or an alkyl having from 1 to 4 carbon atoms,

R^{10} has from 1 to 16 carbon atoms and is an alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkaryl, aralkyl, or aryl group, optionally substituted or interrupted with silane, silicon, oxygen, halogen, carbonyl, hydroxyl, ester, carboxylic acid, urea, urethane, carbamate, amine, amide, sulfur, sulfonate, or sulfone;

(b) urethane acrylates or ureide acrylates represented by the formula:



$$\left[H_2C=\underset{G}{C}-\overset{O}{\overset{\|}{C}}-O-R^{11}-X-\overset{O}{\overset{\|}{C}}-\overset{H}{N}- \right]_z R^{12}$$

where:

G is hydrogen, halogen, or an alkyl having from 1 to 4 carbon atoms;

R^{11} is a divalent alkyl, cycloalkyl, aromatic, or arylalkyl group, bound through a carbon atom or carbon atoms thereof indicated at the –O- atom and -X- atom or group;

X is -O-, -NH-, or -N(alkyl)-, in which the alkyl radical has from 1 to 8 carbon atoms;

z is 2 to 6; and

R^{12} is a z-valent cycloalkyl, aromatic, or arylalkyl group bound through a carbon atom or carbon atoms thereof to the one or more NH groups; or

(c) a di- or tri-(meth)acrylate selected from polyethylene glycol di(meth)acrylates, bisphenol-A di(meth)acrylates, tetrahydrofurane di(meth)acrylates, hexanediol di(meth)acrylate, trimethylol propane tri(meth)acrylate, and the like, as well as combinations of any two or more thereof.

[0068] Suitable polymerizable (meth)acrylate monomers include triethylene glycol dimethacrylate, tripropylene glycol diacrylate, tetraethylene glycol dimethacrylate, diethylene glycol dimethacrylate, 1,4-butanediol diacrylate, 1,6-hexanediol dimethacrylate, pentaerythritol tetraacrylate, trimethylol propane triacrylate, trimethylol propane trimethacrylate, di-pentaerythritol monohydroxypentaacrylate, pentaerythritol triacrylate, bisphenol-A-ethoxylate dimethacrylate, trimethylolpropane ethoxylate triacrylate, trimethylolpropane propoxylate triacrylate, bisphenol-A-diepoxide dimethacrylate, and the like, as well as combinations of any two or more thereof.

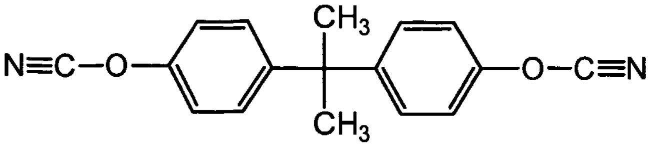
[0069] Additionally, (meth)acrylate monomers contemplated for use herein include polyethylene glycol di(meth)acrylates, bisphenol-A di(meth)acrylates, tetrahydrofurane (meth)acrylates and di(meth)acrylates, citronellyl acrylate and citronellyl methacrylate, hydroxypropyl (meth)acrylate, hexanediol di(meth)acrylate, trimethylol propane tri(meth)acrylate, tetrahydrodicyclopentadienyl (meth)acrylate, ethoxylated trimethylol propane triacrylate, triethylene glycol acrylate, triethylene glycol methacrylate, and the like, as well as combinations of any two or more thereof.

[0070] Exemplary cyanate esters contemplated for use in the practice of the present invention include compounds such as those described in U.S Patent Nos. 5,358,992, 5,447,988, 5,489,641, 5,646,241, 5,718, 941 and 5,753,748, each of which are hereby incorporated by reference herein in their entirety. For instance, cyanate esters useful as a component in the inventive compositions may be chosen from dicyanatobenzenes, tricyanatobenzenes, dicyanatonaphthalenes, tricyanatonaphthalenes, dicyanato-biphenyl, bis(cyanatophenyl)methanes and alkyl derivatives thereof, bis(dihalocyanatophenyl)propanes, bis(cyanatophenyl)ethers, bis(cyanatophenyl)sulfides, bis(cyanatophenyl)propanes, tris(cyanatophenyl)phosphites, tris(cyanatophenyl)phosphates, bis(halocyanatophenyl)methanes, cyanated novolac, bis[cyanatophenyl(methylethylidene)]benzene, cyanated bisphenol-terminated thermoplastic oligomers, and the like, as well as combinations of any two or more thereof.

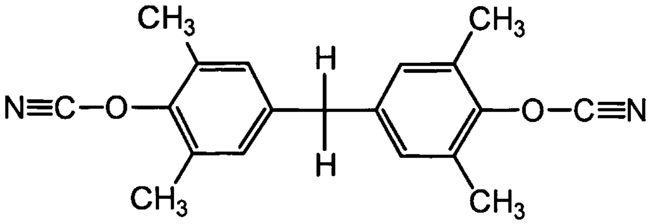
[0071] More specifically contemplated for use herein are aryl compounds having at least one cyanate ester group on each molecule; such compounds may generally be represented by the formula $Ar(OCN)_m$, where Ar is an aromatic radical and m is an integer from 2 to 5. The aromatic radical Ar should contain at least 6 carbon atoms, and may be derived, for example, from aromatic hydrocarbons, such as phenyl, biphenyl, naphthalene, anthracene, or the like. The aromatic radical Ar may also be derived from a polynuclear aromatic hydrocarbon in which at least two aromatic rings are attached to each other through a bridging group. Also included are aromatic radicals derived from novolac-type phenolic resins -- i.e., cyanate esters of these phenolic resins. Ar may also contain further ring-attached, non-reactive substituents.

[0072] Examples of such cyanate esters include, for instance, 1,3-dicyanatobenzene; 1,4-dicyanatobenzene; 1,3,5-tricyanatobenzene; 1,3-, 1,4-, 1,6-, 1,8-, 2,6- or 2,7-dicyanatonaphthalene; 1,3,6-tricyanatonaphthalene; 4,4'-dicyanato-biphenyl; bis(4-cyanatophenyl)methane and 3,3',5,5'-tetramethyl bis(4-cyanatophenyl)methane; 2,2-bis(3,5-dichloro-4-cyanatophenyl)propane; 2,2-bis(3,5-dibromo-4-dicyanatophenyl)propane; bis(4-cyanatophenyl)ether; bis(4-cyanatophenyl)sulfide; 2,2-bis(4-cyanatophenyl)propane; tris(4-cyanatophenyl)-phosphite; tris(4-cyanatophenyl)phosphate; bis(3-chloro-4-cyanatophenyl)methane; cyanated novolac; 1,3-bis[4-cyanatophenyl-1-(methylethylidene)]benzene, cyanated bisphenol-terminated polycarbonate or other thermoplastic oligomer, and the like, as well as combinations of any two or more thereof.

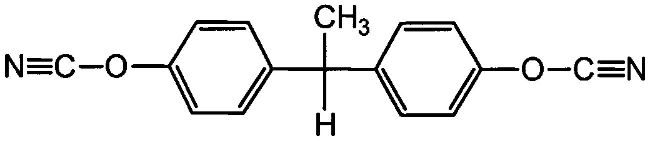
[0073] Particularly desirable cyanate esters contemplated for use herein are available commercially from Ciba Specialty Chemicals, Tarrytown, New York under the tradename "AROCY" [1,1-di(4-cyanatophenylethane)]. The structures of three "AROCY" cyanate esters are shown below:



"AROCY" B-10



"AROCY" M-30



"AROCY" L-10

[0074] Divinyl compounds contemplated for use in the practice of the present invention are present such that there is no greater than one equivalent of divinyl compound plus the polycyclic olefin per equivalent of bismaleimide. The divinyl compounds have the following structure:

$$CHR^9 = CR^9 - M_{0,1} - D - M_{0,1} - CR^9 = CHR^9$$

where:

each R^9 is independently hydrogen, lower alkyl or aryl,

each M is independently -O-, -O-C(O)-, -C(O)- or -C(O)O-, and

D is a monovalent or a polyvalent moiety comprising organic or organosiloxane radicals, and combinations of two or more thereof.

