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(54) Titre : BANDE ADHESIVE AUTOCOLLANTE, ANTISTATIQUE RESISTANT A DE HAUTES TEMPERATURES
(54) Title: HIGH TEMPERATURE RESISTANT ANTISTATIC PRESSURE-SENSITIVE ADHESIVE TAPE

(57) Abrégé/Abstract:
There is provided a heat-resistant anti-static pressure-sensitive adhesive tape comprising a substrate having opposing surfaces, at least one of said surfaces bearing thereon an acrylic microparticulate adhesive wherein the microparticles have an average diameter of 1 to 250 micrometers, wherein the microparticles have a surface bearing thereon an ionic conductive material formed from a polymer electrolyte base polymer and at least one ionic salt selected from the group consisting of salts of alkali metals and salts of alkaline earth metals, said adhesive being bonded to said substrate by means of a primer, said primer comprising at least one phenolic resin and at least one rubbery compound, said adhesive tape being capable of surviving immersion in molten solder at 260°C for at least 5 seconds.

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HIGH TEMPERATURE RESISTANT ANTISTATIC PRESSURE-SENSITIVE ADHESIVE TAPE

Abstract

There is provided a heat-resistant anti-static pressure-sensitive adhesive tape comprising a substrate having opposing surfaces, at least one of said surfaces bearing thereon an acrylic microparticulate adhesive wherein the microparticles have an average diameter of 1 to 250 micrometers, wherein the microparticles have a surface bearing thereon an ionic conductive material formed from a polymer electrolyte base polymer and at least one ionic salt selected from the group consisting of salts of alkali metals and salts of alkaline earth metals, said adhesive being bonded to said substrate by means of a primer, said primer comprising at least one phenolic resin and at least one rubbery compound, said adhesive tape being capable of surviving immersion in molten solder at 260°C for at least 5 seconds.

HIGH TEMPERATURE RESISTANT ANTISTATIC PRESSURE-SENSITIVE ADHESIVE TAPE

Background of the Invention

Field of the Invention

The invention relates to pressure-sensitive adhesive tape constructions which are useful for masking printed circuit boards (PCBs) at the high temperatures associated with wave soldering operations. These adhesive tapes, which comprise ionically conductive polymeric microparticulate adhesive formulations, provide tapes extremely resistant to tribocharging, thereby protecting electronic components from static charge buildup. In addition, the adhesive masking tape, upon removal from a PCB, does not contaminate the surface of the board with adhesive residue.

Description of the Art

The process of wave soldering is commonly used for permanently attaching electronic components to printed circuit boards. Various methods are used to mask or cover areas of the board during the wave soldering attachment process where solder is not desired. It is known, for example, to achieve such masking by use of self-adhesive tapes based on high-temperature-resistant polyimide film coated with a silicone-based adhesive. However, the removal of such tapes from the surface of electronic assemblies causes tribocharging accompanied by static charges which can damage sensitive electronic components and cause contamination of the printed circuits by silicone.

Electrically conductive tapes are also useful for the masking purpose. Electrically conductive tapes do not tribocharge as readily as those made from insulating materials such as silicones. The use of conductive

tapes, in assembly operations, therefore, will reduce the failure rate of electronic components.

Several different types of conductive tape are known for use at ambient temperatures. United States patents 3,104,985, 3,832,598 and 4,749,612 describe adhesive tapes with a coating of carbon black in a binder which is taught to dissipate electrostatic charges. Various patents also disclose multiple layer tape structures wherein one of the layers, usually a buried layer, is electrically conductive.

For example, Japanese Patent Publication J 63012681-A discloses a tape with an intermediate, antistatic polymer layer situated between a polyolefin support and a rubber adhesive layer.

European Patent Publication EP 0422919-A2 discloses a tape having a layer of conductive particles or conductive foil surrounded by binder, situated between a polymer film support and a silicone adhesive. The use of a high temperature film support, polyimide, combined with silicone binder and adhesive, is stated to yield a tape which will perform well as a wave solder masking tape at temperatures unsuitable for earlier antistatic tapes, i.e., this tape will survive in a wave solder bath for up to 5 seconds at 250°C.

Antistatic or conductive tapes which rely on the use of conductive particles require high loading of these particles for sufficient electrostatic charge neutralization. The effect of the conductive particles must be active at the surface of an otherwise insulative adhesive for static free masking of electronic assemblies. Charge transfer to the underlying layer of conductive particles requires a conductive pathway through the adhesive. However, high particulate loading often leads to loss of adhesion and undesirable transfer of contaminating material. This problem must be balanced

against the use of additional polymeric binder which may electrically insulate adjacent conductive particles and thus cause increased tribocharging while reducing transfer.

The need for balance between particle loading and polymeric binder could be avoided with an inherently conductive adhesive layer. However, there is no known disclosure of a wave solder masking tape using an inherently conductive adhesive in direct contact with the printed circuit board. Whether conductive in nature or not, most non-silicone adhesives will not survive the wave soldering process, and are thus not useful for such an application.

The current inventors have discovered an inherently conductive adhesive useful at the high temperatures required by wave solder baths. When coated onto a highly temperature resistant material bearing a specific primer thereon, a tape construction is provided which is useful for wave soldering applications without the problems of previously disclosed wave solder masking tapes.

