



(51) International Patent Classification:

H01B 1/22 (2006.01) *H05K 1/09* (2006.01)
H01B 1/24 (2006.01) *G06F 3/041* (2006.01)

(21) International Application Number:

PCT/CN2014/093259

(22) International Filing Date:

8 December 2014 (08.12.2014)

(25) Filing Language:

English

(26) Publication Language:

English

(71) Applicants: **ABLESTIK (SHANGHAI) LTD.** [CN/CN];
No. 323 Mai Gui South Road, Bonded Area, Wai Gao
Qiao, Shanghai 200131 (CN). **HENKEL ELECTRON-
ICS MATERIALS LLC** [US/US]; 14000 Jamboree Road,
Irvine, California 92606 (US).

(72) Inventors: **YU, Yuanyuan**; Room 502, No.61, Lane619,
Helong Rd., Shanghai 200131 (CN). **XIA, Bo**; 112
Pendant, Irvine, California 92620 (US). **WU, Junjun**;
PuDong New District, JinAn East Rd 88, Building 2 Room
1101, Shanghai 201204 (CN). **SHAIKH, Aziz**; 16421
Winecreek Road, San Diego, California 92127 (US).

(74) Agent: **NTD UNIVATION INTELLECTUAL PROP-
ERTY AGENCY LTD.**; Room 1802, 18th Floor, Block

A, Investment Plaza, 27 Jinrongdajie, Xicheng District,
Beijing 100033 (CN).

(81) Designated States (unless otherwise indicated, for every
kind of national protection available): AE, AG, AL, AM,
AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY,
BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM,
DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT,
HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR,
KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG,
MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM,
PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC,
SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN,
TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every
kind of regional protection available): ARIPO (BW, GH,
GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ,
TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU,
TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE,
DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU,
LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK,
SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ,
GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: ELECTRICALLY CONDUCTIVE COMPOSITIONS, PROCESS AND APPLICATIONS

(57) Abstract: Electrically conductive compositions based on electrically conductive particles, use of said electrically conductive composition in a method for preparing electrically conductive meshes and the manufactured conductive meshes, as well as a touch panel displays comprising an electrically conductive mesh on a substrate are provided.



WO 2016/090532 A1

Electrically conductive compositions, process and applications

Technical field

The present invention relates to electrically conductive compositions based on electrically conductive particles and their use in electrically conductive meshes. The electrically conductive compositions according to the present invention can be used in touch screens.

Background of the invention

Touch screen sensors detect the location of an object (e.g. a finger or a stylus) applied to the surface of a touch screen display or the location of an object positioned near the surface of a touch screen display. These sensors detect the location of the object along the surface of the display, e.g. in the plane of a flat rectangular display. Examples of touch screen sensors include capacitive sensors, resistive sensors and projected capacitive sensors. Such sensors include electrically conductive elements that overlay the display. These elements are combined with electronic components that use electrical signals to probe the elements in order to determine the location of an object near or in contact with the display.

In the field of touch screen sensors, there is a need to have improved control over the electrical properties of the touch screen sensors, without compromising optical quality of the display. In general, optical quality can be expressed in terms of visible light transmittance, haze, and sensor visibility. The quality is determined by observing the sensor as it is assembled in the touch screen by human eyes. Typically, in metal mesh touch sensor, a transparent micro patterned conductive region includes a metal mesh structure, which is used as a touch screen sensor. The geometry of the micro patterned mesh structure can be defined with parameters such as, but not limited to, the width and height of the mesh traces (sometimes referred to as "lines") used for the micro pattern, the density of the lines, and the uniformity of the density of the lines. The micro pattern usually has a line width of less than 5 μm (such fine line is not visible to human eyes), a trace height of less than 5 μm , and an open area fraction between 95% and 99.99%. The space between the mesh lines (transparent area) is usually between several hundred microns and several millimetres. In this way, very high transparency of the touch screen sensor can be achieved. The micro patterned mesh structure can be for example diamond shaped, hexagon shaped or randomly shaped. The electrical conductivity of the touch screen sensor is related to the density of the lines and the geometry of the lines.

In one form of the metal mesh technologies, first a mesh pattern consisting of grooves having a suitable width and height is formed on a substrate surface. The grooves are subsequently filled with electrically conductive composition. Any residue composition during the filling process is removed from the substrate surface during a cleaning step, followed by curing or sintering the electrically conductive composition in the mesh grooves at elevated temperature to form the solid conductive metal mesh structure. The ease of cleaning and the amount of residue composition on the surface are very important factors to determine the product yield loss due to visual defects of the surface caused by the excess residue.