[0075] In one embodiment D is a monovalent or polyvalent radical selected from the group consisting of hydrocarbyl, substituted hydrocarbyl, heteroatom-containing hydrocarbyl, substituted heteroatom-containing hydrocarbyl, hydrocarbylene, substituted hydrocarbylene, heteroatom-containing hydrocarbylene, substituted heteroatom-containing hydrocarbylene, polysiloxane, polysiloxane-polyurethane block copolymer, and combinations of two or more thereof, optionally containing one or more linkers selected from the group consisting of a covalent bond, -O-, -S-, -NR-, -O-C(O)-, -O-C(O)-O-, -O-C(O)-NR-, -NR-C(O)-, -NR-C(O)-O-, -NR-C(O)-NR-, -S-C(O)-, -S-C(O)-O-, -S-C(O)-NR-, $-O-S(O)_2-$, $-O-S(O)_2-O-$, $-O-S(O)_2-NR-$, -O-S(O)-, -O-S(O)-O-, -O-S(O)-NR-, -O-NR-C(O)-, -O-NR-C(O)-O-, -O-NR-C(O)-NR-, -NR-O-C(O)-, -NR-O-C(O)-O-, -NR-O-C(O)-NR-, -O-NR-C(S)-, -O-NR-C(S)-O-, -O-NR-C(S)-NR-, -NR-O-C(S)-, -NR-O-C(S)-O-, -NR-O-C(S)-NR-, -O-C(S)-, -O-C(S)-O-, -O-C(S)-NR-, -NR-C(S)-, -NR-C(S)-O-, -NR-C(S)-NR-, $-S-S(O)_2-$, $-S-S(O)_2-O-$, $-S-S(O)_2-NR-$, -NR-O-S(O)-, -NR-O-S(O)-O-, -NR-O-S(O)-NR-, $-NR-O-S(O)_2-$, $-NR-O-S(O)_2-O-$, $-NR-O-S(O)_2-NR-$, -O-NR-S(O)-, -O-NR-S(O)-O-, -O-NR-S(O)-NR-, $-O-NR-S(O)_2-O-$, $-O-NR-S(O)_2-NR-$, $-O-NR-S(O)_2-$, $-O-P(O)R_2-$, $-S-P(O)R_2-$, $-NR-P(O)R_2-$, where each R is independently hydrogen, alkyl or substituted alkyl, and combinations of any two or more thereof.

[0076] In a further embodiment, the above divinyl compounds include those where D is

(a) saturated straight chain alkyl or branched chain alkyl, optionally containing optionally substituted aryl moieties as substituents on the alkyl chain or as part of the backbone of the alkyl chain, and where the alkyl chains have up to about 20 carbon atoms;

(b) a siloxane having the structure: $-(C(R^3)_2)_d-[Si(R^4)_2-O]_f-Si(R^4)_2-(C(R^3)_2)_e-$, $-(C(R^3)_2)_d-C(R^3)-C(O)O-(C(R^3)_2)_d-[Si(R^4)_2-O]_f-Si(R^4)_2-(C(R^3)_2)_e-O(O)C-(C(R^3)_2)_e-$, or $-(C(R^3)_2)_d-C(R^3)-O(O)C-(C(R^3)_2)_d-[Si(R^4)_2-O]_f-Si(R^4)_2-(C(R^3)_2)_e-C(O)O-(C(R^3)_2)_e-$ where:

each R^3 is independently hydrogen, alkyl or substituted alkyl,
each R^4 is independently hydrogen, lower alkyl or aryl,
$d = 1\text{-}10$,
$e = 1\text{-}10$, and
$f = 1\text{-}50$;

(c) a polyalkylene oxide having the structure:

$[(CR_2)_r\text{-}O\text{-}]_f\text{-}(CR_2)_s\text{-}$

where:

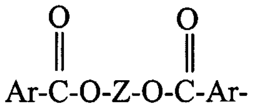
each R is independently hydrogen, alkyl or substituted alkyl,

$r = 1\text{-}10$,

$s = 1\text{-}10$, and

f is as defined above;

(d) aromatic groups having the structure:



$$\mathrm{Ar{-}\overset{O}{\overset{\parallel}{C}}{-}O{-}Z{-}O{-}\overset{O}{\overset{\parallel}{C}}{-}Ar{-}}$$

where each Ar is a monosubstituted, disubstituted or trisubstituted aromatic or heteroaromatic ring having in the range of 3 up to 10 carbon atoms, and Z is:

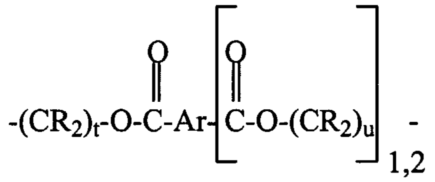
(i) saturated straight chain alkylene or branched chain alkylene, optionally containing saturated cyclic moieties as substituents on the alkylene chain or as part of the backbone of the alkylene chain, or

(ii) polyalkylene oxides having the structure:

$-[(CR_2)_r\text{-}O\text{-}]_q\text{-}(CR_2)_s\text{-}$

where each R is independently defined as above, r and s are each defined as above, and q falls in the range of 1 up to 50;

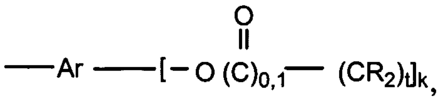
(e) di- or tri-substituted aromatic moieties having the structure:



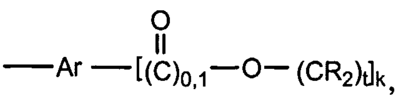
$$\mathrm{-(CR_2)_t{-}O{-}\overset{O}{\overset{\parallel}{C}}{-}Ar{-}\left[\overset{O}{\overset{\parallel}{C}}{-}O{-}(CR_2)_u\right]_{1,2}{-}}$$

where each R is independently defined as above, t falls in the range of 2 up to 10, u falls in the range of 2 up to 10, and Ar is as defined above;

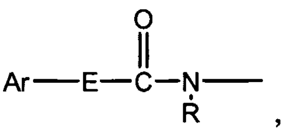
(f) aromatic groups having the structure:



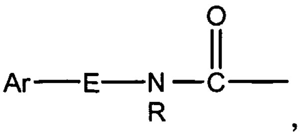
$-Ar-[-O(\overset{O}{\overset{\|}{C}})_{0,1}-(CR_2)_t]_k$,



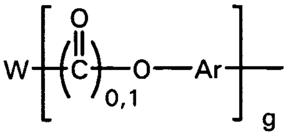
$-Ar-[(\overset{O}{\overset{\|}{C}})_{0,1}-O-(CR_2)_t]_k$,



$Ar-E-\overset{O}{\overset{\|}{C}}-\underset{R}{N}-$,

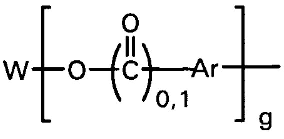


$Ar-E-\underset{R}{N}-\overset{O}{\overset{\|}{C}}-$,



$W-[(\overset{O}{\overset{\|}{C}})_{0,1}-O-Ar]_g-$

or



$W-[O-(\overset{O}{\overset{\|}{C}})_{0,1}-Ar]_g-$

where:

each R is independently defined as above,

$t = 2\text{-}10$,

$k = 1, 2$ or 3,

$g = 1$ up to about 50,

each Ar is as defined above,

E is -O- or $-NR^5-$, where R^5 is hydrogen or lower alkyl;

and

W is

(i) straight or branched chain alkyl, alkylene, oxyalkylene, alkenyl, alkenylene, oxyalkenylene, ester, or polyester,

(ii) a siloxane having the structure $-(C(R^3)_2)_d-[Si(R^4)_2-O]_f-Si(R^4)_2-(C(R^3)_2)_e-$, $-(C(R^3)_2)_d-C(R^3)-C(O)O-(C(R^3)_2)_d-[Si(R^4)_2-O]_f-Si(R^4)_2-(C(R^3)_2)_e-O(O)C-(C(R^3)_2)_e-$, or $-(C(R^3)_2)_d-C(R^3)-O(O)C-(C(R^3)_2)_d-[Si(R^4)_2-O]_f-Si(R^4)_2-(C(R^3)_2)_e-C(O)O-(C(R^3)_2)_e-$ where,

each R^3 is independently hydrogen, alkyl or substituted alkyl,

each R^4 is independently hydrogen, lower alkyl or aryl,

$d = 1\text{-}10$,

$e = 1\text{-}10$, and

$f = 1\text{-}50$; or

(iii) a polyalkylene oxide having the structure:

$-[(CR_2)_r\text{-}O\text{-}]_f\text{-}(CR_2)_s\text{-}$

where:

each R is independently hydrogen, alkyl or substituted alkyl,

$r = 1\text{-}10$,

$s = 1\text{-}10$, and

f is as defined above;

optionally containing substituents selected from hydroxy, alkoxy, carboxy, nitrile, cycloalkyl or cycloalkenyl;

(g) a urethane group having the structure:

$R^7\text{-}U\text{-}C(O)\text{-}NR^6\text{-}R^8\text{-}NR^6\text{-}C(O)\text{-}(O\text{-}R^8\text{-}O\text{-}C(O)\text{-}NR^6\text{-}R^8\text{-}NR^6\text{-}C(O))_v\text{-}U\text{-}R^8\text{-}$

where:

each R^6 is independently hydrogen or lower alkyl;

each R^7 is independently an alkyl, aryl, or arylalkyl group having 1 to 18 carbon atoms;

each R^8 is an alkyl or alkyloxy chain having up to about 100 atoms in the chain, optionally substituted with Ar;

U is -O-, -S-, -N(R)-, or $-P(L)_{1,2}$- where R as defined above, and where each L is independently =O, =S, -OR or -R; and

$v = 0\text{-}50$;

(h) polycyclic alkenyl; or

(i) mixtures of any two or more thereof.

[0077] Epoxy resins contemplated for use herein include C4-C28 alkyl glycidyl ethers; C2-C28 alkyl- and alkenyl-glycidyl esters; C1-C28 alkyl-, mono- and poly-phenol glycidyl ethers; polyglycidyl ethers of pyrocatechol, resorcinol, hydroquinone, 4,4'-

dihydroxydiphenyl methane (or bisphenol F, such as RE-404-S or RE-410-S available commercially from Nippon Kayuku, Japan), 4,4'-dihydroxy-3,3'-dimethyldiphenyl methane, 4,4'-dihydroxydiphenyl dimethyl methane (or bisphenol A), 4,4'-dihydroxydiphenyl methyl methane, 4,4'-dihydroxydiphenyl cyclohexane, 4,4'-dihydroxy-3,3'-dimethyldiphenyl propane, 4,4'-dihydroxydiphenyl sulfone, and tris(4-hydroxyphenyl)methane; polyglycidyl ethers of transition metal complex chlorination and bromination products of the above-mentioned diphenols; polyglycidyl ethers of novolacs; polyglycidyl ethers of diphenols obtained by esterifying ethers of diphenols obtained by esterifying salts of an aromatic hydrocarboxylic acid with a dihaloalkane or dihalogen dialkyl ether; polyglycidyl ethers of polyphenols obtained by condensing phenols and long-chain halogen paraffins containing at least two halogen atoms; N,N'-diglycidyl-aniline; N,N'-dimethyl-N,N'-diglycidyl-4,4'-diaminodiphenyl methane; N,N,N',N'-tetraglycidyl-4,4'-diaminodiphenyl methane; N,N'-diglycidyl-4-aminophenyl glycidyl ether; N,N,N',N'-tetraglycidyl-1,3-propylene bis-4-aminobenzoate; phenol novolac epoxy resin; cresol novolac epoxy resin; and combinations thereof.

[0078] Among the commercially available epoxy resins suitable for use herein are polyglycidyl derivatives of phenolic compounds, such as those available under the tradenames EPON 828, EPON 1001, EPON 1009, and EPON 1031, from Shell Chemical Co.; DER 331, DER 332, DER 334, and DER 542 from Dow Chemical Co.; GY285 from Ciba Specialty Chemicals, Tarrytown, New York; and BREN-S from Nippon Kayaku, Japan. Other suitable epoxy resins include polyepoxides prepared from polyols and the like and polyglycidyl derivatives of phenol-formaldehyde novolacs, the latter of which are available commercially under the tradenames DEN 431, DEN 438, and DEN 439 from Dow Chemical Company. Cresol analogs are also available commercially ECN 1235, ECN 1273, and ECN 1299 from Ciba Specialty Chemicals. SU-8 is a bisphenol A-type epoxy novolac available from Shell Chemicals (formerly, Interez, Inc.). Polyglycidyl adducts of amines, aminoalcohols and polycarboxylic acids are also useful in this invention, commercially available resins of which include GLYAMINE 135, GLYAMINE 125, and GLYAMINE 115 from F.I.C. Corporation; ARALDITE MY-720, ARALDITE MY-721, ARALDITE 0500, and ARALDITE 0510 from Ciba Specialty Chemicals and PGA-X and PGA-C from the Sherwin-Williams Co. And of course combinations of the different epoxy resins are also contemplated for use herein.

[0079] Adhesive compositions of the invention optionally contain at least one free radical initiator. As employed herein, the term "free radical initiator" refers to any chemical species which, upon exposure to sufficient energy (e.g., light, heat, or the like), decomposes into two parts which are uncharged, but which each possesses at least one unpaired electron. Preferred as free radical initiators for use in the practice of the present invention are compounds which decompose (i.e., have a half life in the range of about 10 hours) at temperatures in the range of about 70 up to 180°C.

[0080] Free-radical cure initiators contemplated for use in the practice of the present invention include for example, peroxides (e.g., peroxy esters, peroxy carbonates, hydroperoxides, alkylperoxides, arylperoxides, and the like), azo compounds, and the like. Preferably, free radical initiators contemplated for use in the practice of the present invention include peroxides (e.g., dicumyl peroxide, dibenzoyl peroxide, 2-butanone peroxide, tert-butyl perbenzoate, di-tert-butyl peroxide, 2,5-bis(tert-butylperoxy)-2,5-dimethylhexane, bis(tert-butyl peroxyisopropyl)benzene, and tert-butyl hydroperoxide), azo compounds (e.g., 2,2'-azobis(2-methylpropanenitrile), 2,2'-azobis(2-methylbutanenitrile), 1,1'-azobis(cyclohexanecarbonitrile)), and the like.

[0081] Alternatively, invention compositions cure without the need for a cure initiator. For example, invention compositions may cure upon exposure to electromagnetic radiation (e.g., visible light, ultraviolet light).

[0082] Adhesive compositions according to the present invention typically contain in the range of about 1 wt% up to about 95 wt% thermosetting monomer, in the range of about 0.2 wt% up to about 2.0 wt% cure initiator, and in the range of about 0.05 wt% up to about 95 wt% spacer. Preferably, invention adhesive compositions contain in the range of about 5 wt% up to about 85 wt% thermosetting monomer, and 0.05 wt% up to about 50 wt% spacer. Most preferably, invention adhesive compositions contain in the range of about 10 wt% up to about 75 wt% thermosetting monomer, and 0.05 wt% up to about 10 wt% spacer.

[0083] As readily recognized by those of skill in the art, invention adhesive compositions are useful in a wide variety of applications, including the preparation of multichip modules such as those described in U.S. Patent No. 5,323,060 (incorporated by reference herein in its entirety), the methods described in U.S. Patent No. 5,286,679 (incorporated by reference herein in its entirety), the preparation of semiconductor integrated circuit devices such as those described in U.S. Patent No. 5,140,404 (incorporated by reference herein in its entirety), the preparation of semiconductor chip assemblies such as those described in U.S. Patent No. 6,465,893 (incorporated by reference herein in its entirety), and the like.

[0084] Reference is now made to the figures, where several stacked die structures are illustrated. For example, Figure 1 illustrates a stacked structure where device **3** and device **5** are mounted on substrate **1**, employing invention adhesive as shown at **20** and **22**. Note that the presence of organic spacer in invention adhesive maintains a substantially constant bondline across the full dimension of the assembly. In the embodiment illustrated in Figure 1, device **3** is smaller in dimension than device **5**. As readily understood by those of skill in the art, additional devices could be mounted atop device **5**, thereby providing an even higher density product.

[0085] As another example, Figure 2 illustrates a stacked assembly where the multiple devices stacked onto the substrate are all substantially the same size. Thus, the invention adhesive employed between device **3** and **5'** can fill only the space between the two devices being mounted, not including the wire bond **15**, or alternatively, invention adhesive can completely fill the space between the two devices, including the wire bond **15**. In this way, additional protection can be provided to the wire bond structure.