Adhesive tapes of the invention comprise ionically charged acrylic microparticulate adhesives. Polymeric microparticles having polymer electrolytes on the surface of each polymer particle provide conductive particles which are useful as antistatic adhesive compositions. Surprisingly such adhesives exhibit high temperature resistance when placed in a wave solder bath.

Particulate adhesives are also known in the art, and have been coated on a variety of substrates and used primarily in applications requiring a low level of adhesion, e.g., repositionability. Such spheres and their use in aerosol adhesive systems having repositionable properties are disclosed in U.S. Pat. No. 3,691,140 (Silver). These microparticles are prepared by aqueous suspension polymerization of alkyl acrylate

monomers and ionic comonomer, e.g., sodium methacrylate, in the presence of an emulsifier. The use of a water-soluble, substantially oil-insoluble ionic comonomer is critical to preventing coagulation or agglomeration of the microparticles. However, particulate adhesives disclosed in the prior art have all been useful as repositionable adhesives for such applications as Post-It™ brand notes, and other removable items. Pressure-sensitive tapes made with this type of adhesive are likely to be considered unsuitable for use as antistatic tapes due to their lack of conductivity, and ease of removal. Further, acrylic adhesives are typically not considered to be heat resistant in nature.

Adhesive tapes of the invention provide antistatic tapes which are extremely effective in dissipating electrostatic charge and may be used in sensitive applications without worry about adhesive transfer.

Summary of the Invention

The invention provides a high-temperature resistant, antistatic, pressure-sensitive adhesive tape comprising a polymeric film support bearing a primer which causes a non-tribocharging, microparticulate adhesive to strongly adhere to the backing. This tape has the capacity to survive immersion in molten solder, at elevated temperature, essentially unchanged for periods of up to 5 seconds, preferably up to 20 seconds.

More specifically, the invention provides a heat-resistant anti-static pressure-sensitive adhesive tape comprising a substrate having opposing surfaces, at least one surface bearing thereon, a microparticulate adhesive having an average diameter of at least 1 micrometer, wherein the microparticles have a surface bearing thereon an ionic conductive material formed from a polymer electrolyte base polymer, and at least one ionic salt

selected from the group consisting of salts of alkali metals and salts of alkaline earth metals, said adhesive being adhered to said substrate by means of a primer composition, said primer comprising at least one phenolic resin and at least one rubbery compound,

said adhesive tape surviving in a wave-solder bath for at least 5 seconds.

According to one aspect of the present invention, there is provided a heat-resistant anti-static pressure-sensitive adhesive tape comprising a substrate having opposing surfaces, at least one of said surfaces bearing thereon an acrylic microparticulate adhesive wherein the microparticles have an average diameter of 1 to 250 micrometers, wherein the microparticles have a surface bearing thereon an ionic conductive material formed from a polymer electrolyte base polymer and at least one ionic salt selected from the group consisting of salts of alkali metals and salts of alkaline earth metals, said adhesive being bonded to said substrate by means of a primer, said primer comprising at least one phenolic resin and at least one rubbery compound, said adhesive tape being capable of surviving immersion in molten solder at 260°C for at least 5 seconds.

According to another aspect of the present invention, there is provided a heat-resistant anti-static pressure-sensitive adhesive tape described herein, wherein said at least one phenolic resin is a phenol-formaldehyde resin.

According to still another aspect of the present invention, there is provided a heat-resistant anti-static pressure-sensitive adhesive tape described herein, wherein

said primer coating comprises at least one rubbery compound selected from the group consisting of a butyl rubber, an acrylonitrile-butadiene copolymer, an acrylonitrile-butadiene-styrene copolymer, a styrene-butadiene-styrene copolymer, a styrene-ethylene butylene-styrene copolymer, polychloroprene, polybutadiene, polyisoprene, and a styrene-isoprene-styrene copolymer.

According to yet another aspect of the present invention, there is provided a heat-resistant anti-static pressure-sensitive adhesive tape described herein, wherein said primer coating comprises a mixture of acrylonitrile-butadiene-styrene copolymer and polychloroprene.

According to a further aspect of the present invention, there is provided a heat-resistant anti-static pressure-sensitive adhesive tape described herein, wherein said microparticulate adhesive comprises a polymer of monomers comprising: a) at least 70 parts of at least one alkyl (meth)acrylate or vinyl ester, b) correspondingly, up to 30 parts of at least one polar monomer, to make 100 parts monomer, and wherein said ionic conductive material comprises a polymer electrolyte formed from a polymer electrolyte base polymer selected from the group consisting of polyethylene oxide, polyphenylene oxide, polyphenylene sulfide, polyethylene sulfide, polyethyleneimine, polypropylene oxide, polybutylene oxide, polybutylene sulfide, and polybutylene imine, said polymer electrolyte base polymer is added in an amount of from 0.1 part to 10 parts per 100 parts monomer.

According to yet a further aspect of the present invention, there is provided a heat-resistant anti-static pressure-sensitive adhesive tape described herein, wherein said ionic conductive material comprises from 0.01 moles to

10 moles of at least one salt of an alkali metal or alkaline earth metal per mole of the polymer electrolyte base polymer.

According to still a further aspect of the present invention, there is provided a heat-resistant anti-static pressure-sensitive adhesive tape described herein, wherein said salt is selected from the group consisting of LiCl, $LiNO_3$, $LiCF_3SO_3$, $LiSO_4$, LiOH, KOH, NaSCN, NaI, $BaSO_3CF_3$, and NH_4OH.

