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(54) **ELECTRICALLY CONDUCTIVE PRESSURE SENSITIVE ADHESIVES, METHOD OF MANUFACTURE, AND USE THEREOF**

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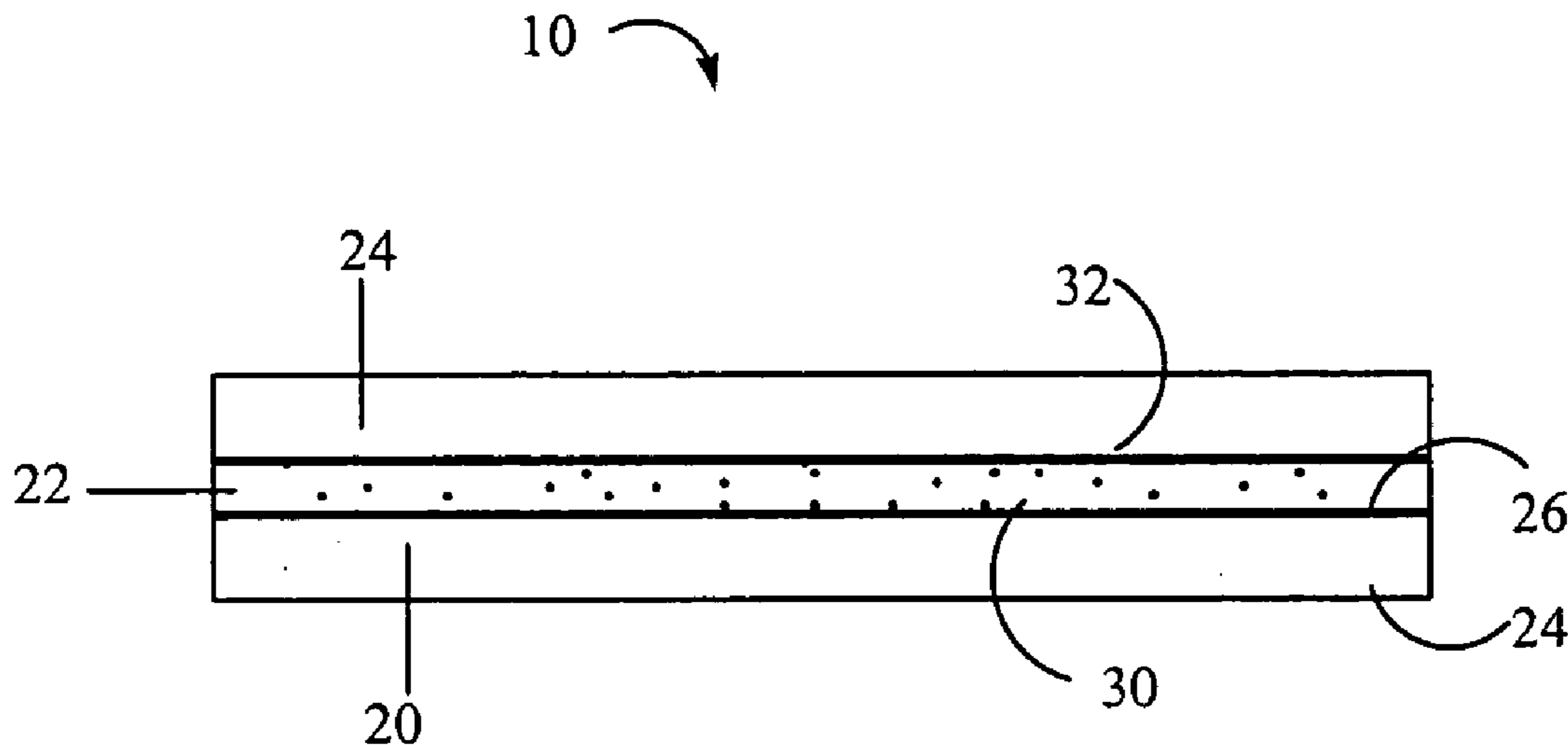
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(57) **ABSTRACT**

An adhesive, comprising a pressure-sensitive adhesive composition; and carbon nanotubes in an amount effective to render the pressure-sensitive adhesive composition electrically conductive. Such adhesives are of particular use with gasketing materials.



