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(54) Title: ELECTRICALLY CONDUCTIVE MEMBER HAVING EXPANDABLE WIRING

(57) **Abstract**: A conductive article, comprising (A) a wiring formed by drying a conductive paste containing an aqueous polyurethane dispersion and conductive particles and (B) a flexible substrate; and a method of producing a conductive article carrying an expandable wiring, comprising the steps of (1) forming a conductive paste by mixing an aqueous polyurethane dispersion with conductive particles and (2) coating and drying the conductive paste on an expandable substrate.

DESCRIPTION

ELECTRICALLY CONDUCTIVE MEMBER HAVING EXPANDABLE WIRING

FIELD OF THE INVENTION

[0001]

The present invention relates to an electrically conductive member having expandable or elastic wiring, and a method of preparing the same. In particular, the present invention relates to an electrically conductive member having an expandable wiring comprising conductive particles bonded by a polyurethane dispersion as a binder and formed on a flexible substrate.

BACKGROUND ART

[0002]

The conventional electronic devices were equipped with electronic parts on a silicone, glass or other substrate. Therefore, a metal wiring was required to have electrical resistances and frequency characteristics, and characteristics such as expandability and flexibility were required only by limited products such as flexible cables. However, for these several years, gained are growing attention to a flexible electronic device technology such as organic semiconductors and a continuous roll-to-roll process using plastic substrates. As a result, the metal wiring is increasingly required to have expandability and flexibility. The expandable flexible wiring is a material which is important in not only the field of electronic devices such as a wearable computer and a flexible device, but also the fields of medical materials such as artificial muscle or artificial skin requiring the expandability.

[0003]

The expandable flexible wiring can be prepared by making a thin film of metal on a silicone rubber substrate by a vapor deposition, a plating process, a photoresist processing or the like. However, because the thin film of metal can expand at only several percents, the thin film of metal is prepared in the form of zigzag, the form of continuous horseshoe or the form of undulation, or a wrinkly thin film of metal is prepared on a pre-stretched silicone rubber substrate. All of materials have a resistance value increased in at least double digit, when the materials are stretched at several ten percents. Both of a stable volume resistivity and a high expandability are not achieved.

In order to provide an electric device having the stable volume resistivity and the high expandability, there is proposed a method comprising complexing the carbon nanotubes (CNT) having a high aspect ratio with a polymer (for example, T. Sekitani, T. Someya: "Stretchable active-matrix organic light-emitting diode display using printable expandable conductors," Nature Materials, 8(6), 494-499, 2009 (Non-patent Document 1)) and the like.

[0004]

Thus, many of expandable flexible wirings are a system having a silicone rubber substrate and expandable conductive materials positioned and attached on the silicone rubber substrate. The silicone rubber has characteristics such as high heat-resistance and high weather-resistance, but a surface energy is low, and an intimate adherence to the different materials is weak. Non-patent Document 1 reports the problem that when the expandable wiring is greatly stretched, the electrically conductive material is peeled off from the substrate before disappearance of electrical conductivity.

As the solution thereof, the intimate adherence is improved by modifying a surface of the silicone rubber and a cover coat is equipped on a polymer conductor for the purpose of preventing the peel-off, but there is a disadvantage that the process is very complicated.

The use other binder resins (for example, a polyester resin and a polyurethane resin) is also proposed (for example, JP-A-10-162647 (Patent Document 1)). However, the electrical conductivity at the time of expansion and contraction is not considered.

[PRIOR ART DOCUMENTS]

[Patent Document]

[0005]

[Patent Document 1] JP-A-10-162647

[Non-patent Document]

[0006]

[Non-patent Document 1] T. Sekitani, T. Someya: "Stretchable active-matrix organic light-emitting diode display using printable elastic conductors," Nature Materials, 8(6), 494-499, 2009

SUMMARY OF INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0007]

An object of the invention is to provide an expandable conductive member having a wiring, which can be produced by a simple process, can be bent or folded, and can keep an electrical conductivity without breakage even if the electrically conductive member is expanded and contracted larger than conventionally expanded and contracted.

MEANS FOR SOLVING THE PROBLEMS

[0008]

The present invention provides an electrically conductive member comprising:
(A) a wiring prepared by drying a mixture of a polyurethane dispersion with electrically conductive particles; and
(B) a flexible substrate.

Further, the present invention provides a method of preparing an electrically conductive member, comprising:
mixing a polyurethane dispersion with electrically conductive particles,
applying the resultant mixture to a flexible substrate and conducting dry.

Additionally, the present invention provides an expandable wiring prepared by:
mixing a polyurethane dispersion with electrically conductive particles, and
drying the mixture.