[0086] As yet another example, Figure 3 illustrates a stacked assembly where a flipped chip **11** serves as the substrate, making electrical contact with the remainder of the device through solder bumps **10**. The remainder of the assembly can be prepared in a variety of ways, for example, as shown in Figures 1 and 2. For simplicity, the same format for devices **3** and **5** is shown here as is illustrated in Figure 1.

[0087] Adhesive compositions according to the invention optionally contain in the range of about 0.1 up to about 10 wt % of at least one coupling agent, based on the total weight of the composition. Preferably, when employed, the coupling agent is present in the range of about 0.2 wt % up to about 5 wt %. Coupling agents contemplated for use in the practice of the present invention include siloxanes, silicate esters, metal acrylate salts, titanates, and the like.

[0088] Invention adhesive compositions may optionally contain at least one filler. Fillers contemplated for optional use in the practice of the present invention are other than the spacers and may optionally be conductive (electrically and/or thermally). Electrically conductive fillers contemplated for use in the practice of the present invention include, for example, silver, nickel, gold, cobalt, copper, aluminum, graphite, silver-coated graphite, nickel-coated graphite, alloys of such metals, and the like, as well as mixtures thereof. Both powder and flake forms of filler may be used in the adhesive compositions of the present invention. Preferably, the flake has a thickness of less than about 2 microns, with planar dimensions of about 20 to about 25 microns. Flake employed herein preferably has a surface area of about 0.15 to 5.0 m^2/g and a tap density of about 0.4 up to about 5.5 g/cc. It is presently preferred that powder employed in the practice of the invention has a diameter of about 0.5 to 15 microns. If present, the filler typically comprises in the range of about 1 % up to about 95 % by weight of the adhesive composition.

[0089] Thermally conductive fillers contemplated for optional use in the practice of the present invention include, for example, boron nitride, silicon carbide, diamond, graphite, beryllium oxide, magnesia, silica, alumina, and the like. The particle size of these fillers will be in the range of about 0.5 microns up to about 25 microns. Preferably, the particle size is about 20 microns.

[0090] Electrically and/or thermally conductive fillers are optionally (and preferably) rendered substantially free of catalytically active metal ions by treatment with chelating agents, reducing agents, nonionic lubricating agents, or mixtures of such agents. Such treatments are described in U.S. Patent No. 5,447,988, which is incorporated by reference herein in its entirety.

[0091] Optionally, a filler may be used that is neither an electrical nor thermal conductor. Such fillers may be desirable to impart some other property to the adhesive formulation such as, for example, reduced thermal expansion of the cured adhesive, reduced dielectric constant, improved toughness, increased hydrophobicity, and the like. Examples of such fillers include fluorinated hydrocarbon polymers (e.g., TEFLON™), thermoplastic polymers, thermoplastic elastomers, mica, fused silica, glass powder, and the like.

[0092] Invention adhesive compositions comprising at least one coupling agent and at least one filler typically contain in the range of about 1 wt % up to about 95 wt% at least one thermosetting monomer, in the range of about 0.2 wt % up to about 2.0 wt % at least one cure initiator, in the range of about 0.5 wt % up to about 5 wt % at least one coupling agent, in the range of about 1 wt % up to about 95 wt% at least one filler, and in the range of about 0.05 wt% up to about 50 wt% a spacer. Preferably, invention adhesive compositions contain in the range of about 5 wt% up to about 85 wt% thermosetting monomer, in the range of about 10 wt % up to about 85 wt% at least one filler, and in the range of about 0.05 wt% up to about 50 wt% spacer. Most preferably, invention adhesive compositions contain in the range of about 10 wt% up to about 75 wt% thermosetting monomer, in the range of about 30 wt % up to about 80 wt% at least one filler, and 0.05 wt% up to about 10 wt% spacer.

[0093] In a further aspect of the invention, there are provided die-attach pastes comprising invention adhesive compositions and optionally a filler different from the spacers constructed from one or more organic polymers. When present in an invention die-attach paste, the filler typically comprises in the range of about 10 up to 90 wt % of the total die-attach paste and the invention adhesive composition comprises in the range of about 10 up to 80 wt % of the total die-attach paste.

[0094] In another aspect of the invention, there are provided methods for creating a substantially uniform bond line between a device and a substrate comprising subjecting a sufficient quantity of an invention adhesive composition positioned between the substrate and the device to conditions suitable to cure the adhesive composition, where spacers control bond line thickness between the device and the substrate. In particular, the bond line thickness is determined by the size of the spacers. Devices contemplated for use in the practice of the present invention include any surface mount component such as, for example, semiconductor die (e.g., wire bonded, flipped chip, and the like), resistors, capacitors, and the like. Preferably, devices contemplated for use in the practice of invention methods are semiconductor dies. Substrates contemplated for use include metal substrates (e.g., lead frames) and organic substrates (e.g., laminates, ball grid arrays, polyamide films, and the like).

[0095] Conditions suitable to cure invention die attach compositions comprise subjecting the above-described assembly to a temperature of less than about 300° C for about 0.5 up to about 2 minutes. This rapid, short duration heating can be accomplished in a variety of ways, e.g., with an in-line heated rail, a belt furnace, or the like.

[0096] Alternatively, conditions suitable to cure invention die attach compositions comprise subjecting the above-described assembly to a temperature in the range of about 120°C up to about 200°C for a period of about 15 minutes up to about 60 minutes. These conditions can be readily produced in a variety of ways, such, for example, by placing the above-described assembly in a curing oven.

[0097] In a further aspect of the invention, there are provided methods for controlling adhesive gap thickness between a device and a substrate, the method comprising subjecting a sufficient quantity of an invention adhesive composition positioned between the substrate and the device to conditions suitable to cure the adhesive composition, where the spacers control adhesive gap thickness between the device and the substrate.

[0098] In a still further aspect of the invention, there are provided methods for maintaining planarity across an adhesive bond line, the method comprising subjecting a sufficient quantity of an invention adhesive composition positioned between a substrate and a device to conditions suitable to cure the adhesive composition, where the spacers maintain planarity across the bond line between the device and the substrate.

[0099] In yet another aspect of the invention, there are provided methods for creating substantially uniform bond lines between at least two semiconductor dice attached to a substrate in a stacked arrangement, the method comprising subjecting a sufficient quantity of an invention adhesive composition positioned between the substrate and each of the dice to conditions suitable to cure the adhesive composition. As readily recognized by those of skill in the art, in some applications, it may be desirable for invention adhesive to substantially completely fill the gap between the surfaces being adhesively attached. In other applications, it may be desirable that invention adhesive formulation not completely fill the gap between the surfaces being adhesively attached. As further recognized by those of skill in the art, the dice bonded can be the same or different sizes.

[00100] In a still further aspect of the invention, there are provided methods for adhesively attaching at least two semiconductor dice to a substrate in a stacked arrangement without the need for a spacer die, the method comprising subjecting a sufficient quantity of an invention adhesive composition positioned between the substrate and each of the dice to conditions suitable to cure the adhesive composition. As readily recognized by those of skill in the art, in some applications, it may be desirable for invention adhesive to substantially completely fill the gap between the surfaces being adhesively attached. In other applications, it may be desirable that invention adhesive formulation not completely fill the gap between the surfaces being adhesively attached. As further recognized by those of skill in the art, the dice bonded can be the same or different sizes.

[00101] In another aspect of the invention, there are provided methods for controlling bond line thickness between semiconductor dice in an assembly comprising a plurality of semiconductor dice in a stacked arrangement, the method comprising subjecting an adhesive composition positioned between each of the dice to conditions suitable to cure the adhesive composition. As readily recognized by those of skill in the art, in some applications, it may be desirable for invention adhesive to substantially completely fill the gap between the surfaces being adhesively attached. In other applications, it may be desirable that invention adhesive formulation not completely fill the gap between the surfaces being adhesively attached. As further recognized by those of skill in the art, the dice bonded can be the same or different sizes.

[00102] In accordance with yet another aspect of the present invention, there are provided assemblies of components adhered together employing invention adhesive compositions. Thus, for example, assemblies comprising a first article permanently adhered to a second article by a cured aliquot of invention adhesive compositions are provided. Articles contemplated for assembly employing invention compositions include memory devices, ASIC devices, microprocessors, flash memory devices, and the like.