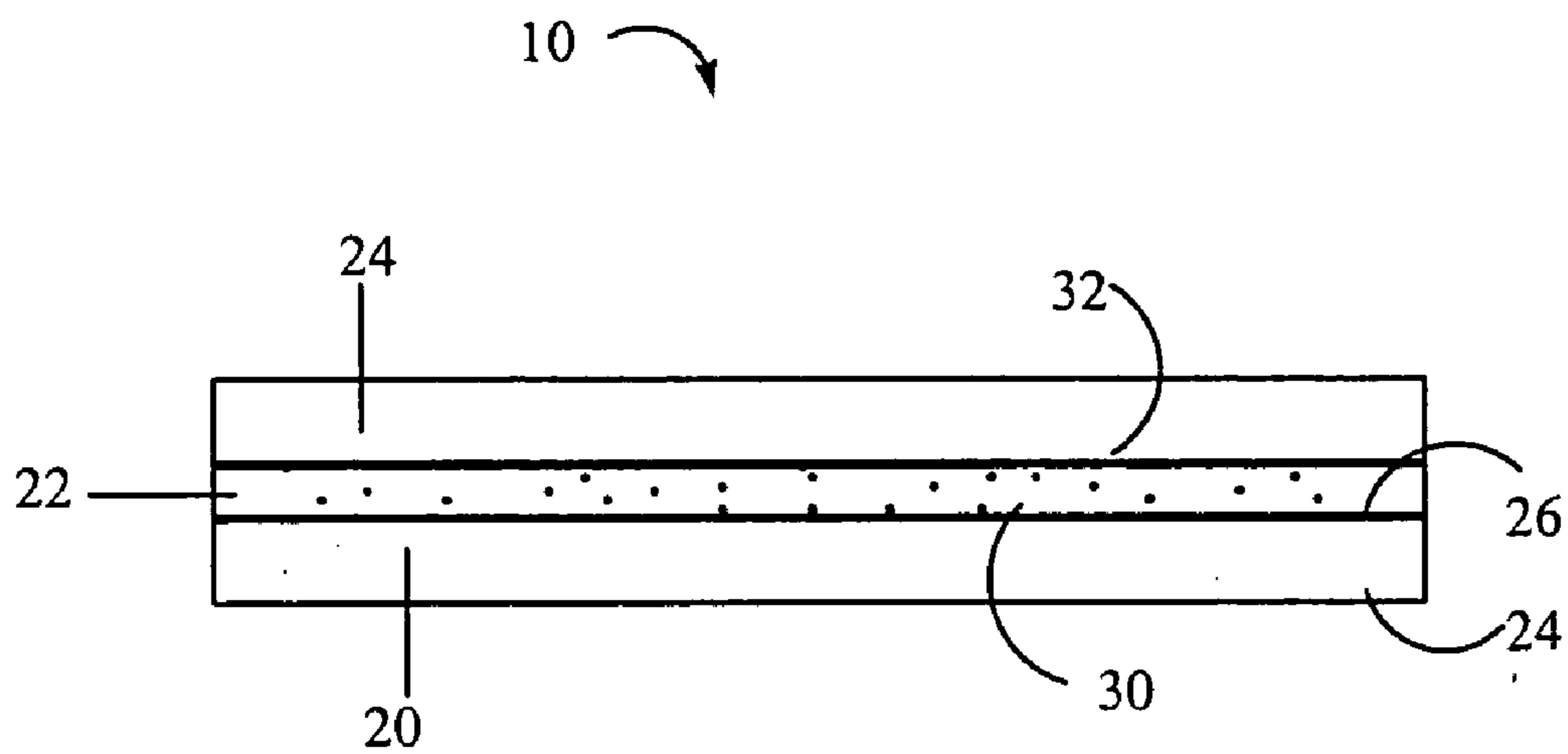


FIGURE 1

**ELECTRICALLY CONDUCTIVE PRESSURE
SENSITIVE ADHESIVES, METHOD OF
MANUFACTURE, AND USE THEREOF**

**CROSS-REFERENCE TO RELATED
APPLICATION**

[0001] This application claims the benefit of the filing of U.S. Provisional Application No. 60/493,181, filed Aug. 6, 2003, which is incorporated herein by reference in its entirety.

BACKGROUND

[0002] This invention relates to electrically conductive pressure sensitive adhesives, methods of manufacture, and uses thereof.

[0003] Electrically conductive materials, particularly elastomers and foams, are of utility in a wide variety of applications such as electrical contacting devices, in sensors, and in applications requiring EMI/RFI shielding and/or electrostatic dissipation. Electrically conductive addition cure silicone compositions have been described, for example, in U.S. Pat. No. 5,932,145 to Mitani et al., U.S. Pat. No. 6,017,587 to Kleyer et al., European Patent No. 0 839 870, and European Patent No. 0 971 367. Other electrically conductive elastomers and foams are also known, for example polyurethanes and polyolefins.

[0004] It is often desirable in the above applications to use an electrically conductive adhesive, particularly a pressure-sensitive adhesive (PSA), to adhere the elastomer or foam to a substrate. Electrical conductivity is most often achieved in PSAs by adding electrically conductive fillers such as particulate polyaniline (see U.S. Pat. No. 5,645,764); particulate metals such as silver or copper (see U.S. Pat. No. 3,475,213 and U.S. Pat. No. 4,258,100); and carbonyl nickel powder (U.S. Pat. No. 3,762,946). Incorporation of enough filler to produce the desired conductivity can be difficult, however, especially without significantly adversely affecting the properties of the adhesive such as tack, peel strength, shear, and the like.