Generally, in present invention, the wiring is expandable. Preferably, each of the substrate and the electrically conductive member is expandable. The term "expandable" means that, when a force is applied, an elongation rate is at least 5% (at least 1.05 times based on the original length), for example, at least 20% (at least 1.2 times based on the original length), preferably at least 50% (at least 1.5 times based on the original length), more preferably at least 100% (at least 2 times based on the original length), particularly preferably at least 300% (at least 4 times based on the original length); and when the force is removed, the original length is recovered.

EFFECTS OF THE INVENTION

[0009]

The electrically conductive member of the present invention can be produced by a simple process. Without the need of using the adhesive which adheres the wiring to the substrate, the electrically conductive member can be produced. The electrically conductive members can be bent, particularly can be folded with expandability, in the state that the wiring is outside or inside. Even if the electrically conductive member is folded or expanded, the electrically conductive member can keep enough electrical conductivity. Even if the electrically conductive member is folded or expanded, the wiring can keep an intimate contact with the flexible substrate. Even if the electrically conductive member of the present invention is stretched larger (for example, the elongation rate of 300%, in particular, the elongation rate of 500%) in comparison with conventional conductive members, the electrical conductivity can be kept without breakage of the electrically conductive member.

In the present invention, fine elongate particles having a major axis equal to or less than 3 micrometers and an aspect ratio of 10 to 200 can be used as the electrical conductive particles. Good electrical conductivity at the time of the expansion can be obtained by using inexpensive electrically conductive particles having a flake shape or a grain shape, without using such fine elongate particles which are expensive.

MODES FOR CARRYING OUT THE INVENTION

[0010]

The electrically conductive member of the present invention can be prepared by applying, to the flexible substrate, an electrically conductive paste comprising electrically conductive particles and a polyurethane dispersion, and drying a film of the electrically conductive paste.

[0011]

[Polyurethane Dispersion]

In present invention, the polyurethane dispersion is dried (removal of water or an organic solvent which are a dispersing medium), and works as a binder which bonds electrically conductive particles. The polyurethane dispersion is an aqueous dispersion wherein a polyurethane is dispersed in water or an oily dispersion wherein a polyurethane is dispersed in an organic solvent.

The polyurethane dispersion may be a one-liquid type or a two-liquid type, is particularly a one-liquid type. The one-liquid type can increase a content of the electrically conductive particles.

The polyurethane is a polymer prepared by reacting a polyisocyanate, a polyol and optionally a chain extender.

[0012]

The polyurethane dispersion used in the present invention is preferably a product prepared by optionally chain-extending a polyurethane which is prepared by reacting a polyol such as a polyester polyol and a polyether polyol with a polyisocyanate, in the presence of a chain extender which is a low molecular weight compound having at least two active hydrogen atoms, such as a diol and a diamine, and stably dispersing or dissolving the polyurethane in water, and the product may be as conventionally known. In addition to the aqueous dispersion wherein a polyurethane is dispersed in water, there can be used an oily dispersion wherein a polyurethane is dispersed in an organic solvent.

[0013]

The following methods can be used as a method of stably dispersing or dissolving the polyurethane resin in water to produce the aqueous polyurethane dispersion:

(1) a method (a self-emulsification type, ionic) wherein ionic groups (for example, an anionic group such as a carboxyl group or a cationic group such as a amino-based group) are introduced into a side chain or an end of the polyurethane polymer, and neutralizing a part or all of said ionic groups to give hydrophilicity, thereby dispersing or dissolving the polyurethane resin in water by self emulsification;

(2) a method (a self-emulsification type, nonionic) wherein a hydrophilic polyol such as polyethylene glycol is used as a polyol of the polyurethane main material to give a water-soluble polyurethane, thereby dispersing or dissolving the polyurethane resin in water; and

(3) a method (forced emulsification type) of dispersing the polyurethane resin in water by using an external emulsifier.

[0014]

The amount of the ionic group may be from 0.1 mol to 20 mol, for example, from 0.2 mol to 10 mol, based on one mol of polyurethane. In order to neutralize the ionic group, there can be used a base such as alkali metal hydroxides (e.g., sodium hydroxide and potassium hydroxide), alkaline-earth metal hydroxides (e.g., calcium hydroxide and magnesium hydroxide), ammonia, amines (e.g., triethylamine), acids such as inorganic acids (e.g., hydrochloric acid, sulfuric acid and nitric acid) and organic acids (in particular, carboxylic acids having 1-10 carbon atoms, e.g., acetic acid). The amount of the neutralizer may be from 0.1 to 5 parts by weight, based on 100 parts by weight of the aqueous dispersion. Generally, the amount of the neutralizer is preferably the amount of neutralizing 5 % to100 % by weight of the ionic group.