The metal mesh structure can be made from highly electrically conductive metals or metal alloys consisting of micron or sub-micron sized metal particles. Silver particles are often used to form the conductive mesh lines, to ensure high conductivity of the mesh structure. However, the surface of the cured silver line usually has a high reflectance and can be detected by human eyes. This visibility compromises the optical quality of the touch screen sensor, and consequently, the display comprising said touch screen sensor, and thus is one of the key drawbacks of this technology.

In order to reduce the reflectance of the surface of the metal mesh structure, it is known to paint a dark overlay of a black ink coating on top of the conductive metal mesh lines. By doing so there will be additional process step, prolonging the overall process and therefore, increasing the process time and cost. The added step can also lead to additional yield loss.

Another solution known in the prior art is to add black dye material (e.g. carbon black or organic black dye) to the conductive composition to reduce the surface reflectance of the cured metal mesh surface. However, this may lead to non-uniform colour appearance on the film surface if the dye is not evenly distributed. Moreover, the conductivity of the cured metal mesh will decrease, due to insulating properties of the organic black dye material and lower conductivity of carbon black than silver.

Accordingly, there remains a need to provide an electrically conductive composition having the ability to be cured or sintered at relatively low temperatures, and having sufficient adhesion to the substrate, high electrical conductivity and low reflectance after curing or sintering. Furthermore, it is desired that the residue composition can be simply removed from the substrate surface outside the grooves before curing.

Summary of the invention

The present invention relates to an electrically conductive composition comprising: a) electrically conductive particles selected from first particles, having an aspect ratio equal to or greater than 1 and less than 2.0, wherein said first particles are selected from spherical

particles, faceted particles, pyramidal particles and mixtures thereof; or a mixture of said first particles and second particles, wherein said second particles are non-spherical particles having an aspect ratio of greater than 2.0; b) a resin; and c) at least one organic solvent.

The present invention further relates to a method to prepare a transparent electrically conductive mesh comprising the electrically conductive composition according to the present invention, and the obtained electrically conductive mesh structure.

Furthermore, the present invention encompasses use of the electrically conductive mesh structure in touch sensor technology.

Finally, the present invention encompasses a touch panel display comprising an electrically conductive mesh on a substrate, wherein said mesh comprises cured or sintered composition according to the present invention.

Detailed description of the invention

In the following passages the present invention is described in more detail. Each aspect so described may be combined with any other aspect or aspects unless clearly indicated to the contrary. In particular, any feature indicated as being preferred or advantageous may be combined with any other feature or features indicated as being preferred or advantageous.

In the context of the present invention, the terms used are to be construed in accordance with the following definitions, unless a context dictates otherwise.

As used herein, the singular forms “a”, “an” and “the” include both singular and plural referents unless the context clearly dictates otherwise.

The terms “comprising”, “comprises” and “comprised of” as used herein are synonymous with “including”, “includes” or “containing”, “contains”, and are inclusive or open-ended and do not exclude additional, non-recited members, elements or method steps.

The recitation of numerical end points includes all numbers and fractions subsumed within the respective ranges, as well as the recited end points.

All percentages, parts, proportions and then like mentioned herein are based on weight unless otherwise indicated.

When an amount, a concentration or other values or parameters is/are expressed in form of a range, a preferable range, or a preferable upper limit value and a preferable lower limit value, it should be understood as that any ranges obtained by combining any upper limit or preferable value with any lower limit or preferable value are specifically disclosed, without considering whether the obtained ranges are clearly mentioned in the context.

All references cited in the present specification are hereby incorporated by reference in their entirety.

Unless otherwise defined, all terms used in disclosing the invention, including technical and scientific terms, have the meaning as commonly understood by one of the ordinary skill in the art to which this invention belongs to. By means of further guidance, term definitions are included to better appreciate the teaching of the present invention.

The present invention provides an electrically conductive composition comprising: a) electrically conductive particles selected from first particles, having an aspect ratio equal to or greater than 1 and less than 2.0, wherein said first particles are selected from spherical particles, faceted particles and mixtures thereof; or a mixture of said first particles and second particles, wherein said second particles are non-spherical particles having an aspect ratio of greater than 2.0; b) a resin or a mixture of resins; and c) at least one organic solvent.