According to another aspect of the present invention, there is provided a heat-resistant anti-static pressure sensitive adhesive tape described herein, wherein the at least one alkyl (meth)acrylate comprises one of more component selected from the group consisting of isooctyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, isononyl (meth)acrylate, isoamyl (meth)acrylate, isodecyl (meth)acrylate, and butyl (meth)acrylate, the at least one vinyl ester comprises one or more component selected from the group consisting of vinyl 2-ethylhexanoate, vinyl caproate, vinyl laurate, vinyl pelargonate, vinyl hexanoate, vinyl propionate, vinyl decanoate, and vinyl octanoate, and the at least one polar monomer comprises one or more component selected from the group consisting of N-vinyl-2-pyrrolidone, N-vinyl caprolactam, acrylonitrile, vinyl acrylate, diallyl phthalate, acrylic acid, methacrylic acid, itaconic acid, an hydroxyalkyl acrylate, a cyanoalkyl acrylate, an acrylamide, and a substituted acrylamide.

According to yet another aspect of the present invention, there is provided a heat-resistant anti-static pressure-sensitive adhesive tape described herein, wherein said substrate is selected from the group consisting of polyimide, polyphenylene sulfide, heat-treated non-woven

material, fiberglass, metallized polymeric film, ceramic sheet material, and metal foil.

According to yet another aspect of the present invention, there is provided a heat-resistant anti-static pressure-sensitive adhesive tape described herein, wherein said substrate is polyimide.

Preferably, the heat-resistant anti-static pressure-sensitive adhesive tape of the invention comprises an adhesive polymer of monomers comprising:

a) at least 70 parts of at least one alkyl (meth)acrylate or vinyl ester,

b) correspondingly, up to 30 parts of at least one polar monomer, to make 100 parts monomer,

and wherein said ionic conductive material comprises a polymer electrolyte formed from a polymer electrolyte base polymer, said polymer electrolyte base polymer added in an amount of from 0.1 part to 10 parts, said adhesive being adhered to said substrate by means of a primer composition, said primer comprising at least one phenolic formaldehyde resin and at least one rubbery compound selected from the group consisting of butyl rubbers, acrylonitrile-butadiene, acrylonitrile-butadiene-styrene copolymers, styrene-butadiene-styrene, styrene-ethylene butylene-styrene, polychloroprene, polybutadiene, polyisoprene, styrene-isoprene-styrene, and mixtures thereof,

said adhesive tape surviving in a wave-solder bath for at least 10 seconds.

As used herein, these terms have the following meanings.

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1. The term "polymer electrolyte base polymer" means a polymer which is capable of forming a polymeric species containing electron donating atoms which may be associated with acceptor atoms during formation of the microparticle.

2. The term "polymer electrolyte functional unit" means the group containing the electron donating species.

3. The term "microparticle" means a particle having a diameter of from 1 micrometer to 250 micrometers.

4. The term "tribocharging" means electrostatic charge generation associated with friction or separation between separable surfaces.

5. The term "droplet" means the liquid stage of the microparticles prior to the completion of polymerization.

6. The term "cavity" means a space within the walls of a droplet or microparticle when still in the suspension or dispersion medium prior to drying, and thus containing whatever medium was used.

7. The term "void" means an empty space completely within the walls of a polymerized microparticle.

8. The term "hollow" means containing at least one void or cavity.

9. The term "solid" means voids or cavity-free.

10. The term alkyl (meth)acrylate means an alkyl acrylate or alkyl methacrylate.

11. The term "modified surface" means a surface which has been subjected to a priming, coating or treatment such as chemical or radiation treatment such that the original properties of the surface have been changed.

As used herein, all parts, percents, and ratios are by weight, unless specifically stated otherwise.

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Detailed Description of the Invention

Alkyl acrylate or methacrylate monomers useful in preparing the microparticles and conductive pressure-sensitive adhesives for use in tapes of this invention are those monofunctional unsaturated acrylate or methacrylic esters of non-tertiary alkyl alcohols, the alkyl groups of which have from 4 to about 14 carbon atoms. Such acrylates are oleophilic, water emulsifiable, have limited water solubility, and as homopolymers, generally have glass transition temperatures below about -20°C. Included within this class of monomers are, for example, isooctyl acrylate, 4-methyl-2-pentyl acrylate, 2-methylbutyl acrylate, isoamyl acrylate, sec-butyl acrylate, n-butyl acrylate, 2-ethylhexyl acrylate, isodecyl methacrylate, isononyl acrylate, isodecyl acrylate, and the like, singly or in mixtures.

Preferred acrylates include isooctyl acrylate, isononyl acrylate, isoamyl acrylate, isodecyl acrylate, 2-ethylhexyl acrylate, n-butyl acrylate, sec-butyl acrylate, and mixtures thereof. Acrylate or methacrylate or other vinyl monomers which, as homopolymers, have glass transition temperatures higher than about -20°C, e.g., tert-butyl acrylate, vinyl acetate, and the like, may be utilized in conjunction with one or more of the acrylate or methacrylate monomers provided that the glass transition temperature of the resultant polymer is below about -20°C. When methacrylate monomer is the sole alkyl acrylate utilized, a crosslinking agent, infra, must be included.