[0005] There accordingly remains a need in the art for compositions and methods whereby pressure sensitive adhesives can be provided with electrical conductivity without significant adverse effect on one or more physical properties desired for a particular application.

BRIEF SUMMARY

[0006] The above-described drawbacks and disadvantages are alleviated by a pressure sensitive adhesive comprising a pressure sensitive adhesive composition and carbon nanotubes in an amount effective to render the pressure sensitive adhesive electrically conductive. Use of carbon nanotubes allows the pressure sensitive adhesive compositions to attain a volume resistivity of about 10^{-3} ohm-cm to about 10^8 ohm-cm without significantly adversely affecting the properties of the compositions such as peel strength, tack, and shear.

[0007] Further disclosed is the above-described composition in the form of a tape, and an article comprising the electrically conductive pressure sensitive adhesive disposed on a substrate. The adhesives, tapes, and articles are of particular utility in applications such as EMI/RFI shielding,

sensors, electrical contacts, and the like. The above discussed and other features and advantages of the present invention will be appreciated and understood by those skilled in the art from the following detailed description.

BRIEF DESCRIPTION OF THE FIGURE

[0008] The invention is illustrated by the following Figure, which is a cross-sectional view of an embodiment of an adhesive tape of the present invention.

DETAILED DESCRIPTION

[0009] The inventors hereof have unexpectedly found that carbon nanotubes can be used to confer high electrical conductivity to pressure sensitive adhesives without significantly affecting the physical properties of the adhesives. The adhesives are particularly suitable for use in adhering elastomers and foams that can provide electromagnetic shielding and/or electrostatic dissipation to articles. Uses include applications involving complicated geometries and forms, such as in computers, personal digital assistants, cell phones, medical diagnostics, and other wireless digital devices, electronic goods such as cassette and digital versatile disk players, as well as in automobiles, ships and aircraft, and the like, where high strength to weight ratios are desirable.

[0010] As used herein, the term "carbon nanotube" is inclusive of a variety of very small carbon fibers having average diameters of less than or equal to about 2000 nanometers (nm) and having graphitic or partially graphitic structures. Suitable carbon nanotubes include those wherein the outer surface of the graphitic or carbon layers is derivatized, for example bonded to a plurality of oxygen-containing groups such as carbonyl, carboxylic acid, carboxylic acid ester, epoxy, vinyl ester, hydroxy, alkoxy, isocyanate, or amide group, or derivatives thereof, for example, sulfhydryl, amino, or imino groups.

[0011] Suitable carbon nanotubes for imparting electrical conductivity to the pressure sensitive adhesive compositions have diameters of about 0.5 to about 2000 nm, with aspect ratios greater than or equal to about 5. Preferably, the carbon nanotubes have an aspect ratio greater than or equal to about 10, more preferably greater than or equal to about 100, and even more preferably greater than or equal to about 1000. Carbon nanotubes as defined herein include vapor grown carbon nanofibers (VGCF) and multi-wall and single carbon nanotubes obtained from processes such as laser ablation, carbon arc, chemical vapor deposition and other processes.

[0012] The VGCF have diameters of about 3.5 to about 2000 nm and are generally produced by chemical vapor deposition. Within this range, the VGCF generally have diameters of greater than or equal to about 3, preferably greater than or equal to about 4.5, and more preferably greater than or equal to about 5 nm. Also desirable within this range are diameters of less than or equal to about 1000, preferably less than or equal to about 500, and more preferably less than or equal to about 100, and even more preferably less than or equal to about 50 nm. The VGCF may be hollow or solid and may have outer surfaces comprising amorphous or graphitic carbon. Solid VGCF are often referred to as carbon nanofibers. VGCF typically exist in the form of clusters, often referred to as aggregates or agglomerates, which may or may not contain embedded catalyst particles utilized in their production.

[0013] Other carbon nanotubes are presently produced by laser-evaporation of graphite or by carbon arc synthesis, yielding fullerene-related structures that comprise graphene cylinders that may be open or closed at either end with caps containing pentagonal and/or hexagonal rings. These nanotubes may have a single wall of carbon, and are therefore generally called single wall carbon nanotubes. Preferred single wall carbon nanotubes have a diameter of about 0.5 to about 3 nm. Within this range it is desirable to use single wall carbon nanotubes having diameters of greater than or equal to about 0.6, preferably greater than or equal to about 0.7 nm. Also desirable within this range are single wall carbon nanotubes having diameters less than or equal to about 2.8, preferably less than or equal to about 2.7, and more preferably less than or equal to about 2.5 nm.