[0015]

Examples of the polyisocyanate include:

aromatic diisocyanates such as 4,4'-diphenyl methane diisocyanate, 2,4' diphenyl methane diisocyanate, 2,2'-diphenyl methane diisocyanate, 2,4-toluene diisocyanate, 2,6-toluene diisocyanate, 4,4'-diphenyl ether diisocyanate, 2,2'-diphenyl propane-4,4'-diisocyanate, 3,3'-dimethyl diphenyl methane-4,4'-diisocyanate, 4,4'-diphenyl propane diisocyanate, 1,2-phenylene diisocyanate, 1,3-phenylene diisocyanate, 1,4-phenylene diisocyanate, 1,4-naphthalene diisocyanate, 1,5-naphthalene diisocyanate and 3,3'-dimethoxydiphenyl-4,4'-diisocyanate,

aliphatic diisocyanates such as 1,6-hexamethylene diisocyanate, 1,4-tetramethylene diisocyanate and lysine diisocyanate,

araliphatic diisocyanates such as o-xylene diisocyanate, m-xylene diisocyanate, p-xylene diisocyanate and tetramethyl xylene diisocyanate, and

cycloaliphatic diisocyanate such as isophorone diisocyanate, hydrogenated toluene diisocyanate, hydrogenated xylene diisocyanate, hydrogenated diphenyl methane diisocyanate and hydrogenated tetramethyl xylene diisocyanate.

Also, so-called modified polyisocyanates such as an adduct modified product, a burette modified product, an isocyanurate modified product, a uretimine modified product, a uretdione modified product, a carbodiimide modified product of these diisocyanates can be used. Further, polyisocyanates which are called as polymeric products such as polyphenylene polymethylene polyisocyanate and crude toluene diisocyanate can be used.

These polyisocyanates can be used alone or a mixture of at least two.

[0016]

Examples of the polyol include a polyester polyol, a polycarbonate polyol and a polyether polyol. The molecular weight, which is the number-average molecular weight, of the polyol may be from 300 to 10,000, preferably from 400 to 5,000, more preferably from 400 to 2,500.

[0017]

The polyester polyol may have the number-average molecular weight of preferably from 400 to 6,000, more preferably from 600 to 3,000. The hydroxyl number of the polyester polyol is preferably from 22 to 400 mg KOH/g, more preferably from 50 to 200 mg KOH/g, most preferably from 80 to 160 mg KOH/g. The polyester polyol has the number-average OH functionality of preferably 1.5 to 6, more preferably 1.8 to 3, particularly preferably 2.

As the polyester polyol, there may be used an ester of a diol and optionally a polyol (triol or tetraol) with a dicarboxylic acid and optionally a polycarboxylic acid (tricarboxylic acid and tetracarboxylic acid), or an ester of polycarboxylic acid with a lower alcohol to produce a polyester.

[0018]

Examples of the suitable diol include ethylene glycol, butylene glycol, diethylene glycol, triethylene glycol, polyalkylene glycols (for example, polyethylene glycol), propanediol, butane-1,4-diol, hexane-1,6-diol, neopentyl glycol and neopentyl glycol hydroxypivalate ester, and last three compounds are desirable. Examples of the polyol optionally used together may include trimethylol propane, glycerol, erythritol, penta erythritol, trimethylol benzene and tris-hydroxyethyl isocyanurate.

Examples of the suitable dicarboxylic acid include phthalic acid, isophthalic acid, terephthalic acid, tetrahydrophthalic acid, hexahydrophthalic acid, cyclohexane dicarboxylic acid, adipic acid, azelaic acid, sebacic acid, glutaric acid, tetrachlorophthalic acid, maleic acid, fumaric acid, itaconic acid, malonic acid, suberic acid, 2-methylsuccinic acid, 3,3-diethylglutaric acid and 2,2-dimethylsuccinic acid. If anhydrides of these acids are present, the anhydrides also can be used. In the present invention, the anhydride is included in "acid". If the average functionality is larger than 2, a monocarboxylic acid such benzoic acid and hexane carboxylic acid can be used.

[0019]

Examples of suitable polycarbonate polyol use, as raw materials, carbonate esters such as alkylene carbonates, dialkyl carbonates and diaryl carbonates. Example of the alkylene carbonate include ethylene carbonate, trimethylene carbonate, 1,2-propylene carbonate, 1,2-butylene carbonate, 1,3-butylene carbonate and 1,2-pentylene carbonate. Examples of the dialkyl carbonates include dimethyl carbonate, diethyl carbonate and di-n-butyl carbonate. Examples of the diaryl carbonates include diphenyl carbonate. Among them, it is preferable to use ethylene carbonate, dimethyl carbonate and/or diethyl carbonate.

[0020]

Examples of the suitable polyether polyol can be prepared by reacting a starting compound which contains reactive hydrogen atoms with alkylene oxides, for example, an ethylene oxide, propylene oxide, butylene oxide, styrene oxide, tetrahydrofuran, epichlorohydrin or an alkylene oxide mixture of these, in known manners.