Useful vinyl ester monomers are those which form homopolymers having glass transition temperatures below about 10°C. Such esters comprise 2 to 14 carbon atoms, and includes such monomers as vinyl 2-ethylhexanoate,

vinyl caprate, vinyl laurate, vinyl pelargonate, vinyl hexanoate, vinyl propionate, vinyl decanoate, vinyl octanoate, and the like.

Useful polar monomers include moderately polar monomers such as N-vinyl-2-pyrrolidone, N-vinyl caprolactam, acrylonitrile, vinyl acrylate, and diallyl phthalate, as well as strongly polar monomers such as acrylic acid, methacrylic acid, itaconic acid, hydroxyalkyl acrylates, cyanoalkyl acrylates, acrylamides, substituted acrylamides. When more than one polar monomer is used, mixtures may include monomers having similar or unlike polarities, e.g., one moderately polar and one strongly polar monomer or two monomers from one group.

The conductive microparticles and the pressure-sensitive adhesives made therefrom comprise at least 70 parts by weight of at least one alkyl (meth)acrylate ester or vinyl ester and correspondingly, up to 30 parts by weight of one or more polar monomers.

Polymer electrolyte base polymers suitable for use include polyethylene oxide, polyphenylene oxide, polyphenylene sulfide, polyethylene sulfide, polyethyleneimine, polypropylene oxide, polybutylene oxide, polybutylene sulfide, polybutylene imine, and the like. Polyethylene oxide is preferred. Useful amounts of the polymer electrolyte base polymer in microparticles of the invention range from 0.1 part to 10 parts, preferably from 1 part to 5 parts, based on 100 parts monomer weight.

The conductive properties of the polymeric microparticles may be further enhanced by the addition of ionic salts to adhesive compositions which contain the microparticles. It is believed that the ionic salts become associated with the electron donating groups present in the amorphous polymer domains.

Salts used for this purpose include salts of alkali metals, and alkaline earth metals, including but not limited to, NaI, NaSCN, $BaCF_3So_3$, NaBr, $NaClO_4$, LiCl, $LiNO_3$, $LiCF_3SO_3$, $LiSO_4$, LiOH and KOH. Lithium salts are preferred for the present invention, especially lithium nitrate.

Microparticles may be prepared by various emulsification processes, which are varied depending on whether hollow or solid microparticles are desired. Aqueous suspensions of hollow microparticles may be prepared by a "two-step" emulsification process which first involves forming a water-in-oil emulsion of an aqueous solution of polar monomer(s) in oil phase monomer, i.e., at least one (meth)acrylate or vinyl ester monomer, with a polymer electrolyte base polymer, using an emulsifier having a low hydrophilic-lipophilic balance (HLB) value. Suitable emulsifiers are those having an HLB value below about 7, preferably in the range of about 2 to about 7. Examples of such emulsifiers include sorbitan monooleate, sorbitan trioleate, and ethoxylated oleyl alcohol such as Brij™ 93, available from Atlas Chemical Industries, Inc.

Thus, in this first step, oil phase monomer(s), polymer electrolyte base polymer, emulsifier, a free radical initiator, and, optionally, a crosslinking monomer or monomers as defined below are combined, and an aqueous solution of all or a portion of the polar monomer(s) is agitated and poured into the oil phase mixture to form a water-in-oil emulsion. The polymer electrolyte base polymer may be added to either the oil phase or the water phase. A thickening agent, e.g., methyl cellulose may also be included in the aqueous phase of the water-in-oil emulsion. In the second step, a water-in-oil-in-water emulsion is formed by dispersing the water-in-oil emulsion of the first step into an aqueous phase containing an emulsifier having an HLB value above about 6. The aqueous phase may also contain any portion of the polar monomer(s) which was not added in step one. Examples of such emulsifiers include ethoxylated sorbitan monooleate, ethoxylated lauryl alcohol, and alkyl sulfates. In both steps, when an emulsifier is utilized, its concentration should be greater than its critical micelle concentration, which is herein defined as the minimum concentration of emulsifier necessary for the formation of micelles, i.e., sub-microscopic aggregations of emulsifier molecules. Critical micelle concentration is slightly different for each emulsifier, usable concentrations ranging from 1.0×10^{-4} to about 3.0 moles/liter. Additional detail concerning the preparation of water-in-oil-in-water emulsions, i.e., multiple emulsions, may be found in various literature references, e.g., Surfactant Systems: Their Chemistry, Pharmacy, & Biology, (D. Attwood and A. T. Florence, Chapman & Hall Ltd, New York City, 1983).

The final process step of this method involves the application of heat or radiation to initiate polymerization of the monomers. Useful initiators are

those which are normally suitable for free radical polymerization of acrylate or vinyl ester monomers and which are oil-soluble and of very low solubility in water. However, when the polar monomer is N-vinyl pyrrolidone, the use of benzoyl peroxide as the initiator is recommended.

Examples of such initiators include azo compounds, hydroperoxides, peroxides, and the like, and photoinitiators such as benzophenone, benzoin ethyl ether, and 2,2-dimethoxy-2-phenyl acetophenone.

Use of a water-soluble polymerization initiator causes formation of substantial amounts of latex. The extremely small particle size of latex particles renders any significant formation of latex undesirable. The initiator is generally used in an amount ranging from 0.01 percent up to 10 percent by weight of the total polymerizable composition, preferably up to 5 percent.