[0014] Carbon nanotubes having multiple concentrically arranged walls produced by laser-evaporation of graphite or by carbon arc synthesis are generally called multiwall carbon nanotubes. Multiwall nanotubes used in the polymeric foams and elastomers generally have diameters of about 2 nm to about 50 nm. Within this range it is generally desirable to have diameters greater than or equal to about 3, preferably greater than or equal to about 4, and more preferably greater than or equal to about 5 nm. Also desirable within this range are diameters of less than or equal to about 45, preferably less than or equal to about 40, more preferably less than or equal to about 35, even more preferably less than or equal to about 25, and most preferably less than or equal to about 20 nm. Single wall or multiwall carbon nanotubes generally exist in the form of clusters, (also often referred to as agglomerates and aggregates) and may or may not contain embedded catalyst particles utilized in their production. Single wall carbon nanotubes tend to exist in the form of ropes due to Van der Waal forces, and clusters formed by these ropes may also be used. Single wall nanotubes may be metallic or semi-conducting. It is preferable to use compositions having as high a weight percentage of metallic carbon nanotubes as possible for purposes of electromagnetic shielding.

[0015] Carbon nanotubes containing impurities such as amorphous carbon or soot, as well as catalytic materials such as iron, nickel, copper, aluminum, yttrium, cobalt, sulfur, platinum, gold, silver, or the like, or combinations comprising at least one of the foregoing catalytic materials, may also be used. In one embodiment, the carbon nanotubes may contain impurities in an amount less than or equal to about 80 weight percent (wt %), preferably less than or equal to about 60 wt %, more preferably less than or equal to about 40 wt %, and most preferably less than or equal to about 20 wt %, based upon the total weight of the carbon nanotubes and the impurities.

[0016] Effective amounts of VGCF, single wall, and/or multiwall carbon nanotubes, alone or in combination, will vary depending on the nature of the adhesive, the nature of the nanotubes, the intended use, the desired electrical conductivity, and similar factors, and can be readily determined by one of ordinary skill in the art. In general, the nanotubes will comprise about 0.0001 to about 50 wt % of the total weight of the pressure sensitive adhesive composition. Within this range, it is generally desirable to have the carbon nanotubes present in an amount of greater than or equal to about 0.05, preferably greater than or equal to about 0.1 of the total weight of the adhesive composition. Also desirable

are carbon nanotubes present in an amount less than or equal to about 40, preferably less than or equal to about 20, and more preferably less than or equal to about 5 wt % of the total weight of the composition.

[0017] Other electrically conductive fillers may be used in addition to the carbon nanotubes, for example carbon black, carbon fibers such as PAN fibers, metal-coated fibers or spheres such as metal-coated glass fibers, metal-coated carbon fibers, metal-coated organic fibers, metal-coated ceramic spheres, metal-coated glass beads and the like, inherently conductive polymers such as polyaniline, polypyrrole, polythiophene in particulate or fibril form, conductive metal oxides such as tin oxide or indium tin oxide, and combinations comprising at least one of the foregoing conductive fillers may also be used. The amount of these fillers is preferably selected so as to not adversely affect the final properties of the pressure sensitive adhesive compositions. Typical amounts, when present, are about 0.1 to about 50 wt % based on the total weight of the composition. Within this range it is generally desirable to have an amount of greater than or equal to about 1.0, preferably greater than or equal to about 5 wt % of the total weight of the composition. Also desirable is an amount of less than or equal to about 40, more preferably less than or equal to about 25 wt %, of the total weight of the composition.

[0018] The term "pressure sensitive adhesive" or "PSA" is used herein in its conventional sense to mean that the composition is formulated to have a glass transition temperature, surface energy, and/or other properties such that it exhibits some degree of tack at normal room temperature. Thus, the constituent polymers and/or copolymers of the composition generally will have a glass transition temperature of less than about 0° C. such that the mass of the composition is tacky at ambient temperatures and is thereby bondable under an applied pressure to a surface or other substrate. In general, the formulation of the adhesive composition specifically may be selected to exhibit an affinity, as may be measured by lap shear, die shear, static or dynamic shear, peel, or other adhesion, to the material forming the substrate or substrates involved in the particular application, but which affinity is less than to the material forming a backing layer as described below. Such adhesion affinities may depend particularly on the surface energy of the materials involved, and may be developed from surface tension, valence, polar, electrostatic, van der Waals, or other attractive forces, mechanical interlocking action, or a combination thereof.

[0019] In use, pressure sensitive adhesives are generally provided in the form of a tape. An exemplary embodiment of a pressure sensitive adhesive tape is shown generally at FIG. 1, and comprises tape 10, which may have an overall thickness of between about 0.5 and about 10 mils, may be provided in the form of, or as formed from, a sheet, roll, tape, die-cut part, or the like. Tape 10, which may be of an indefinite length and/or width, includes a backing strip, sheet, or other generally flat layer 20, an adhesive layer 22 on at least one side or portion of backing layer 20, and, optionally, a release liner 24 for covering adhesive layer 22 during shipping and handling. Although adhesive layer 22 is shown as being coated on substantially the entirety of backing layer 20, adhesive layer 22 may alternatively be applied in a pattern or otherwise to cover only a portion of backing layer 20. For most applications, backing layer 20

can have a thickness of about 0.5-8 mils (0.013-0.203 mm), with adhesive layer **22** having a thickness of about 0.5-2.5 mils (0.013-0.064 mm).