[0021]

The amount of the polyol may be from 20% by weight to 70% by weight, for example, from 30% by weight to 60% by weight in the synthesized polyurethane resin, but is not limited to this.

[0022]

The chain extender may be used according to necessity. The chain extender is a low-molecular weight compound having at least two active hydrogen atoms, such as diols and diamines. Specific examples of the chain extender include hydrazine, and alkylenediamines such as ethylenediamine, propylene diamine, 1,4-butylene diamine, piperazine and alkylene oxide diamine.

[0023]

Examples of the alkylene oxide diamine include:
dipropyl amine propylene glycol, dipropyl amine dipropylene glycol, dipropyl amine tripropylene glycol, dipropyl amine poly(propyleneglycol), dipropyl amine ethyleneglycol, dipropyl amine poly(ethylene glycol), dipropylamine 1,3-propane diol, dipropylamine 2-methyl 1,3-propanediol, dipropylamine 1,4-butanediol, dipropylamine 1,3-butanediol, dipropylamine 1,6-hexanediol and dipropylamine cyclohexane-1,4-dimethanol.

[0024]

Also, a compound containing two isocyanate-reactive groups and an ionic group or a latently ionic group capable of forming the ionic group can be used as the chain extender. The ionic group or the latently ionic group can be selected from a tertiary or quaternary ammonium group, a group which can be converted into such a group, a carboxyl group, a carboxylate group, a sulfone acid radical and a sulfonate group.

Examples of the suitable compound include a sodium salt of diamonosulfonates, for example, N-(2-aminoethyl)-2-aminoethanesulfonic acid and a sodium salt of N-(2-aminoethyl)-2-aminopropionic acid. Also, a mixture of these mentioned chain extender can be used.

[0025]

The amount of the chain extender is not limited and may be from 0.1% by weight to 20% by weight, for example, 0.5% by weight to 15% by weight in the polyurethane resin.

[0026]

The aqueous polyurethane dispersion contains water as a medium in addition to the polyurethane resin. The aqueous polyurethane dispersion may contain an organic solvent which does not contain the isocyanate-reactive group, for example, ethyl acetate, acetone, methyl ethyl ketone and N-methyl pyrrolidone. The amount of the organic solvent is not limited in particular, and may be from 10 parts by weight to 100 parts by weight, based on 100 parts by weight of water in polyurethane dispersions.

[0027]

Examples of a method of stably dispersing the polyurethane resin in an organic solvent in order to prepare the oily polyurethane dispersion include the following method: A method of reacting the polyurethane resin with a vinyl monomer giving a polymer insoluble in the organic solvent, in the organic solvent which contains the polyurethane resin prepared by polyaddition of a polyvalent isocyanate and a polyhydric alcohol and soluble in the organic solvent, to give the polyurethane resin dispersion wherein the polymerized polyurethane resin is dispersed in the organic solvent.

Herein, examples of the organic solvent include aliphatic hydrocarbon solvents such as n-hexane, n-pentane and n-octane; cycloaliphatic saturated hydrocarbon solvents such as cyclohexane; aromatic hydrocarbon solvents such as toluene and xylene; ketone solvents such as methyl isobutyl ketone and cyclohexanone; alcohol solvents such as ethyl alcohol and butyl alcohol; and ester solvents such as ethyl acetate and butyl acetate.

[0028]

Examples of the polyvalent isocyanate include trylene diisocyanate, isophorone diisocyanate, diphenylmethane diisocyanate, hydrogenated diphenylmethane diisocyanate, hexamethylene diisocyanate, xylylene diisocyanate, hydrogenated xylylene diisocyanate, tetramethyl xylylene diisocyanate, trimethyl hexamethylene diisocyanate and 1,5- naphthalene diisocyanate.

Examples of the polyhydric alcohol include alkylene glycols and monocyclic and polycyclic polyhydric polyols. Specific examples of the polyhydric alcohol include neopentyl glycol, ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, propylene glycol, dipropylene glycol, tripropylene glycol, tetrapropylene glycol, butanediol, pentanediol, hexanediol, heptane diol, octane diol, nonane diol, decane diol and/or derivatives thereof substituted with a alkyl group, an aralkyl groups, an alkoxy group or the like.

[0029]

Examples of the vinyl monomer include alkyl (meth) acrylate esters such as methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate and butyl (meth)acrylate; carboxyl group-containing vinyl monomers, phosphate group-containing vinyl monomers, sulfo group-containing vinyl monomers and halogen atom-containing vinyl monomers, for example, (meth)acrylic acid, itaconic acid, a crotonic acid, maleic acid, fumaric acid, tetrahydrophthalic anhydrite and monoalkyl esters of these polybasic acids, a (meth)acryloxyethyl phosphate, p-sulfostyrene, sulfoethyl acrylamide, and 2-chloroethyl ester, 2-hydroxy-3-chloropropyl ester, 2,3-dibromopropyl ester of (meth)acrylic acid or these acids; epoxy group-containing vinyl monomers such as glycidyl (meth) acrylate.