Aqueous suspensions of hollow conductive microparticles may also by prepared by a "one-step" emulsification process comprising aqueous suspension polymerization of at least one alkyl (meth)acrylate ester monomer or vinyl ester monomer and at least one polar monomer and a polymer electrolyte base polymer in the presence of at least one emulsifier capable of producing a water-in-oil emulsion inside the droplets which is substantially stable during emulsification and polymerization. As in the two-step emulsification process, the emulsifier is utilized in concentrations greater than its critical micelle concentration. In general, high HLB emulsifiers are required, i.e., emulsifiers having an HLB value of at least about 25, will produce stable cavity-containing droplets during the polymerization, and are suitable for use in this one-step process. Examples of such emulsifiers include alkylarylether sulfates such as sodium alkylarylether

sulfate, e.g., Triton™ W/30, available from Rohm and Haas, alkylarylpolyether sulfates such as alkylarylpoly(ethylene oxide) sulfates, preferably those having up to about 4 ethyleneoxy repeat units, and alkyl sulfates such as sodium lauryl sulfate, ammonium lauryl sulfate, triethanolamine lauryl sulfate, and sodium hexadecyl sulfate, alkyl ether sulfates such as ammonium lauryl ether sulfate, and alkylpolyether sulfates such as alkyl poly(ethylene oxide) sulfates, preferably those having up to about 4 ethyleneoxy units. Alkyl sulfates, alkyl ether sulfates, alkylarylether sulfates and mixtures thereof are preferred as they provide a maximum void volume per microparticle for a minimum amount of surfactant. Nonionic emulsifiers, e.g., Siponic™ Y-500-70 (ethoxylated oleyl alcohol), commercially available from Alcolac, Inc, and Pluronic™ P103 (a block copolymer of polypropylene oxide and polyethylene oxide commercially from BASF Corporation) can be utilized alone or in conjunction with anionic emulsifiers. Polymeric stabilizers may also be present but are not necessary.

The composition may also contain a crosslinking agent such as a multifunctional (meth)acrylate, e.g., butanediol diacrylate or hexanediol diacrylate, or other multifunctional crosslinker such as divinylbenzene. When used, crosslinker(s) is (are) added at a level of up to 1 percent, preferably up to 0.5 percent, of the total polymerizable composition.

Solid microparticles also useful in tapes of the invention may be made by a similar one-step process comprising aqueous suspension polymerization of at least one alkyl (meth)acrylate ester monomer or vinyl ester monomer, at least one polar monomer and a polymer electrolyte base polymer in the presence of an suspension stabilizer. It is not necessary to use a high HLB

emulsifier because the droplets formed need not be cavity-containing droplets. Examples of such useful lower HLB emulsifiers include ammonium lauryl sulfate such as Standapol™ A, available from Hercules and other steric or electrosteric polymeric stabilizers such as (poly)vinyl alcohol, polyacrylic acid, polymethacrylic acid, polyacrylamide, polyvinyl pyrrolidone, polyvinyl methylether, and the like.

Microsphere preparation may be modified by withholding the addition or all or part of the polymer electrolyte base polymer, and polar monomers until after polymerization of the oil phase is initiated; however, the components must be added to the polymerizing mixture prior to 100% polymer conversion.

Discrete conductive polymeric microparticles may also be prepared via suspension polymerizations disclosed in U.S. Pat. No. 3,691,140, US 4,166,152, US 4,636,432, US 4,656,218, and US 5,045,569, for preparing adhesive compositions.

The conductive microparticles are normally tacky, elastomeric, insoluble but swellable in organic solvents, and small, typically having diameters of at least 1 micrometer, preferably in the range of 1 to 250 micrometers, more preferably from about 1 to 50 micrometers. They may be solid, contain a single void, or multiple voids.

Following polymerization, an aqueous suspension of the microparticles is obtained which is stable to agglomeration or coagulation under room temperature conditions. The suspension may have non-volatile solids contents of from 10 to 50 percent by weight. Upon prolonged standing, the suspension separates into two phases, one phase being aqueous and substantially free of polymer, the other phase being an aqueous suspension of conductive microparticles. Where high HLB emulsifiers

are used the droplets have one or more cavities which, upon drying, become voids. Both phases may contain a minor portion of small latex particles. Decantation of the microparticle-rich phase provides an aqueous suspension having a non-volatile solids content on the order of about 40-50 percent which, if shaken with water, will readily redisperse.

The adhesion properties of the microparticles may be altered by addition of tackifying resin and/or plasticizer. Preferred tackifiers for use herein include hydrogenated rosin esters commercially available from companies such as Hercules Inc., under such trade names as Foral™ 65, Foral™ 85, Foral™ 105, and Tacolyn™. Other useful tackifiers include those based on t-butyl styrene. Useful plasticizers include dioctyl phthalate, 2-ethyl hexyl phosphate, tricresyl phosphate, and the like.

It is also within the scope of this invention to include various other components to the adhesives used in tapes of the invention, such as pigments, fillers, including additional conductive fillers, stabilizers, or various polymeric additives.

Tapes of the invention may be produced by coating microparticle-containing compositions of the invention onto a variety of high-temperature resistant primed substrates. Suitable substrates include polymeric films such as polyimide and poly-phenylene sulfide, heat-treated non-wovens, fiberglass, metallized polymeric film, ceramic sheet material, metal foils, etc. The substrate, or tape backing, as it is sometimes called, must be able to withstand temperatures of at least 200°C and preferably about 260°C, without degrading or releasing the adhesive from the surface.