[0020] Backing layer **20** has a first side or surface **24** and an opposing second side or surface **26**. Adhesive layer **22** may be coated or laminated on, or otherwise bonded to or in intimate contact with second side **26** of the backing layer **20** to provide the laminar structure of tape **10**. Depending on the intended application, a second adhesive layer **22** may be coated on backing layer first side **24** (not shown). Adhesive layer **22** has an inner face **30** adhesively or otherwise bonded to second side **26**, and an opposite outer face **32** that is adhesively bondable under an applied pressure to a surface of a substrate.

[0021] Backing layer **20** may be formed of a synthetic, natural, or glass fiber fabric, paper, or foamed or unfoamed plastic, resin, elastomer, or other polymeric or other material conventionally used in tape construction. In one embodiment, backing layer **20** is removable after bonding of adhesive layer **22** to the surface of a substrate. A second substrate may then be applied to the exposed face **30**. In another embodiment, for example EMI shielding applications, backing layer **20** can be formed of an electrically-conductive material such as a conductive polymer, a conductive metal foil, or a cloth plated with a conductive metal such as copper, aluminum, nickel, silver, or alloys or mixtures comprising at least one of the foregoing conductive metals. Where similar materials are used for the substrate and backing layer **20**, the backing layer second side **26** may be coated, prior to the application of the adhesive layer, with a higher surface energy "tie" layer so as to increase the affinity of the adhesive layer **22** thereto relative to the substrate surface. Such tie layer may be formed as a chemical bond coat, such as a thermoplastic dissolved in a solvent, which is applied to the side **26** and dried or otherwise cured thereon to form an intermediate tie layer between the side and the adhesive layer **22**. Alternatively, other known surface treatments may be employed such as cleaning or roughening the side **26** with one or more of compressed gas, chemical or solvent etching/cleaning, grit blasting, such as with aluminum oxide or other abrasive, or plasma, such as may be generated from the ionization of oxygen, argon, or another gas or mixture of gases.

[0022] Exemplary release liners **24** include face stocks or other films of polyolefins, plasticized polyvinyl chloride, polyesters, cellulose, metal foils, composites, and waxed, siliconized, or other coated paper or plastic having a relatively low surface energy to be removable without appreciable lifting of the adhesive layer **22** from the backing layer **20**.

[0023] Manufacture of the pressure sensitive adhesives is by processes recognized in the art. In general, the compositions for formation of the adhesive, additives, e.g., catalyst, crosslinking agent, additional fillers, and the like (which are described in further detail below), and the carbon nanotubes are mixed, frothed and/or blown if desired, shaped (e.g., cast), then cured, if applicable. Stepwise addition of the various components may also be used, e.g., the carbon nanotubes may be provided in the form of a masterbatch, and added after the other components are mixed.

[0024] During manufacture, it is generally desirable to disentangle any clusters, aggregates or agglomerates of

carbon nanotubes with minimal damage to the aspect ratio, in order to provide enhanced electrical conductivity, in particular enhanced electromagnetic shielding or electrostatic dissipative properties at lower weight percentages of nanotubes. It may therefore be desirable that any mixing during manufacture be carried out at as low a viscosity as possible, as mixing at lower viscosities substantially reduces the shear forces acting on the nanotubes. Accordingly, it may be desirable to use a removable solvent or diluent (e.g., an organic solvent and/or water) during mixing, to substantially reduce the melt viscosity of the composition. The diluent may be removed after some or all of the dispersion of the nanotubes in the elastomer is completed. Alternatively, the nanotubes may be pre-dispersed at a higher concentration in at least one of the adhesive components, i.e., masterbatch. In the preparation of foamed adhesives, it may be desirable to introduce desired blowing agents into the composition prior to the introduction of the nanotubes to facilitate dispersion while minimizing damage to the nanotubes. The blowing of the foam may produce a similar effect, in that it disentangles nanotubes with low or minimal damage to the aspect ratio, because the expansion of any polymer trapped in a nanotube cluster or agglomerate or aggregate may cause the disentangling of the individual nanotubes with minimal damage. Thus, mixing nanotubes with the polymer at a reduced viscosity and subsequently foaming the polymer may achieve excellent conductivity at low loading levels, because of the preservation of nanotube aspect ratio. Low carbon nanotube loading aids in preserving the desirable physical properties of the adhesives.

[0025] Accordingly, in the production of commercial quantities of tape **10**, the formulation for the adhesive layer **22** may be compounded in a conventional mixing apparatus as an admixture of a PSA composition, the carbon nanotubes, any additional fillers and/or additives, and a solvent or diluent. The formulation may be coated or otherwise applied to side **26** of the backing layer **20** in a conventional manner such as, for example, by a direct process such as spraying, knife coating, roller coating, casting, drum coating, dipping, dispensing, extrusion, screen printing, or like, or an indirect transfer process. After coating, the resultant film may be dried to remove the solvent or otherwise cured or cooled to develop an adherent film on backing layer **20**. Curing, where used, is inclusive of polymerization, crosslinking, vulcanization, or otherwise chemical or physical changes that result in formation of a generally solid film from the applied composition. As a result of the inherent tack of the PSA film, an adhesive and/or mechanical bond may be developed between the layers **20** and **22** to form the integral, laminate structure of tape **10**. Alternatively, the adhesive layer **22** may be separately formed and laminated under conditions of elevated temperature and/or pressure to the backing layer **20** in a separate operation.