[0030]

The amount of the polyurethane resin may be about 10-70% by weight, particularly about 30-50 % by weight in the aqueous polyurethane dispersion and the oily polyurethane dispersions.

[0031]

A volume-average particle diameter of the polyurethane resin particles in the aqueous polyurethane dispersions and the oily polyurethane dispersions is preferably from 10 nm to 1,000 nm, particularly from 50 nm to 500 nm. The measurement of the average particle diameter can be conducted by a laser scattering particle size distribution measurement instrument (HPPS laser spectrometer manufactured by Malvern Instruments Ltd.).

[0032]

In present invention, the polyurethane dispersion is preferably the aqueous polyurethane dispersion. The aqueous polyurethane dispersion which can be used for present invention may be a solid content of 30 to 60% by weight, and is preferably an aqueous polyester polyurethane dispersion based on (1) a polyester urethane, and (2) water and optionally a solvent, without considering additives present in the dispersion. The aqueous polyester polyurethane dispersion may have a viscosity at 23 degrees Celsius of 30 to 5000 mPa.s and pH of 6 to 9, and the polyester polyurethane present in the aqueous dispersion may have a weight-average molecular weight of 1,500 to 100,000, preferably 2,000 to 45,000 (Mw, in terms of polystyrene standard, measured by gel permeation chromatography).

However, the aqueous polyurethane dispersions which can be used for present invention are not limited to the above-mentioned aqueous polyester polyurethane dispersions, and may be, for example, an aqueous polyether polyurethane dispersion, an aqueous polycarbonate polyurethane dispersion, and an aqueous polyurea dispersion.

[0033]

In these aqueous dispersions, a so-called anionic dispersion having ionic groups introduced into polymer main chain through a bifunctional polyol component additionally containing, for example, a sulfone acid group, a sulfonate group or a carboxyl group in the amount of 0.5 to 2 mol per one mol of polymer; a cationic dispersion having ammonium ionic groups; and a nonionic dispersion having no ionic groups.

[0034]

The polyisocyanate is preferably an aliphatic diisocyanate, a cycloaliphatic diisocyanate or a modified product thereof. The polyol is preferably a polyester polyol. An elastomer (a binder) formed from (usually provided by drying) the polyurethane dispersion of the present invention hardly makes a color change and can be extended at an elongation rate of at least 300% (at least 4 times based on original length), particularly at least 500% (at least 6 times based on original length). The elastomer containing conductive particles also can be extended at the elongation rate which is similar to the elastomer which does not contain conductive particles.

[0035]

[Electrically Conductive Particles]

The electrically conductive particles may be any of particles conventionally used as an electrical conductivity-imparting agent. Examples of the electrically conductive particles include furnace black such as Ketjen black and Vulcan; carbon black such as acetylene black, thermal black and the channel black; vapor phase growth carbon fibers such as amorphous carbon powder, natural graphite powder, artificial graphite powder, expansion graphite powder, pitch microbeads and carbon fiber; and carbon fine particles such as carbon nanotubes and carbon nanofibers. Other examples of the electrically conductive particles include metal fine powder such as Ag, Cu, Sn, Pb, Ni, Li, Bi, In and alloys thereof; metal oxide fine powder such as ZnO, SnO_2, In_2O_3, CuI and TiO_2/SnO_2/Sb-doped; metal flakes such as the Al; metal fibers such as Al, Ni and stainless steel; metal-surface-coated glass beads, and metal-plated carbon. These may be used alone or a blend of at least two.

The shape of the electrically conductive particles may be spherical, needle-shaped (oval spherical), flake (scale) or amorphous, and is not particularly limited.

[0036]

The size of the electrically conductive particle may be average particle size of about 0.1 micrometers to about 10 micrometers, for example, from about 0.5 micrometers to about 5 micrometers. When the shape of the electrically conductive particle is granular, the average particle diameter is preferably from 0.5 micrometers to 5 micrometers. When the shape of the electrically conductive particle is elongate (as in the case of carbon fiber and a metal flake), elongate fine particles (for example, nanotubes and nanorods) are preferable wherein the major axis is equal to or less than 3 micrometers, and an aspect ratio is within the range from 10 to 200. The flake may have an average particle size of 1 micrometer to 10 micrometers, and a thickness of 100 nm to 500 nm.

The electrically conductive particle (for example, metal fine power) may be coated with a dispersing agent such as higher fatty acids or natural high molecular weight compounds to prevent particles from adhering to each other.

The amount of the electrically conductive particle may be from 70 parts by weight to 99 parts by weight, for example, from 80 parts by weight to 97 parts by weight, particularly from 85 parts by weight to 95 parts by weight, based on 100 parts by weight of total of the electrically conductive particles and polyurethane (solid content).