The surface(s) bearing the microparticulate adhesive thereon are primed surfaces. Primers useful in tapes of the invention comprise at least one phenolic resin and at least one rubbery component.

Useful rubbery components include natural rubbers such as butyl rubbers, and various synthetic compounds, including but not limited to, acrylonitrile-butadiene, acrylonitrile-butadiene-styrene copolymers, styrene-butadiene-styrene, styrene-ethylene butylene-styrene, polychloroprene, polybutadiene, polyisoprene, styrene-isoprene-styrene, and mixtures thereof. Preferred primers contain mixtures of two or more rubbery compounds, such as acrylonitrile-butadiene, and polychloroprene.

Useful phenolic resins, include but are not limited to, phenol formaldehyde resin, available commercially from Union Carbide under the trade names UCAR BKR-2620, and UCAR CK-1635, novolak resins and the like, and mixtures thereof. Preferred primers contain from 40 to 120, preferably from 40 to 100 parts of phenolic resin per 100 parts of rubbery compound.

The primer may further comprise additives such as tackifying agents, antioxidants, colorants, viscosity adjusting agents, solvents and other conventional additives, which may be used in such amounts as are known in the art.

Preferred tackifying agents include hydrogenated rosin esters, include those available from Hercules under such trade names as Piccolyte™, Foral™, Pentalyn™, and the like.

Preferred primers include from 15 to 100 parts of tackifier.

Coating of the adhesive and the primer may be carried out by conventional methods such as knife coating, Meyer bar coating, and other conventional means

known in the art for coating adhesives such as use of an extrusion die.

The tape may be commercialized in roll form, or may be divided into segments for sale, such as strips or labels. Additionally, the adhesive may be provided between two substrates, e.g., the adhesive is coated onto a polyimide substrate, which may be provided on a low adhesion backsize or other easily removable surface for individual use.

These and other aspects of the invention are illustrated by the following examples which should not be viewed as limiting in scope.

Glossary

IOA	Isooctyl Acrylate
AA	Acrylic Acid
PEO	Polyethylene Oxide
PEO (750)	Acrylate terminated PEO having a MW of about 750)
BPER	70% Benzoyl Peroxide, Lucidol™ 70
PEODMA	Polyethylene Oxide Dimethacrylate [$(PEO)_9DMA$]
1,6 HDDA	1,6 Hexanediol Diacrylate
ALS	Ammonium Lauryl Sulfate
Standapol™ A	Ammonium Lauryl Sulfate from Hercules
Santivar A	Antioxidant di-tertiary amyl hydroquinone
Piccolyte™ S115	Polyterpene resin (tackifier)
Zirex™	Zinc Resinate (tackifier)

Phenolic Resins:

CK-1635	Phenol-Formaldehyde Resin, also designated CK-1635 UCAR, manufactured by Union Carbide
BKR-2620	Phenol-Formaldehyde Resin, also designated BKR-2620 UCAR, manufactured by Union Carbide.

Test Methods

Tribocharging Measurements of Antistatic Coatings

The separation of materials which have been laminated to each other causes the generation of electrical charge on the surfaces which were previously in contact. It is possible to calculate the magnitude of the electrical charge as a measure of volts generated.

Voltages were conveniently measured using a 3M 711 Charge Analyser, available from Minnesota Mining and Manufacturing Co. This equipment includes a voltage sensor, mounted in a suitable enclosure. The enclosure is provided with a digital read-out of voltage measured with respect to a stainless steel plate which is horizontally disposed and insulatively attached above the enclosure. Static charge development may be measured for adhesive tapes of the invention by laminating the tape with its adhesive face in contact with the surface of the stainless steel plate.

A strip of tape, 1.0" wide x 6.0" long is applied to the upper surface of the stainless steel plate using a 3 lb roller. The steel plate is then grounded to zero the digital display. Next, a free end of the tape is grasped and using a uniformly applied force, the tape is peeled away from the surface of the steel plate at a rate of 1.0 ft/sec. The voltage developed on the steel plate is displayed via digital read-out. After this reading is noted, the detector is zeroed by grounding the steel

plate. The tape which was previously peeled from the steel plate, is next positioned as close as possible to the steel plate without touching it. A second reading of voltage is displayed which represents the voltage residing on the surface of the tape.

It is possible to determine the voltage generated during separation of adhesive tapes of the invention from a printed circuit board by attachment of a suitable board to the surface of the stainless steel plate. Adhesive tape is then attached to the circuit board using the procedure described previously for the steel plate. Upon peeling the tape from the circuit board a voltage reading is displayed which reflects the charge generated on the surface of the circuit board. Following the process of zeroing the instrument, by grounding, the residual charge on the tape is measured by positioning the peeled tape in close proximity to the steel plate.

Tribocharging during unwind of a roll of tape is also measured using the 3M 711 Charge Analyser. In this case a length of tape approximately 1.0 ft. long is unwound from a roll of adhesive tape but not removed from it. When the unwound length is placed in close proximity to the previously grounded steel plate, a voltage reading is displayed which represents the magnitude of the charge on the tape.