[0026] A variety of pressure sensitive adhesive formulations may be suitable for use with the carbon nanotubes, and include film-forming materials such as a natural or synthetic rubber or elastomer, or other resin, plastic, or polymer exhibiting rubber-like properties of compliancy, resiliency or compression deflection, low compression set, flexibility, and an ability to recover after deformation. Examples of such materials include styrene-butadienes, styrene-isoprenes, polybutadienes, polyisobutylenes, polyurethanes, silicones, fluorosilicones and other fluoropolymers, chlorosulfonates, butyls, neoprenes, nitriles, polyisoprenes, plas-

ticized nylons, polyesters, polyvinyl ethers, polyvinyl acetates, polyisobutylenes, ethylene vinyl acetates, polyolefins, and polyvinyl chlorides, copolymer rubbers such as ethylene-propylene (EPR), ethylene-propylene-diene monomer (EPDM), styrene-isoprene-styrene (SIS), styrene-butadiene-styrene (SBS), nitrile-butadienes (NBR) and styrene-butadienes (SBR), blends such as ethylene or propylene-EPDM, EPR, or NBR, and mixtures, blends, and copolymers thereof.

[0027] These materials may be compounded with a tackifier, which may be a resin such as glyceryl esters of hydrogenated resins, thermoplastic terpene resins, petroleum hydrocarbon resins, coumarone-indene resins, synthetic phenol resins, low molecular weight polybutenes, or a tackifying silicone. Generally, the tackifying resin may be compounded into the resin material at between about 40-150 parts per hundred parts of the resin.

[0028] Additional fillers and additives may be included in the PSA composition depending upon the requirements of the particular application, for example conventional wetting agents or surfactants, pigments, dyes, and other colorants, opacifying agents, anti-foaming agents, anti-static agents, coupling agents such as titanates, chain extending oils, lubricants, stabilizers, emulsifiers, antioxidants, thickeners, and/or flame retardants such as aluminum trihydrate, antimony trioxide, metal oxides and salts, intercalated graphite particles, phosphate esters, brominated diphenyl compounds such as decabromodiphenyl oxide, borates, phosphates, halogenated compounds, glass, silica, silicates, and mica. Typically, these fillers and additives are blended or otherwise admixed with the formulation, and may comprise between about 0.05-80% or more by total volume thereof.

[0029] Aqueous pressure sensitive adhesive compositions are useful with carbon nanotubes, for example those comprising a mechanically stable aqueous emulsion of polyethylene particles having an average molecular weight ranging from about 7,000 to 40,000 as described in U.S. Pat. No. 3,734,686; ethylene polymer latexes containing ethylene polymer particles of submicron size prepared by dispersing in water an ethylene polymer and a water-soluble block copolymer of ethylene oxide and propylene oxide as described in U.S. Pat. No. 3,418,26; latexes prepared from copolymers of ethylene and C₃-C₂₀ α -olefins as in U.S. Pat. No. 5,574,091; or compositions comprising homogenous ethylene/ α -olefin interpolymers and substantially random interpolymers as disclosed in U.S. Pat. No. 6,521,696.

[0030] Another useful type of pressure sensitive adhesive composition is based on (meth) acrylates (i.e., acrylates and methacrylates). Such compositions include, for example, copolymers derived from compositions containing, based on the total weight of the monomer components, about 50 to about 99 weight percent of C₄-C₁₈ alkyl esters of (meth)acrylic acids, about 1 to about 50 weight percent of polar ethylenically unsaturated comonomers such as itaconic acid, certain substituted acrylamides such as N,N-dimethyl acrylamide, N-vinyl-2-pyrrolidone, or n-vinyl caprolactam, acrylonitrile, acrylic acid, glycidyl acrylate, and the like, and optionally, up to about 25 weight percent of a non-polar ethylenically unsaturated comonomer such as cyclohexyl acrylate, n-octyl acrylamide, t-butyl acrylate, methyl methacrylate, and the like, and/or a tackifier.