[00103] In yet another aspect of the present invention, there are provided assemblies comprising a substrate and plurality of semiconductor dice positioned on the substrate in a stacked arrangement, where each of the semiconductor die is adhered to either the substrate or another die by a cured aliquot of invention adhesive composition.

[00104] In a still further aspect of the invention, there are provided bond lines in an assembly where the assembly comprises at least one semiconductor die, at least one substrate, and an adhesive composition positioned therebetween, where the thickness of the bond line is determined by a plurality of spacers in the adhesive formulation. Preferably, the assembly contains bondlines with a thickness in the range of about 1 mil up to about 8 mils.

[00105] In yet another aspect of the present invention, there are also provided adhesive film compositions suitable for use in die-attach and other applications. Such compositions comprise an adhesive composition, as described above, and a thermoplastic elastomer. The latter is a block copolymer having at least one unit of the general formula (A-B) or (A-B-A), where A is a non-elastomeric polymer block and B is an elastomeric polymer block that is the polymerization product of optionally substituted olefin monomers and/or optionally substituted conjugated diene monomers.

[00106] As employed herein, the term "block copolymer" refers to polymers composed of two or more different polymer subunits joined together. An elastomeric polymer block is a polymer subunit that exhibits rubber-like properties; i.e. it is soft at room temperature and deforms under stress but recovers upon the removal of stress. A non-elastomeric polymer block is a polymer subunit that is hard at room temperature and does not stretch. Polybutadiene is an example of an elastomeric polymer block, while polystyrene is an

example of a non-elastomeric block.

[00107] Thermoplastic elastomers contemplated for use in the practice of the present invention include, for example, polystyrene-polybutadiene-polystyrene block copolymers, polystyrene-polyisoprene-polystyrene block copolymers, polystyrene-polydimethylbutadiene-polystyrene block copolymers, polybutadiene-polyacrylonitrile block copolymers, and the like. Preferably, the block copolymer is a polystyrene-polybutadiene-polystyrene block copolymer or a polybutadiene-polyacrylonitrile block copolymer.

[00108] In a further aspect of the invention, there are provided assemblies employing such adhesive film formulations and methods for making the same. Thus the invention provides methods for adhesively attaching a device to a substrate comprising subjecting a sufficient quantity of an invention adhesive composition positioned between a substrate and a device to conditions suitable to cure the adhesive formulation. Devices contemplated for use in the practice of the present invention include any surface mount component such as, for example, semiconductor die, resistors, capacitors, and the like. Preferably, devices contemplated for use in the practice of invention methods are semiconductor dies. Substrates contemplated for use include metal substrates (e.g., lead frames), organic substrates (e.g., laminates, ball grid arrays, polyamide films), and the like.

[00109] Various conditions are suitable to cure invention adhesive film compositions. For example, some embodiments comprise subjecting invention film adhesive compositions to a temperature of at least about 150°C but less than about 300°C for about 0.5 up to about 2 minutes. This rapid, short duration heating can be accomplished in a variety of ways, e.g., with an in-line heated rail, a belt furnace, or the like. Alternative embodiments comprise subjecting invention film adhesive compositions to a temperature in the range of about 120°C up to about 200°C for a period of about 15 minutes up to about 60 minutes. These conditions can be readily produced in a variety of ways, such as, for example, by placing invention film adhesive compositions in a curing oven. In still other alternative embodiments, conditions suitable to cure invention film adhesive compositions may comprise subjecting invention film adhesive compositions to a pre-cure at temperatures high enough to increase the viscosity of the liquid adhesive and reduce tackiness but low enough to prevent a complete cure. Articles to which such pre-cured adhesive film compositions have been applied may then, at some later time, be subjected to a final cure as described above to give the fully cured adhesive.

[00110] The invention will now be described in greater detail by reference to the following non-limiting examples.

EXAMPLE

[00111] This Example presents bondline data for three different invention adhesive compositions, DR48, DR51, and DR50. Each of these invention compositions was prepared from the same base composition containing the following components:

X-Bismaleimide (described in U.S. Patent Nos. 6,034,194 and 6,034,195)	34.75 %
Ricon 130 (Sartomer)	13.38 %
Ricon 130 MA (Sartomer)	5.06 %
(Glycidoxypropyl) trimethoxysilane (Aldrich)	2.0 %
TEFLON™ (DuPont)	42 %
Perkadox 16 (Akzo Chemicals)	1.12 %
Triganox 141 (Akzo Chemicals)	1.69

[00112] In addition to the components listed above, invention composition DR48 contained 3 to 4 mil spacers, invention composition DR51 contained 4 to 5 mil spacers, and invention composition DR50 contained 5 to 6 mil spacers.

[00113] The bondline data presented in Table 1 were obtained on parts comprising a 300 x 300 x 14 mil die on top of a 500 x 500 x 14 mil die, with a placement force of 10N, and cured on a Hot-Block at 150°C for 1 minute.

Table 1

	Average Bondline (from four corners)			Max Bondline Tilt (Max Corner - Min Corner)		
	DR48	DR51	DR50	DR48	DR51	DR50
	3.3	4.6	5.5	0.1	0.1	0.4
	3.2	4.5	5.3	0.4	0.2	0.3
	3.2	4.5	5.3	0.3	0.6	0.1
	3.8	4.3	5.3	0.2	0.4	0.1
	3.2	4.5	5.4	0.3	0.4	0.4
	3.3	4.2	4.1	0.4	0.2	0.3
	3.3	4.4	5.6	0.1	0.1	0.2
	3.3	4.4	5.3	0.5	0.1	0.3
	3.4	4.4	5.4	0.2	0.6	0.3
	3.6	4.3	5.3	0.5	0.3	0.3
x-bar	3.36	4.41	5.25	0.30	0.30	0.27

(All values above are in mils)

[00114] As readily ascertained from the bondline data shown in Table 1, each invention composition provides a bondline thickness which corresponds to the size of the spacers chosen for each formulation. For example, invention composition DR51 which contains 4 to 5 mil spacers, provides a bondline thickness of 4.41 mils. In addition, the data presented in Table 1 clearly indicate that each invention composition provides substantially uniform planarity across the entire bondline.

[00115] The data presented in Table 2 were obtained on an electrically conductive adhesive using 1.5 mil spacers to control the bond line to >1 mil. Thus, adhesive (with or without added 1.5 mil spacer) was applied to a 78 x71 mil die and subjected to rapid cure (240°C for 23 seconds, followed by an additional 27 seconds at 290°C).

Table 2

Property	Control	Invention (0.1 wt% 1.5 mil spacer)
Cured average BLT	~0.4 mil	1.4 mil
RT Die Shear	15.1 +/- 2.5 kg-f	13.8 +/- 2.7 kg-f
245°C Die Shear	3.6 +/- 0.5 kg-f	3.4 +/- 0.8 kg-f
RT Die Shear after MSL L1 260°C	17.4 +/- 1.5 kg-f	17.6 +/- 2.5 kg-f
245°C Die Shear after MSL L1 260°C	3.7 +/- 0.5	4.4 +/- 0.9
Electrical test at wire bond, no. of failures	0/1200	0/420

[00116] As can be readily ascertained from the data presented in Table 2, the presence of spacer maintains a consistent bondline, while exerting no significant effect on such properties as die shear strength or electrical properties of the modified adhesive. Similarly, it is observed that the presence of spacers as contemplated herein has substantially no effect on the fracture toughness of the underlying adhesive to which the spacers are added.

WHAT IS CLAIMED IS:

1. An adhesive composition comprising at least one thermosetting monomer, optionally at least one cure initiator, and a plurality of spacers, wherein the spacers are constructed from one or more organic polymers.

2. The adhesive composition of claim 1, further comprising inorganic filler material.

3. The adhesive composition of claim 1, wherein the spacers are substantially spherical.

4. The adhesive composition of claim 3, wherein the spacers have a particle size in the range of about 0.02 mils up to about 25 mils.

5. The adhesive composition of claim 4, wherein the spacers have a particle size in the range of about 0.1 mils up to about 15 mils.

6. The adhesive composition of claim 1, wherein the organic polymers are substantially uncrosslinked.

7. The adhesive composition of claim 1, wherein the organic polymers are partially crosslinked.

8. The adhesive composition of claim 1, wherein the organic polymers are substantially completely crosslinked.

9. The adhesive composition of claim 1, wherein the organic polymers are polymerization products of optionally substituted ethylenically unsaturated monomers.