[0037]

[Other Additives]

The electrically conductive paste comprising the electrically conductive particles and the aqueous polyurethane dispersion may contain or may not contain an additive in addition to the electrically conductive particles and the aqueous polyurethane dispersion.

Examples of such an additive include an organic electrically conductive material, a liquid electrically conductive material, a dispersing agent and a coloring agent.

The amount of the additive may be, for example, at most 50 parts by weight, particularly from 0.1 parts by weight to 30 parts by weight, based on 100 parts by weight of total of the electrically conductive particle and the polyurethane (solid content).

[0038]

[Flexible Substrate]

Examples of the flexible substrate include paper, a fabric (for example, a cotton fabric and a polyester fabric), a resin (for example, polyethylene terephthalate (PET), vinyl chloride (PVC), polyethylene and polyimide) and an elastomer (for example, an expandable polyurethane).

The flexible substrate is preferably an expandable material, particularly an elastomer. The flexible substrate is preferably an expandable polyurethane substrate (generally, an elastomer).

[0039]

The flexible substrate can be folded, and can be expanded in surface direction (in one axis or two axes).

The shape and size (an area and a thickness) of the flexible substrate are not particularly limited. The shape may be a square, a circle or the like. The dimension may be from 1 mm^2 to 300 cm^2 in area, and from 0.1 mm to 1 cm in thickness.

[0040]

The expandable polyurethane substrate may be a urethane elastomeric material without limiting a composition of the material, if it generally has an elongation rate of at least 5%. The expandable polyurethane substrate preferably has the elongation rate of at least 50%, particularly at least 200%.

The material constituting the polyurethane in the expandable polyurethane substrate may be those described for the aqueous polyurethane dispersion. The expandable polyurethane substrate is the polymer prepared by reacting a polyisocyanate and a polyol, and optionally a chain extender. The polyisocyanate may be an aliphatic diisocyanate, a cycloaliphatic diisocyanate or modified product thereof. The polyol may be a polyester polyol.

[0041]

The electrically conductive members of the present invention can be prepared by a method comprising steps of

(1) mixing an aqueous polyurethane dispersions and electrically conductive particles to give an electrically conductive paste, and

(2) applying the electrically conductive paste to a flexible substrate, and drying the electrically conductive paste.

The expandable wiring comprising the electrically conductive paste can be prepared by applying, to the flexible substrate, the electrically conductive paste comprising the electrically conductive particles and the polyurethane dispersion, and drying a film of the electrically conductive paste.

[0042]

The electrically conductive paste may be applied to the substrate in the state that the substrate (expandable substrate) is stretched (stretch wiring). The stretch may be in monoaxial direction or in biaxial directions (perpendicular to each other). The degree of the stretch may be from 5% to 500%, particularly from 10% to 300%, based on the original length (that is, length at the time of no stretch).

[0043]

In a normal wiring, the electrical conductivity remarkably decreases when the substrate is stretched. In the stretch wiring, the decrease of the electrical conductivity can be prevented when the substrate is stretched, since the degree of overlapping of the electrically conductive particles is large. The electrically conductive paste is applied on the substrate with stretching the substrate, and then the electrically conductive paste is dried. The stretch wiring can give a large stretch of the electrically conductive member and a small decrease of electrical conductivity even in the stretched state. For example, the electrically conductive paste may be applied to the substrate in the state that the substrate is stretched in one direction at stretch degree of 2 times (for example, double or triple).

[0044]

If the process of applying the electrically conductive paste on the substrate can apply the electrically conductive paste of the present invention to the substrate surface, the application process is not particularly limited. For example, the application process may be conducted by a printing method or a coating method. Examples of the printing method include a screen print process, an offset print process, an ink-jet process, a flexography process, a gravure print process, a stamping process, a dispensing process, a squeegee print process, a silk screen print, a spraying process and a brush coating process. The thickness of the applied electrically conductivity paste is, for example, 0.01 micrometers to 1,000 micrometers.

[0045]

A process of heating the electrically conductivity paste applied to the substrate may be performed, for example, in a non-oxidative atmosphere such as an inert gas atmosphere (for example, a nitrogen gas), in an air atmosphere, in a vacuum atmosphere, in an oxygen or mixture gases atmosphere or in a gas flow atmosphere. The heating temperature may be from 20 degrees Celsius to 100 degrees Celsius, and the heating time may be from 0.1 hours to 50 hours, for example, from 0.2 hours to 5 hours.

The thickness and the width of the wiring resulting after heating are not limited. The thickness of the wiring may be from 0.01 micrometers to 1,000 micrometers, for example, from 0.05 micrometers to 400 micrometers. The width of the wiring may be from 0.01 mm to 10 mm.