[0031] Other additives such as crosslinking agents may also be present, for example include di- and triacrylates, for

instance 1,6-hexanediol diacrylate; and photoinitiators such as 1-hydroxycyclohexyl phenyl ketone or 2,2-dimethoxy-2-phenylacetophenone, which are commercially available from Ciba-Geigy under the trade names respectively of IRGACURE 184 and IRGACURE 651, or other photoinitiators for ethylenically-unsaturated monomers which are well known in the art. Cross-linking agents and photoinitiators, are each generally used in amounts of about 0.005 to about 0.5 weight percent, based on total weight of monomer composition. Suitable (meth)acrylate pressure sensitive adhesives are disclosed, for example, in U.S. Pat. No. 4,223,067; U.S. Pat. No. 4,181,752 U.S. Pat. No. 5,183,833; U.S. Pat. No. 5,645,764, and U.S. Pat. No. Re. 24,906. Suitable compositions are also commercially available, for example from Ashland Chemicals under the trade name AEROSSET.

[0032] The (meth)acrylate containing monomer mixture may be polymerized by various techniques, preferably photoinitiated bulk polymerization as described, for example, in U.S. Pat. No. 5,620,795, wherein the polymerizable comonomers and a photoinitiator are mixed together in the absence of solvent and partially polymerized to a viscosity of about 500 to about 50,000 cps to achieve a coatable syrup. Alternatively, the monomers may be mixed with a thixotropic agent such as fumed hydrophilic silica to achieve a coatable thickness. A crosslinking agent, the carbon nanotubes, and any other components (including any tackifiers) are then added to the prepolymerized syrup. Alternatively, these components (including any tackifiers but with the exception of the crosslinking agent) can be added directly to the monomer mixture prior to pre-polymerization.

[0033] The resulting composition is coated onto a substrate (which may be transparent to ultraviolet radiation) and polymerized in an inert (i. e., oxygen free) atmosphere, e.g., a nitrogen atmosphere by exposure to ultraviolet radiation. Examples of suitable substrates include release liners (e.g., silicone release liners) and tape backings (which may be primed or unprimed paper or plastic). A sufficiently inert atmosphere can also be achieved by covering a layer of the polymerizable coating with a plastic film which is substantially transparent to ultraviolet radiation, and irradiating through that film in air as described in the aforementioned Martens et al. patent using ultraviolet lamps. The ultraviolet light source preferably has 90% of the emissions between 280 and 400 nm (more preferably between 300 and 400 nm), with a maximum at 351 nm. Where multi-layer tape constructions are desirable, a variety of conventional techniques may be used. For example, the coatings may be applied concurrently (e.g., through a die coater), after which the entire multi-layer structure is cured at the same time. The coatings may also be applied sequentially whereby each individual layer is partially or completely cured prior to application of the next layer.

[0034] Use of carbon nanotubes enables the production of electrically conductive adhesives having a volume resistivity of about 10⁻³ ohm-cm to about 10⁸ ohm-cm. Within this range, the volume resistivity can be less than or equal to about 10⁶, less than or equal to about 10⁴, or less than or equal to about 10³, and is preferably less than or equal to about 10², more preferably less than or equal to about 10, and most preferably less than or equal to about 1 ohm-cm.

[0035] Use of carbon nanotubes unexpectedly allows the manufacture of pressure sensitive adhesives that have excel-

lent electrical conductivity and physical properties, particularly tack and peel strength. These characteristics permit the adhesives to be used with a variety of articles, particularly where electromagnetic and/or electrostatic dissipative properties are desired. The articles are suitable for use in a variety of commercial applications such as cell phones, global positioning systems, disk drives, personal digital assistants, personal or laptop computers, airplanes, radio receiver or transmitter, network server, cellular communication base station or other telecommunications equipment, or other articles of commerce.

[0036] The following examples, which are meant to be exemplary, not limiting, illustrate compositions and methods of manufacturing of some of the various embodiments of the pressure sensitive adhesives described herein.

EXAMPLES

[0037] As is known, particular values for volume resistivity and electrostatic shielding will depend on the particular test methods and conditions. For example, it is known that volume resistivity and shielding effectiveness may vary with the pressure placed on the sample during the test. Useful electrical equipment and test fixtures to measure volume resistivity in the sample below are as follows. The fixture is a custom fabricated press with gold plated, 2.5 cm×2.5 cm (1 inch×1 inch) square, and electrical contacts. The fixture is equipped with a digital force gauge that allows the operator to control and make adjustments to the force that is applied to the surface of the sample. The Power supply is capable of supplying 0 to 2 amps to the sample surface. The Voltage drop and ohms across the sample are measured using a HP 34420A Nano Volt/Micro Ohmmeter. The electronic components of the fixture are allowed to warm up and, in the case of the HP 34420 A, the internal calibration checks are done. The samples are allowed to equilibrate, for a period of 24 hours, to the conditions of the test environment. Typical test environment is 50% Relative Humidity (% RH) with a room temp of 23° C. (70° F.).

[0038] The sample to be tested is placed between the platens of the test fixture and a load is applied to the surface. The applied load is dependent on the type of sample to be tested, soft elastomers are tested using small loads while solids are tested using a load range from about 10 to 100 pounds per square inch). Once the load has been applied, the current is applied to the sample and the voltage drop through the sample thickness is measured. A typical test would include measurements at 4 different amp settings, 0.5, 1.0, 1.6, and 2.0 amps. For a conductive composite the resulting calculated volume resistivity for all four of the amp settings will be similar. The calculation for the volume resistivity is as follows:

$$\text{Volume resistivity (ohm-cm)} = (E/I) * (A/T)$$

[0039] wherein E=voltage drop (V), I=current (amps), A=area (cm²), and T=thickness (cm).