The electrically conductive composition according to the present invention provides the ability to be cured or sintered at relatively low temperature. The cured or sintered composition according to the present invention has sufficient adhesion to substrate, high electrical conductivity and low reflectance. Furthermore, the residue composition can be simply removed from the substrate surface outside the grooves before curing.

Each of the essential components of the electrically conductive composition according to the present invention are described in details below.

Electrically conductive particles

The electrically conductive composition according to the present invention comprises electrically conductive particles selected from first particles, having an aspect ratio equal to or greater than 1 and less than 2.0, wherein said first particles are selected from spherical particles, faceted particles, pyramidal particles and mixtures thereof; or a mixture of said first particles and second particles, wherein said second particles are non-spherical particles having an aspect ratio of greater than 2.0.

The particles according to the present invention are characterized by the particle shape and size. The particle size is measured by particle size analyser and the particle shape is analysed by scanning electron microscope. In short scattered laser lights from the particles are detected an array of detectors. Theoretical calculation is carried out to fit the measured distribution of scattered light intensity. During the fitting process the particle size distribution is deduced and D10, D50, D90 etc. values are calculated accordingly. The particles according to the present invention have D50 from 10nm to 500 nm and D90 below 1 μm .

By the term “aspect ratio” is meant herein an image projection attribute that describes the proportional relationship between the width of a particle and its height. The particle shapes are observed and the dimensions are measured by SEM, and average value for the aspect ratio is provided.

Electrically conductive first and second particles according to the present invention are selected from the group consisting of metals, metal alloys, metal-containing composites, non-metallic particles and mixtures thereof, preferably selected from the group consisting of silver, gold, platinum, copper, nickel, aluminium, zinc, iron, copper-nickel, silver-copper, silver-nickel, copper-aluminum, silver plated copper, silver plated glass, silver plated graphite, silver plated fibre, graphite, carbon black, carbon nanotubes and mixtures thereof, and more preferably the electrically conductive particles are silver particles.

Silver particles are preferred due to their ideal balance between conductivity and price.

First particles

In one embodiment, the electrically conductive composition according to the present invention comprises electrically conductive first particles having an aspect ratio equal to or greater than 1 and less than 2.0, the aspect ratio is measured as described above. First particles have spherical or faceted or pyramidal shape. First particles may contain only one shape from spherical or faceted or pyramidal shapes. Alternatively, first particles can also be a mixture of any of the two shapes or mixture of all three shapes.

The first particles according to the present invention preferably have an average particle size from 5 nm to 1 μ m, more preferably from 5 nm to 500 nm and even more preferably from 5 nm to 200 nm.

The width of the grooves in metal mesh application is usually less than 5 μ m for large size touch sensor, and less than 2.5 μ m for small sensor. In order to successfully fill into the grooves to form conductive line, the particle size needs to be controlled in the compositions according to the present invention to be less than the width of the grooves. Therefore, preferred size ranges are ideal for the metal mesh application. In addition, silver particles having smaller particle size have darker colour versus silver particles having larger particle size. Especially, particle size from 5 nm to 200 nm have darker colour than larger particles, which is beneficial to reduce the reflectance of the conductive mesh pattern, thus less visible to human eyes.

The composition according to the present invention comprises first particles from 5 % to 85 % by weight of the total weight of the composition, preferably from 60 % to 75 %.

If the composition comprises first particles less than 5% by weight of the total weight of the composition it may lead to low conductivity. On the other hand if the composition comprises first particles more than 85% by weight of the total weight of the composition it may lead to poor adhesion and too high viscosity, since there is not enough solvent or resin binder. Ideal range 60 - 75% by weight of the total weight of the composition provides ideal conductivity and suitable rheology and mechanical properties for the metal mesh application.

The spherical and/or faceted and/or pyramidal particles in the adhesive composition according to the present invention improve the optical properties, meaning they reduce the overall reflectance. Furthermore, the spherical and/or faceted and/or pyramidal particles improve removing of residue adhesive outside the grooves.

Second particles

In one embodiment, the electrically conductive composition according to the present invention comprises mixture of electrically conductive first particles and electrically conductive second particles, wherein said second particles are non-spherical particles with an aspect ratio of greater than 2.0.

If the conductive composition would comprise only second (non-spherical) particles, excellent conductivity could be achieved, however, the optical properties would not be ideal, because the reflectance of the composition would very high.