By application of heat, the aqueous polyurethane dispersion is converted to the polyurethane elastomer which does not contain water, giving the expandable wiring which acts as a binder bonding conductive particles.

EXAMPLES

[0046]

The following Examples and Comparative Examples are shown to specifically illustrate the present invention.

In the following Examples, all percentages are percentages by the weight unless specified otherwise.

[0047]

Example 1

Silver flake particles (AgC-239, manufactured by Fukuda Metal Foil & Powder Co., Ltd.) having an average particle size of 2-3 micrometers were intimately mixed with a bonder by a dispersion machine (ARV-310, manufacture by THINKY Co.) at 2,000 rpm for 3 minutes under vacuum to give an electrically conductive paste. The mixture ratio was 91wt % of the silver particles and 9wt% of the binder (containing water).

The used binder was an aqueous polyurethane dispersion which is Dispercoll U42 (a self-emulsification type anionic dispersion, aliphatic isocyanate/polyester polyol, polyurethane solid content: 50wt%, viscosity: about 500 mPa.s/23 degrees Celsius, pH: 7, Mw: about 20,000, average particle diameter: about 200 nm, manufactured by Beyer MaterialScience AG).

[0048]

Screen-printing of the electrically conductive paste on the substrate was performed. After printing, the electrically conductive paste was dried at 70 degrees Celsius for three hours, giving wirings having 3 mm in width, 20 mm in length and 0.36 mm in thickness. The substrate was a polyurethane (Sizes: 15 mm x 60 mm x thickness 1 mm). The volume resistivity was measured using four terminal probes (Loresta-GP MCP-T610, ASP terminals, manufacture by Mitsubishi Chemical Corp.).

The polyurethane substrate was formed from Dispercoll U42 (a product manufactured by Beyer MaterialScience AG).

The resultant electrically conductive members comprising the expandable polyurethane substrate were stretched to 20%, 40%, 60%, 80% or 600% in monoaxial direction (in the direction parallel to wirings). A volume resistivity was measured in an extended state. Results are shown in Table 1.

[0049]

Comparative Example 1

The same procedure as in Example 1 was repeated except that polychloroprene (polychloroprene water suspension, polychloroprene solid content: 58wt%, Dispercoll C74 manufactured by Beyer MaterialScience AG) was used as the binder and the substrate. Results are shown in Table 1.

Polychloroprene wiring can be stretched to the limitation of around 60%. In contrast, the polyurethane wiring can be stretched to 600% with keeping the electrical conductivity.

[0050]

Table 1

	Example 1	Com. Ex. 1
	Volume resistivity [Ω-cm]	Volume resistivity [Ω-cm]
Elongation rate [%]	Polyurethane wiring Polyurethane substrate (Ag: 91wt%)	Chloroprene wiring Chloroprene substrate (Ag: 91wt%)
0	2.8×10^{-4}	2.1×10^{-5}
20	1.3×10^{-3}	3.9×10^{-3}
40	3.9×10^{-3}	4.3×10^{-2} (Crack)
60	5.6×10^{-3}	1.3×10^{-1}
80	8.8×10^{-3}	(Breakage)
100	8.8×10^{-3}	
200	2.4×10^{-2}	
300	7.2×10^{-2}	
400	8.0×10^{-2}	
500	1.9×10^{-1}	
600	2.5	

[0051]

Example 2 (a method by double stretch wiring)

Samples were made by the following steps.

(i) A polyurethane substrate (15 mm x 60 mm) was stretched to double length. The polyurethane substrate was fixed with a tape.

(ii) An electrically conductive paste was coated on the polyurethane substrate in a width of 3 mm (a length of 50 mm and a thickness of 0.18 mm) in same procedure as in Example 1 except that the mixture ratio of preparing the electrically conductive paste was 83.1wt % of silver particles and 16.9 wt% of the binder (water-containing state)

(iii) The sample was kept in the stretched state for one hour and the electrically conductive paste was air-dried.

(iv) The stretch of the sample was released so that the original length of the polyurethane substrate was recovered. The coated conductive paste having a length of 50 mm recovered in approximately 5 minutes to a length of 30 mm (this length is taken as an initial length).

(v) The sample was dried at 70 degrees Celsius for one hour.

(vi) At the initial length of 30 mm, the stretch and the release of stretch were repeated, and a volume resistivity was measured.

The procedures of extension and release and the measurement were conducted as follows:

[0052]

Operation Number:

1. Initial resistance measurement (elongation of 0%)
2. Stretch to double length (elongation of 100%) and resistance measurement
3. Left standing with release of stretch for one hour, and resistance measurement after length recovery (elongation of 0%).
4. Stretch to triple length (elongation of 200%) and resistance measurement
5. Left standing with release of stretch for one hour, and resistance measurement

Results (double stretch wiring) are shown in Table 2.