[0040] To make volume resistivity measurements, a conductive silicone elastomer is coated with a commercially available pressure sensitive adhesive composition (e.g., Aeroset 1450 from Ashland Chemicals) in an organic solvent and comprising 0.001 to 50 wt % of carbon nanotubes. After as described by the manufacturer, the elastomer is adhered to conductive silicone elastomer from BISCO, and a voltmeter is used to make resistance measurements as

described above. The volume resistivity of such samples is lower than for comparable samples made using a commercially available conductive PSA available from 3M under the trade designation "9713"). The samples can have a volume resistivity of about 10⁻³ ohm-cm to about 10⁸ ohm-cm. Within this range, the volume resistivity can be less than or equal to about 10⁶, less than or equal to about 10⁴, or less than or equal to about 10³, and is preferably less than or equal to about 10², more preferably less than or equal to about 10, and most preferably less than or equal to about 1 ohm-cm.

[0041] Typically, the inventive pressure sensitive adhesive will be bondable to the substrate surface under firm hand pressure, and will exhibit thereon a 180° peel adhesion, such as may be determined in accordance with PSTC-1 (Pressure Sensitive Tape Council Test Methods for Pressure Sensitive Adhesive Tapes, Pressure Sensitive Tape Council, Northbrook, Ill. 60062), of between 0.5-5.0 lb/in initial. Preferably, such adhesion will be observed to increase or "build" on aging.

[0042] While preferred embodiments have been shown and described, various modifications and substitutions may be made thereto without departing from the spirit and scope of the invention. Accordingly, it is to be understood that the present invention has been described by way of illustration and not limitations.

What is claimed is:

1. An adhesive, comprising
 - a pressure-sensitive adhesive composition; and
 - carbon nanotubes in an amount effective to render the pressure-sensitive adhesive composition electrically conductive.
2. The adhesive of claim 1, having a volume resistivity of about 10⁻³ ohm-cm to about 10⁸ ohm-cm.
3. The adhesive of claim 1, having a volume resistivity of less than about 10 ohm-cm.
4. The adhesive of claim 1, having a volume resistivity of less than about 1 ohm-cm.
5. An article comprising the adhesive composition of claim 1 disposed on a substrate.
6. The article of claim 5, wherein the substrate is electrically conductive.
7. The article of claim 6, wherein the substrate has a volume resistivity of about 10⁻³ ohm-cm to about 10⁸ ohm-cm.
8. The article of claim 7, wherein the substrate has a volume resistivity of less than about 10 ohm-cm.
9. The article of claim 7, wherein the substrate has a volume resistivity of less than about 1 ohm-cm.
10. A pressure-sensitive adhesive tape, comprising
 - a backing layer having a first side and a second side opposite said first side; and
 - a pressures-sensitive adhesive layer having a first side and a second side opposite the first side, wherein
 - the first side of the pressure-sensitive adhesive layer is in contact with at least a portion of the first side of the backing layer,
 - the second side is bondable under pressure to a substrate, and

the pressure-sensitive adhesive layer comprises
a pressure-sensitive adhesive composition; and
carbon nanotubes in an amount effective to render
the pressure-sensitive adhesive composition elec-
trically conductive.

11. The tape of claim 10, wherein the backing layer is an electrically conductive polymer.

12. The tape of claim 10, wherein the backing layer is an electrically conductive silicone.

13. The tape of claim 10, wherein the backing layer has a volume resistivity of about 10^{-3} ohm-cm to about 10^8 ohm-cm.

14. The tape of claim 12, wherein the backing layer has a volume resistivity of less than about 10 ohm-cm.

15. The tape of claim 12, wherein the backing layer has a volume resistivity of less than about 1 ohm-cm.

16. An article, comprising

a substrate having a surface; and

the tape of claim 10, wherein the second side of the pressure-sensitive adhesive layer is bonded to at least a portion of the surface of the substrate.

17. The article of claim 16, wherein the tape provides an EMI shielding effectiveness of at least about 60 dB over a frequency range of about 10 to about 10 GRz.

18. The article of claim 16, wherein the initial peel strength between the backing and the surface of the substrate is about 1.5 to about 5.0 lb/in (0.26-0.87 N/m).

19. The article of claim 16, wherein the volume resistivity between the backing and the surface of the substrate is about 10^{-3} ohm-cm to about 10^8 ohm-cm.

20. A method of manufacture of an adhesive, comprising

mixing a pressure-sensitive adhesive formulation in a solvent or diluent with carbon nanotubes;

applying the mixture to a substrate or backing layer;

removing the solvent or diluent; and

optionally curing the adhesive.

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