10. The adhesive composition of claim 1, wherein the organic polymers are polymerization or copolymerization products of α-olefins, (meth)acrylates, vinyl esters, acrylamides, or acrylonitriles.

11. The adhesive composition of claim 1, wherein the organic polymers are polymerization or copolymerization products of (meth)acrylates.

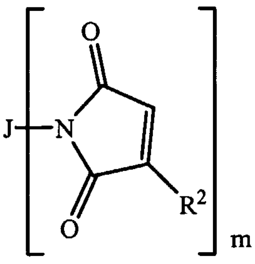
12. The adhesive composition of claim 1, wherein the organic polymer is polymethylmethacrylate.

13. The adhesive composition of claim 12, wherein the polymethylmethacrylate has a molecular weight in the range of about 50,000 up to about 1,500,000.

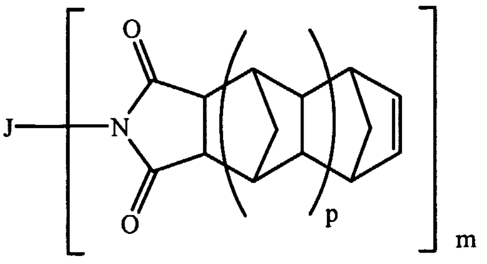
14. The adhesive composition of claim 12, wherein the polymethylmethacrylate has a molecular weight in the range of about 400,000 up to about 500,000.

15. The adhesive composition of claim 1, wherein the thermosetting monomer is selected from the group consisting of maleimide-, nadimide- or itaconamide-containing monomer(s), unsaturated anhydrides, (meth)acrylates, styrenes, cyanate esters, vinyl esters, divinyl compounds, acrylamides, acrylonitriles, allyl amides, and epoxies.

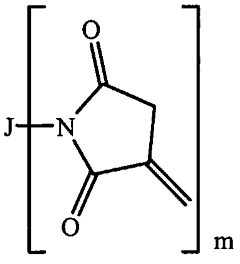
16. The adhesive composition of claim 15, wherein the maleimide-, nadimide-, and itaconimide-containing monomer(s) comprise, respectively, the structures I, II and III:



(I)



(II)



(III)

wherein:

m = 1-15,

p = 0-15,

each R^2 is independently selected from hydrogen or lower alkyl, and

J is a monovalent or a polyvalent moiety comprising organic or organosiloxane radicals, and combinations thereof.

17. The adhesive composition of claim 16, wherein:

J is a monovalent or polyvalent radical selected from the group consisting of hydrocarbyl, substituted hydrocarbyl, heteroatom-containing hydrocarbyl, substituted heteroatom-containing hydrocarbyl, hydrocarbylene, substituted hydrocarbylene, heteroatom-containing hydrocarbylene, substituted heteroatom-containing hydrocarbylene, polysiloxane, polysiloxane-polyurethane block copolymer, and combinations of two or more thereof, optionally containing one or more linkers selected from the group consisting of a covalent bond, -O-, -S-, -NR-, -O-C(O)-, -O-C(O)-O-, -O-C(O)-NR-, -NR-C(O)-, -NR-C(O)-O-, -NR-C(O)-NR-, -S-C(O)-, -S-C(O)-O-, -S-C(O)-NR-, -O-S(O)$_2$-, -O-S(O)$_2$-O-, -O-S(O)$_2$-NR-, -O-S(O)-, -O-S(O)-O-, -O-S(O)-NR-, -O-NR-C(O)-, -O-NR-C(O)-O-, -O-NR-C(O)-NR-, -NR-O-C(O)-, -NR-O-C(O)-O-, -NR-O-C(O)-NR-, -O-NR-C(S)-, -O-NR-C(S)-O-, -O-NR-C(S)-NR-, -NR-O-C(S)-, -NR-O-C(S)-O-, -NR-O-C(S)-NR-, -O-C(S)-, -O-C(S)-O-, -O-C(S)-NR-, -NR-C(S)-, -NR-C(S)-O-, -NR-C(S)-NR-, -S-S(O)$_2$-, -S-S(O)$_2$-O-, -S-S(O)$_2$-NR-, -NR-O-S(O)-, -NR-O-S(O)-O-, -NR-O-S(O)-NR-, -NR-O-S(O)$_2$-, -NR-O-S(O)$_2$-O-, -NR-O-S(O)$_2$-NR-, -O-NR-S(O)-, -O-NR-S(O)-O-,

$-O-NR-S(O)-NR-$, $-O-NR-S(O)_2-O-$, $-O-NR-S(O)_2-NR-$, $-O-NR-S(O)_2-$, $-O-P(O)R_2-$, $-S-P(O)R_2-$, $-NR-P(O)R_2-$, wherein each R is independently hydrogen, alkyl or substituted alkyl, and combinations of any two or more thereof.

18. The adhesive composition of claim 16, wherein:
$m = 1\text{-}6$,
$p = 0\text{-}6$, and
J is

(a) saturated straight chain alkyl or branched chain alkyl, optionally containing substituents selected from hydroxy, alkoxy, carboxy, nitrile, cycloalkyl cycloalkenyl, or optionally substituted aryl moieties as substituents on the alkyl chain or as part of the backbone of the alkyl chain, and wherein the alkyl chains have up to about 20 carbon atoms;

(b) alkylene, oxyalkylene, alkenyl, alkenylene, oxyalkenylene, ester, or polyester, optionally containing substituents selected from hydroxy, alkoxy, carboxy, nitrile, cycloalkyl or cycloalkenyl;

(c) a siloxane having the structure $-(C(R^3)_2)_d-[Si(R^4)_2-O]_f-Si(R^4)_2-(C(R^3)_2)_e-$, $-(C(R^3)_2)_d-C(R^3)-C(O)O-(C(R^3)_2)_d-[Si(R^4)_2-O]_f-Si(R^4)_2-(C(R^3)_2)_e-O(O)C-(C(R^3)_2)_e-$, or $-(C(R^3)_2)_d-C(R^3)-O(O)C-(C(R^3)_2)_d-[Si(R^4)_2-O]_f-Si(R^4)_2-(C(R^3)_2)_e-C(O)O-(C(R^3)_2)_e-$ wherein,

each R^3 is independently hydrogen, alkyl or substituted alkyl,
each R^4 is independently hydrogen, lower alkyl or aryl,
$d = 1\text{-}10$,
$e = 1\text{-}10$, and
$f = 1\text{-}50$;

(d) a polyalkylene oxide having the structure:

$$[(CR_2)_r-O-]_f-(CR_2)_s-$$

wherein:

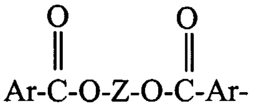
each R is independently hydrogen, alkyl or substituted alkyl,

$r = 1\text{-}10$,

$s = 1\text{-}10$, and

f is as defined above;

(e) aromatic groups having the structure:



$$\mathrm{Ar{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}Z{-}O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}Ar{-}}$$

wherein each Ar is a monosubstituted, disubstituted or trisubstituted aromatic or heteroaromatic ring having in the range of 3 up to 10 carbon atoms, and Z is:

(i) saturated straight chain alkylene or branched chain alkylene, optionally containing saturated cyclic moieties as substituents on the alkylene chain or as part of the backbone of the alkylene chain, or

(ii) polyalkylene oxides having the structure:

$$-[(CR_2)_r\text{-}O\text{-}]_q\text{-}(CR_2)_s\text{-}$$

wherein:

each R is independently defined as above,

$r = 1\text{-}10$,

$s = 1\text{-}10$, and

$q = 1\text{-}50$;

(f) di- or tri-substituted aromatic moieties having the structure:

$$(CR_2)_t\text{-}O\text{-}(C{=}O)\text{-}Ar\text{-}[(C{=}O)\text{-}O\text{-}(CR_2)_a]_{1,2}\text{—}$$

wherein:

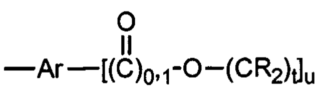
each R is independently defined as above,

$t = 2\text{-}10$,

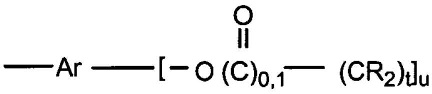
a = 2-10, and

Ar is as defined above;