[0053]

Example 3 (normal wiring)

The same procedure as in Example 1 was repeated except that the steps (i), (ii) and (iii) were omitted (that is, the electrically conductive paste was coated without stretching the substrate) in Example 2.

Results are shown in Table 2.

In the normal wiring, the volume resistivity (Ω-cm) largely increases at the restretch (Operation Number 4). In contrast, in the double stretch wiring, the increase of the volume resistivity is smaller.

[0054]

Table 2

Operation Number	Elongation rate	Example 4 Volume resistivity (Ω-cm) Polyurethane double stretch wiring (Ag: 83.1wt%)	Example 3 Volume resistivity (Ω-cm) Polyurethane normal wiring (Ag: 83.1wt%)
1	0%	1.2×10^{-4}	1.0×10^{-4}
2	100%	4.9×10^{-2}	8.9×10^{-2}
3	0%	2.0×10^{-3}	1.2×10^{-2}
4	200%	1.5×10^{-1}	3.0
5	0%	1.8×10^{-3}	1.0×10^{-2}

[0055]

Example 4

Using paper, cotton cloth, polyimide (PI), PET, vinyl chloride (PVC) (Dimensions of all: 15mm x 60mm x thickness 50 micrometers) as the substrate and using the conductive paste prepared in Example 1, the wiring was printed in the same manner as in Example 1.

The fold test of electrically conductive paste was conducted so that the wiring was outward and the sample was folded perpendicularly to a wiring direction. The resistance values before fold and during fold at 180 degrees were measured by two-terminal method by using a digital multimeter (Agilent 34410A, manufactured by Agilent Technologies Inc.). Ratios of resistance change before and after fold were calculated and shown in Table 3. The results using the chloroprene represents as the binder of the wiring were shown as Comparative Example 2.

It is understood that the polyurethane wiring shows a small ratio of resistance change before and after fold in comparison with the chloroprene wiring even if any type of the substrate is used.

[0056]

Table 3

		Example 4	Comparative Example 2
		Polyurethane wiring	Chloroprene wiring
		Ratio of resistance change before and after fold (Resistance value after fold/ Initial resistance value before fold)	
Subst-rate	PVC	5.6	55
	PI	2.1	4.8
	PET	2.8	17
	Paper	1.5	3.0
	Fabric	2.3	3.6

INDUSTRIAL APPLICABILITY

[0057]

The electrically conductive member of the present invention is soft and expandable and can be uses as various electronic devices such as a part of a sensor (particularly a medical sensor and a sensor for robots), a display, an artificial muscle and a computer.

CLAIMS

1. An electrically conductive member comprising:

(A) a wiring prepared by drying an electrically conductive paste comprising a polyurethane dispersion and electrically conductive particles; and

(B) a flexible substrate.

2. The electrically conductive member according to claim 1, wherein the polyurethane dispersion is an aqueous dispersion wherein a polyurethane is dispersed in water or an oily dispersion wherein a polyurethane is dispersed in an organic solvent.

3. The electrically conductive member according to claim 1 or 2, wherein the polyurethane dispersion is one-liquid type.

4. The electrically conductive member according to claim 2, wherein the aqueous polyurethane dispersion is one prepared by dispersing, in water, a self-emulsification anionic polyurethane comprising a polyester polyol and an aliphatic diisocyanate or an cycloaliphatic diisocyanate.

5. The electrically conductive member according to any one of claims 1 to 4, wherein the electrically conductive particles are metal particles.

6. The electrically conductive member according to claim 5, wherein the metal particles are silver particles.

7. The electrically conductive member according to any one of claims 1 to 6, wherein the flexible substrate (B) is paper, a fabric, a resin or an elastomer.

8. The electrically conductive member according to any one of claims 1 to 7, wherein the flexible substrate (B) is an expandable substrate.

9. The electrically conductive member according to any one of claims 1 to 7, wherein the flexible substrate (B) is an expandable polyurethane substrate.

10. The electrically conductive member according to claim 9, wherein the expandable polyurethane substrate is formed from an aqueous dispersion prepared by dispersing, in water, a self-emulsification anionic polyurethane comprising a polyester polyol and an aliphatic diisocyanate or an cycloaliphatic diisocyanate.

11. The electrically conductive member according to any one of claims 1 to 10, wherein the wiring (A) is expandable.

12. A method of preparing an electrically conductive member having an expandable wiring, comprising steps of
(1) mixing an aqueous polyurethane dispersions and conductive particles to give an electrically conductive paste, and
(2) applying the electrically conductive paste to a flexible substrate, and drying the electrically conductive paste.

13. The method according to claim 12, wherein the electrically conductive paste is

applied to the substrate in the state that the expandable substrate is stretched.

14. An expandable wiring prepared by mixing an aqueous polyurethane dispersion with electrically conductive particles, and drying a mixture of the aqueous polyurethane dispersion and the electrically conductive particles.