In order to improve balance between conductive and optical properties, particles having aspect ratio equal to or greater than 1 and less than 2 may be used in combination with non-spherical particles having aspect ratio greater than 2. Use of a mixture of non-spherical and spherical and/or faceted and/or pyramidal particles may also improve the physical properties of the cured composition, especially, the adhesion of the cured mesh structure to the substrate.

Second particles having an aspect ratio of greater than 2.0 are defined as non-spherical particles. Non-spherical particles according to the present invention can have for example flake or rod-like shape. Non-spherical particles according to the present invention preferably have an aspect ratio greater than 10.0.

Higher aspect ratio provides lower percolation threshold resulting in good conductivity. Lower percolation threshold (which means the loading of silver particles to start forming continuous contact between silver particles and possibly forming electrically continuous paths) due to the high aspect ratio is the fundamental reason for conductivity. In the present application a denser filling of the grooves also contributes to improved conductivity. At last, lower contact resistance between particles is another factor for better conductivity.

The non-spherical particles according to the present invention preferably have an average particle size from 10 nm to 2 μm , and more preferably from 10 nm to 1 μm .

The width of the grooves used in the metal mesh application according to the present invention is less than 5 μm for large size touch sensor, and less than 2.5 μm for small touch sensor. In order to successfully fill the grooves with the conductive particles and to get a conductive line, the particle size must be optimized and controlled. Therefore, selected particle size ranges of the present invention are ideal for the metal mesh application.

When conductive composition according to the present invention comprises a mixture of first particles and second particles, the second particles are present from 10 % to 85 % by weight of the total weight of the composition, preferably from 30 % to 70 % and the first particles are present from 5 to 40 % by weight of the total weight of the composition.

Selected combination of first and second particles provides ideal conductivity having comparable colour. Higher quantity of second particles is preferred. Higher the quantity of first particles in the composition is, more the conductivity of the composition will decrease. However, the colour L^* value is in reverse trend. Higher the quantity of the first particles in the composition is, darker colour is shown. Therefore, in order to provide good conductivity ($VR < 5E-05 \text{ ohm.cm}$) with comparable colour $L^* < 60 \%$, it is preferred that the composition contains higher quantity of the second particles.

In a highly preferred embodiment the weight ratio of second particles to first particles is from 6:1 to 1:2, more preferably from 3:1 to 1:1.

Resin

The electrically conductive composition according to the present invention comprises a resin or mixture of resins. The resin used in the present invention should have good solubility in the solvents used in the compositions. In addition resin should have good solvent release properties during curing or sintering at elevated temperature to ensure complete drying at relatively low temperatures. The resin used in the present invention should have good compatibility with the selected particles. The resin should also have good mechanical and rheological properties to facilitate the groove filling process. As a binder material in-between the particles, the resin should have good conductivity. Finally, resin should have good adhesion to substrates used such as polyethylene terephthalate (PET).

Preferably, resin used in the composition according to the present invention is selected from the group consisting of halogenated thermoplastic resins, phenoxy resins, polyester resins, thermoplastic polyurethanes, polyacrylates, silicones and mixtures thereof, preferably resin is selected from the group consisting of polyvinyl dichloride, polyvinyl dichloride copolymers,

phenoxy resin PKHH and mixtures thereof, and more preferably selected from the group consisting of polyvinyl dichloride and polyvinyl dichloride copolymers and mixtures thereof.

Thermoplastic resins suitable for use herein include vinyl copolymers, polyesters, polyurethanes and the like. In certain embodiments, thermoplastic resins suitable for use herein include halogenated thermoplastic resins.

In certain embodiments, composition according to the present invention comprises a polyvinyl dichloride copolymer comprising a first monomer and second monomer, wherein said first monomer is selected from the group consisting of vinyl acetate, vinyl alcohol, vinyl chloride, vinylidene chloride and styrene and said second monomer selected from the group consisting of a second vinyl acetate, a second vinyl alcohol, a second vinyl chloride, a second vinylidene chloride, a second styrene, acrylate and nitride.

In certain embodiments, the first monomer is vinylidene chloride and a second monomer is vinyl chloride, acrylonitrile or alkyl acrylate.

In certain embodiments, the first monomer is vinylidene chloride and the second monomer is vinyl chloride (e.g. polyvinylidene chloride). In certain embodiments, the first monomer is vinylidene chloride and the second monomer is alkyl acrylate.