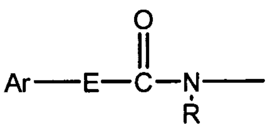
(g) aromatic groups having the structure:



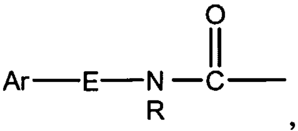
$-Ar-[(\overset{O}{\overset{\|}{C}})_{0,1}-O-(CR_2)_t]_u$,



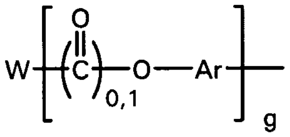
$-Ar-[-O(\overset{O}{\overset{\|}{C}})_{0,1}-(CR_2)_t]_u$,



$Ar-E-\overset{O}{\overset{\|}{C}}-\underset{R}{N}-$,

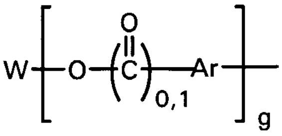


$Ar-E-\underset{R}{N}-\overset{O}{\overset{\|}{C}}-$,



$W\left[(\overset{O}{\overset{\|}{C}})_{0,1}-O-Ar\right]_g$

or



$W\left[O-(\overset{O}{\overset{\|}{C}})_{0,1}-Ar\right]_g$

wherein:

$t = 2\text{-}10$,

$u = 1, 2$ or 3,

$g = 1$ up to about 50,

each R is independently defined as above,

each Ar is as defined above,

E is –O- or $-NR^5-$, wherein R^5 is hydrogen or lower alkyl;

and

W is

(i) straight or branched chain alkyl, alkylene, oxyalkylene, alkenyl, alkenylene, oxyalkenylene, ester, or polyester, optionally containing substituents selected from hydroxy, alkoxy, carboxy, nitrile, cycloalkyl or cycloalkenyl,

(ii) a siloxane having the structure $-(C(R^3)_2)_d-[Si(R^4)_2-O]_f-Si(R^4)_2-(C(R^3)_2)_e-$, $-(C(R^3)_2)_d-C(R^3)-C(O)O-(C(R^3)_2)_d-[Si(R^4)_2-O]_f-Si(R^4)_2-(C(R^3)_2)_e-O(O)C-(C(R^3)_2)_e-$, or $-(C(R^3)_2)_d-C(R^3)-O(O)C-(C(R^3)_2)_d-[Si(R^4)_2-O]_f-Si(R^4)_2-(C(R^3)_2)_e-C(O)O-(C(R^3)_2)_e-$ wherein, each R^3 is independently hydrogen, alkyl or substituted alkyl,

each R^4 is independently hydrogen, lower alkyl or aryl,

$d = 1\text{-}10$,

$e = 1\text{-}10$, and

$f = 1\text{-}50$; or

(iii) a polyalkylene oxide having the structure:

$-[(CR_2)_r\text{-}O\text{-}]_f\text{-}(CR_2)_s\text{-}$

wherein:

each R is independently defined as above,

$r = 1\text{-}10$,

$s = 1\text{-}10$, and

f is defined as above;

optionally containing substituents selected from hydroxy, alkoxy, carboxy, nitrile, cycloalkyl or cycloalkenyl;

(h) a urethane group having the structure:

$$R^7\text{-}U\text{-}C(O)\text{-}NR^6\text{-}R^8\text{-}NR^6\text{-}C(O)\text{-}(O\text{-}R^8\text{-}O\text{-}C(O)\text{-}NR^6\text{-}R^8\text{-}NR^6\text{-}C(O))_v\text{-}U\text{-}R^8\text{-}$$

wherein:

each R^6 is independently hydrogen or lower alkyl;

each R^7 is independently an alkyl, aryl, or arylalkyl group having 1 to 18 carbon atoms;

each R^8 is an alkyl or alkyloxy chain having up to about 100 atoms in the chain, optionally substituted with Ar;

U is -O-, -S-, -N(R)-, or $-P(L)_{1,2}$- wherein R as defined above, and wherein each L is independently =O, =S, -OR or -R; and

$v = 0\text{-}50$;

(i) polycyclic alkenyl; or

(j) mixtures of any two or more thereof.

19. The adhesive composition of claim 18, wherein the maleimide-, nadimide-, itaconamide-containing monomer, or combination of any two or more thereof is liquid at ambient temperature.

20. The adhesive composition of claim 18, wherein J is of sufficient length and has sufficient branching to render the resulting monomer liquid at or about room temperature.

21. The adhesive composition of claim 1, wherein the cure initiator is a free-radical cure initiator.

22. The adhesive composition of claim 21, wherein the free-radical cure initiator is a member selected from the group consisting of peroxy esters, peroxy carbonates, hydroperoxides, alkylperoxides, arylperoxides, and azo compounds.

23. The adhesive composition of claim 1, wherein the composition comprises in the range of about 1 wt% up to about 95 wt% at least one thermosetting monomer, in the range of about 0.2 wt% up to about 2.0 wt% at least one cure initiator, and in the range of about 0.05 wt% up to about 95 wt% at least one organic spacer.

24. The adhesive composition of claim 1, further comprising at least one coupling agent.

25. The adhesive composition of claim 2, wherein the inorganic filler material is conductive.

26. The adhesive composition of claim 25, wherein the inorganic filler material is electrically conductive.

27. The adhesive composition of claim 25, wherein the inorganic filler material is thermally conductive.

28. The adhesive composition of claim 2, wherein the inorganic filler material is non-conductive.

29. The adhesive composition of claim 2, further comprising a filler material constructed from a fluorinated hydrocarbon polymer.

30. The adhesive composition of claim 2, wherein the inorganic filler material is present in the range of about 1 wt % up to about 95 wt%.

31. An adhesive composition comprising in the range of about 1 wt % up to about 95 wt% at least one maleimide-, nadimide-, or itaconamide-containing monomer, in the range of about 0.2 wt % up to about 2.0 wt % at least one cure initiator, in the range of about 0.5 wt % up to about 5 wt % at least one coupling agent, in the range of about 1 wt % up to about 95 wt% at least one filler, and in the range of about 0.05 wt% up to about 50 wt% spacer constructed from one or more organic polymers.

32. A method for creating a substantially uniform bond line between a device and a substrate, the method comprising subjecting a sufficient quantity of an adhesive formulation according to claim 1 positioned between the substrate and the device to conditions suitable to cure the adhesive formulation, wherein the spacers control bond line thickness between the device and the substrate.

33. The method of claim 32, wherein the bond line thickness is determined by the size of the spacers.

34. The method of claim 32, wherein the device is a semiconductor die.

35. A method for controlling adhesive gap thickness between a device and a substrate, the method comprising subjecting a sufficient quantity of an adhesive formulation according to claim 1 positioned between the substrate and the device to conditions suitable to cure the adhesive formulation, wherein the spacers control adhesive gap thickness between the device and the substrate.

36. The method of claim 35, wherein the device is a semiconductor die.

37. A method for maintaining planarity across an adhesive bond line, the method comprising subjecting a sufficient quantity of an adhesive formulation according to claim 1 positioned between a substrate and a device to conditions suitable to cure the adhesive formulation, wherein the spacers maintain planarity across the bond line between the device and the substrate.

38. A method for creating substantially uniform bond lines between at least two semiconductor dice attached to a substrate in a stacked arrangement, the method comprising subjecting a sufficient quantity of an adhesive formulation according to claim 1 positioned between the substrate and each of the dice to conditions suitable to cure the adhesive formulation.

39. A method for adhesively attaching at least two semiconductor dice to a substrate in a stacked arrangement without the need for a spacer die, the method comprising subjecting a sufficient quantity of an adhesive formulation according to claim 1 positioned between the substrate and each of the dice to conditions suitable to cure the adhesive formulation.

40. The method of claim 39 wherein the adhesive formulation substantially completely fills the gap between the surfaces being adhesively attached.

41. The method of claim 39 wherein the adhesive formulation does not completely fill the gap between the surfaces being adhesively attached.

42. A method for controlling bond line thickness between semiconductor dice in an assembly comprising a plurality of semiconductor dice in a stacked arrangement, the method comprising subjecting a sufficient quantity of an adhesive formulation according to claim 1 positioned between each of the dice to conditions suitable to cure the adhesive formulation.