Adhesive Transfer

With tapes of the current invention it is important to prevent adhesive transfer from the tape onto the surface of electronic assemblies which are subject to wave soldering. The test measures the ability of the tape to maintain a strong bond between film support and adhesive even at the elevated temperature of molten solder.

A tape sample (2.5 cm x 7.6 cm) is applied with its adhesive in contact with the surface of a 4.45 cm x 10cm section of dust-free printed circuit board (PCB). A small portion of the tape overlaps an edge portion of the PCB to facilitate subsequent removal. Pressure from a 3 lb roller assures consistent application of the tape samples. These test pieces are then positioned in a molten solder bath so that the tape is held below the surface of the solder for a desired length of time.

After removal from the solder bath, the test pieces are allowed to cool to room temperature. The free end of the tape is grasped and drawn away from the edge of the PCB. Observation is made to determine if the adhesive separates from the film support, thereby leaving an unwanted residue on the surface of the PCB.

Examples

Preparations of Microparticles

Example 1

Acrylic acid (5.4g), polyethylene oxide acrylate (PEO 750) (13.5g), PEODMA (0.15g) and 70% benzoyl peroxide (0.99g) were dissolved in isooctyl acrylate (223.2g). This solution was added to an aqueous solution of surfactant. The surfactant solution comprised Standapol™A, available from Hercules, (8.4g) dissolved in de-ionized water (360g). An emulsion of the isooctyl acrylate solution in the aqueous solution was produced by high shear mixing using an Omni mixer at setting 5. Mixing was continued until the average particle size of the oily droplets was approximately 3µm. Size was determined using an optical microscope.

The resulting oil-in-water emulsion was charged to a 1-liter resin reactor equipped with four baffles, a paddle stirrer and a suitable heat source, such as a

heating mantle. With continuous stirring at a rate of 400 rpm, the reactor and contents were heated to 60°C.

At this point the reactor was degassed with nitrogen. A reaction proceeded in the absence of oxygen. This was allowed to continue for a period of 22 hours while both temperature and stirring rate were maintained. The resulting aqueous suspension contained insoluble particles of approximately 5µm in diameter.

Example 2

Primer Composition for Polyimide Substrate

Ingred.	Parts	% solids
Butadiene/Acrylonitrile	75.00 parts	25.63
Neoprene W.	25.00 parts	8.54
Phenolic Resin BKR-2620	19.90 parts	6.8
Santivar A	3.95 parts	1.35
Piccolyte S115	49.67 parts	16.97
Zirex	49.67 parts	16.97
Phenolic Resin	69.43 parts	23.73
Methyl Ethyl Ketone	329.57 parts	
iso-Propanol	60.00 parts	
Toluene	621.00 parts	

Physical Properties

S.G. of Solids	1.065	S.G. of Solution	0.884
# per Gallon	7.370	% Comb. RHC Soln.	7.67
% Comb. RHC on Solids	34.17	% Theoretical Solids	22.45

Preparation of Primer Solution Materials

Butadiene/Acrylonitrile	75.00 parts	5.755%
Neoprene™ W.	25.00 parts	1.918%
Phenolic Resin BKR-2620	19.90 parts	1.527%
Santivar™ A	3.95 parts	0.303%
Piccolyte™ S115	49.67 parts	3.811%

Zirex™	49.67 parts	3.811%
Phenolic Resin	69.43 parts	5.328%
Methyl Ethyl Ketone	329.57 parts	25.290%
iso-Propanol	60.00 parts	4.604%
Toluene	621.00 parts	47.652%

The resins, tackifiers and antioxidant, indicated above, are dissolved in a mixed solvent comprising methyl ethyl ketone, iso-propanol and toluene to provide a primer coating for film supports. Conventional churns, equipped with stirrers, or similar equipment may be used for primer solution preparation. The solution is inspected for clarity and filtered if necessary.

Example 3

Adhesive Coating Composition

Adhesive[1]	100 parts
Lithium Nitrate	0.40 parts
Lithium Hydroxide	0.28 parts
Ammonium Hydroxide	0.60 parts
Benzotriazole[2]	0.05 parts
Thickener (QR 708)[3]	0.30 parts

[1] 40% solids suspension of Ex. 1

[2] 10% soln. in 1:1 IPA/Water

[3] 50% soln. in IPA

To 100 parts of the adhesive, prepared as previously described, was added a combination of lithium salts, to increase ionic conductivity, ammonium hydroxide for pH adjustment, benzotriazole for corrosion inhibition and a thickener to improve coating characteristics. Each of the additional ingredients was slowly stirred into the adhesive composition and thoroughly mixed prior to coating.

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Example 4

Tape Preparation Using A Primer Coating

The high temperature resistant, antistatic adhesive tape of the present invention was prepared by coating suitable film supports with a primer, which, after drying, was over-coated with a layer of the antistatic adhesive composition.

The primer composition was used as previously described or with addition of 0.5 parts of benzotriazole corrosion protection agent. A knurled roll applied a coating of primer on a 20 μm (1 mil) filled polyimide (Kapton) film. The coated film was dried at 180°F for 1 min. with a resulting primer coating weight of 0.003 gm/sq. ft.

A 75 μm (3 mil) film of adhesive was then coated over the primer layer then dried for 3 mins. at 110°C (230°F).

Examples 5-10C

Tape Properties

The electrical and adhesive properties of tapes including the invention are presented in the following table. Examples 5, C6 and C7 were tested at 10% relative humidity while samples 8, C9 and C10 were tested at 60% relative humidity.