43. An assembly comprising a first article adhered to a second article by a cured aliquot of the adhesive composition according to claim 1.

44. A bond line in an assembly wherein the assembly comprises at least one semiconductor die, at least one substrate, and an adhesive composition positioned therebetween, wherein the thickness of the bond line is determined by a plurality of spacers in the adhesive formulation.

45. The bond line of claim 44, wherein the bond line is in the range of about 1 mil up to about 8 mils.

46. The adhesive composition of claim 1, wherein the spacers include at least one reactive moiety.

47. A die-attach paste comprising an adhesive composition according to claim 1, and optionally a filler different from the spacers constructed from one or more organic polymers.

48. An assembly comprising a substrate and plurality of semiconductor dice positioned on the substrate in a stacked arrangement, wherein each of the semiconductor die is adhered to either the substrate or another die by a cured aliquot of the adhesive composition according to claim 1.

49. An adhesive film formulation comprising:

(a) an adhesive composition according to claim 1, and

(b) a thermoplastic elastomer that is a block copolymer having at least one unit of the general formula (A-B) or (A-B-A), wherein A is a non-elastomeric polymer block and B is an elastomeric polymer block that is the polymerization product of optionally substituted olefin monomers and/or optionally substituted conjugated diene monomers.

50. A method for adhesively attaching a device to a substrate, the method comprising curing an adhesive film formulation according to claim 49 positioned between and contacting a surface of the device and a surface of the substrate.

51. A method according to claim 50, wherein the device is a semiconductor die and the substrate is a lead frame.

52. An assembly comprising a device adhered to a substrate by the method of claim 50.

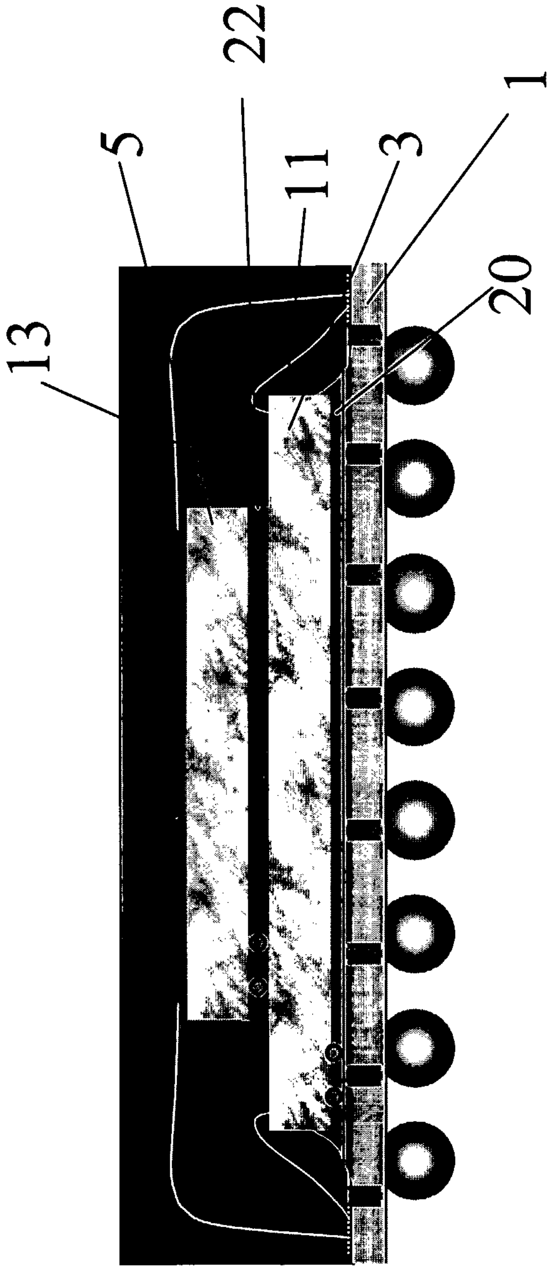


Fig. 1

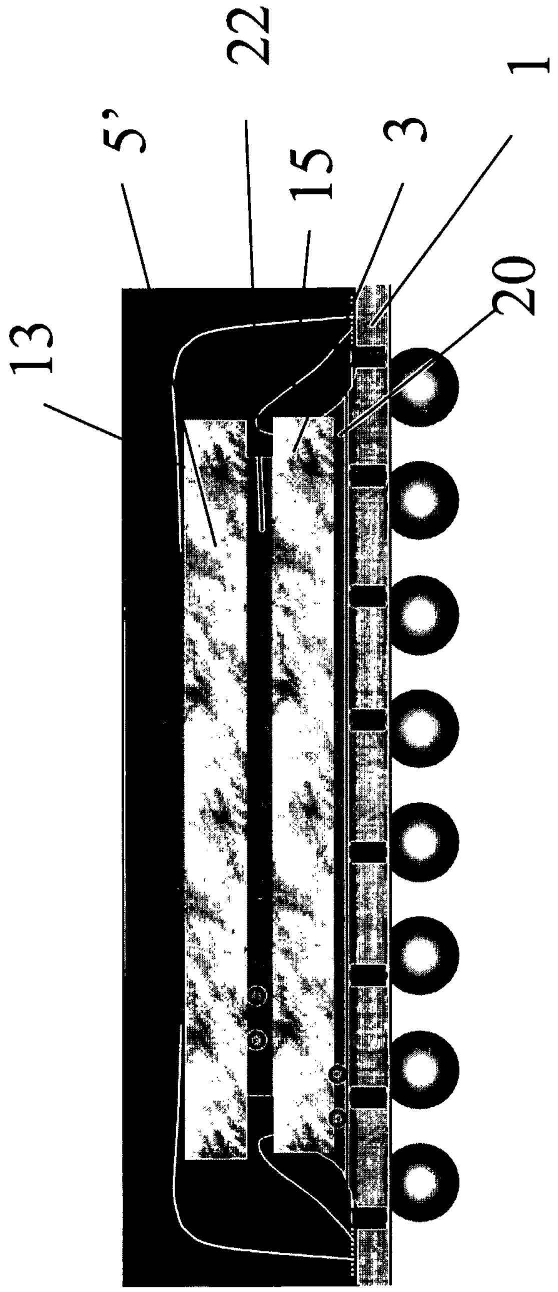


Fig. 2

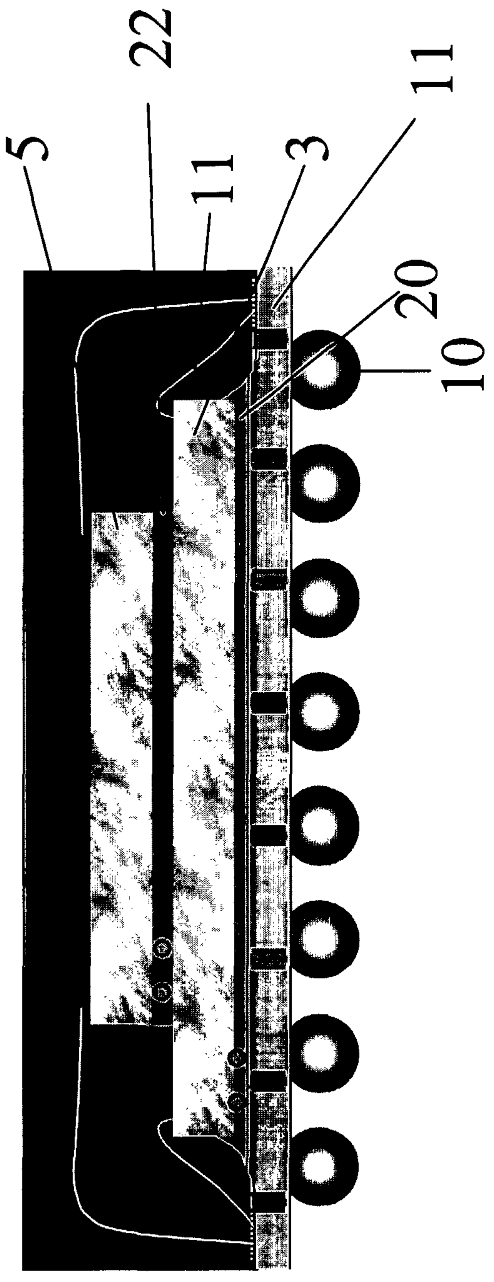


Fig. 3