Examples 5 and 8 are tapes of the current invention. Examples C6 and C9 comprise a commercially available tape known as 3M #92 Tape which has a silicone adhesive. Examples C7 and C10 are a commercially available tape known as 3M #1205.

Note that only the tapes of the invention exhibit both lack of adhesive transfer and low tribocharging.

Tape Identity	Conductivity Ohms/sq.	Tribocharge Volts (3M Tester #711)		Adhesive Transfer*
		Unwind	Removal from PC Board	
Ex. 5	4.8×10^{9}	3.0	35	No transfer
Ex. 6C	1.3×10^{16}	>2000	670	No transfer
Ex. C7	2.7×10^{15}	1414	680	> 30% Transfer
Ex. 8	2.7×10^{8}	2	4	No transfer
Ex. 9C	2.3×10^{14}	1311	581	No transfer
Ex. C10	5.8×10^{15}	1223	566	> 30% Transfer

* Adhesive transfer was measured at 287°C (550°F) with tape samples dipped into molten solder for 5 seconds.

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CLAIMS:

1. A heat-resistant anti-static pressure-sensitive adhesive tape comprising a substrate having opposing surfaces, at least one of said surfaces bearing thereon an acrylic microparticulate adhesive wherein the microparticles have an average diameter of 1 to 250 micrometers, wherein the microparticles have a surface bearing thereon an ionic conductive material formed from a polymer electrolyte base polymer and at least one ionic salt selected from the group consisting of salts of alkali metals and salts of alkaline earth metals, said adhesive being bonded to said substrate by means of a primer, said primer comprising at least one phenolic resin and at least one rubbery compound,

said adhesive tape being capable of surviving immersion in molten solder at 260°C for at least 5 seconds.

2. A heat-resistant anti-static pressure-sensitive adhesive tape according to claim 1, wherein said at least one phenolic resin is a phenol-formaldehyde resin.

3. A heat-resistant anti-static pressure-sensitive adhesive tape according to claim 1, wherein said primer coating comprises at least one rubbery compound selected from the group consisting of a butyl rubber, an acrylonitrile-butadiene copolymer, an acrylonitrile-butadiene-styrene copolymer, a styrene-butadiene-styrene copolymer, a styrene-ethylene butylene-styrene copolymer, polychloroprene, polybutadiene, polyisoprene, and a styrene-isoprene-styrene copolymer.

4. A heat-resistant anti-static pressure-sensitive adhesive tape according to claim 1, wherein said primer coating comprises a mixture of acrylonitrile-butadiene-styrene copolymer and polychloroprene.

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5. A heat-resistant anti-static pressure-sensitive adhesive tape according to claim 1, wherein said microparticulate adhesive comprises a polymer of monomers comprising:

a) at least 70 parts of at least one alkyl (meth)acrylate or vinyl ester,

b) correspondingly, up to 30 parts of at least one polar monomer, to make 100 parts monomer, and wherein said ionic conductive material comprises a polymer electrolyte formed from a polymer electrolyte base polymer selected from the group consisting of polyethylene oxide, polyphenylene oxide, polyphenylene sulfide, polyethylene sulfide, polyethyleneimine, polypropylene oxide, polybutylene oxide, polybutylene sulfide, and polybutylene imine, said polymer electrolyte base polymer is added in an amount of from 0.1 part to 10 parts per 100 parts monomer.

6. A heat-resistant anti-static pressure-sensitive adhesive tape according to claim 1, wherein said ionic conductive material comprises from 0.01 moles to 10 moles of at least one salt of an alkali metal or alkaline earth metal per mole of the polymer electrolyte base polymer.

7. A heat-resistant anti-static pressure-sensitive adhesive tape according to claim 6, wherein said salt is selected from the group consisting of LiCl, $LiNO_3$, $LiCF_3SO_3$, $LiSO_4$, LiOH, KOH, NaSCN, NaI, $BaSO_3CF_3$, and NH_4OH.

8. A heat-resistant anti-static pressure sensitive adhesive tape according to claim 5, wherein the at least one alkyl (meth)acrylate comprises one of more component selected from the group consisting of isooctyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, isononyl (meth)acrylate, isoamyl (meth)acrylate, isodecyl

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(meth)acrylate, and butyl (meth)acrylate, the at least one vinyl ester comprises one or more component selected from the group consisting of vinyl 2-ethylhexanoate, vinyl caproate, vinyl laurate, vinyl pelargonate, vinyl hexanoate, vinyl propionate, vinyl decanoate, and vinyl octanoate, and the at least one polar monomer comprises one or more component selected from the group consisting of N-vinyl-2-pyrrolidone, N-vinyl caprolactam, acrylonitrile, vinyl acrylate, diallyl phthalate, acrylic acid, methacrylic acid, itaconic acid, an hydroxyalkyl acrylate, a cyanoalkyl acrylate, an acrylamide, and a substituted acrylamide.

9. A heat-resistant anti-static pressure-sensitive adhesive tape according to claim 1, wherein said substrate is selected from the group consisting of polyimide, polyphenylene sulfide, heat-treated non-woven material, fiberglass, metallized polymeric film, ceramic sheet material, and metal foil.

10. A heat-resistant anti-static pressure-sensitive adhesive tape according to claim 9, wherein said substrate is polyimide.

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