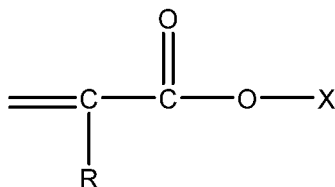
In accordance with certain embodiments, the composition according to the present invention may optionally further comprise one or more thermoset resins selected from the group consisting of epoxy-functionalized resins, acrylates, cyanate esters, silicones, oxetanes, maleimides and the mixtures thereof.

A wide variety of epoxy-functionalized resins are suitable for use herein, e.g. liquid-type epoxy resins based on bisphenol A, solid-type epoxy resins based on bisphenol A, liquid-type epoxy resins based on bisphenol F, multifunctional epoxy resins based on phenol-novolac resin, dicyclopentadiene-type resins, naphthalene-type epoxy resins and the mixtures thereof.

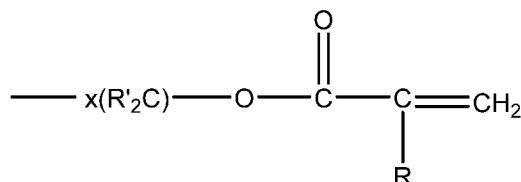
Exemplary epoxy-functionalised resins suitable for use in the present invention include diepoxide of the cycloaliphatic alcohol, hydrogenated bisphenol A, di functional cycloaliphatic glycidyl ester of hexahydrophthalic anhydride and mixtures thereof.

Suitable acrylates for use in the present invention are well known in the art.

Example of suitable (meth)acrylates to be used in the present invention include compounds having a general structure I as follows:



wherein R is H or methyl, and X is selected from (a) an alkyl group having in the range from 8 to 24 carbon atoms, or (b)



wherein R is H or methyl, R' is independently selected from H or methyl and x is integer from 2 to 6.

Preferably, (meth)acrylates are selected from the group consisting of tridecylmethacrylate, 1,6-hexanediol dimethacrylate, 1,10-decanediol diacrylate, 1,10-decanediol dimethacrylate, 1,12-dodecanediol diacrylate, 1,12-dodecanediol dimethacrylate and mixtures thereof.

Suitable cyanate esters for use in the present invention are well known in the art.

Suitable cyanate ester monomers for use in the present invention contain two or more ring forming cyanate ($-\text{O}-\text{C}=\text{N}$) groups, which cyclotrimerize to form substituted triazine rings upon heating. Because no leaving groups or volatile by-products are formed during curing of the cyanate ester monomer, the curing reaction is referred to as addition polymerization. Preferably polycyanate ester monomers that may be used in the present invention are selected from the group consisting of 1,1-bis(4-cyanatophenyl)methane, 1,1-bis(4-cyanatophenyl)ethane, 2,2-bis(4-cyanatophenyl)propane, bis(4-cyanatophenyl)-2,2-butane, 1,3-bis(2-(4-cyanatophenyl)propyl)benzene, bis(4-cyanatophenyl)ether, 4,4'-dicyanatodiphenyl, bis(4-cyanato-3,5-dimethylphenyl)methane, tris(4-cyanatophenyl)ethane, cyanated novolak, 1,3-bis(4-cyanatophenyl)-1-(1-methylethylidene)benzene, cyanated phenol-dicyclopentadiene adduct and the mixtures thereof. Polycyanate ester monomers utilized in the present invention may be readily prepared by reacting appropriate dihydric or polyhydric phenols with a cyanogen halide in the presence of an acid acceptor.

Suitable silicones for use in the present invention are well known in the art.

Suitable silicone-based adhesive formulations for use in the present invention comprise a substantially stoichiometric mixture of hydride-terminated polysiloxane(s) and vinyl-terminated polysiloxane(s). An exemplary hydride-terminated polysiloxane for use herein is a

hydride terminated polydimethylsiloxane. An exemplary vinyl-terminated polysiloxane for use herein is divinyl terminated polydimethylsiloxane.

Suitable resins for use in the present invention are also oxetane containing monomers and/or oligomers.

The electrically conductive composition according to the present invention comprises resin from 1 % to 10 % by weight of the total weight of the composition, preferably from 1 % to 8 % and more preferably from 2 % to 6 %.

Very poor adhesion is provided when the composition comprises resin less than 1% by weight of the total weight of the composition. On the other hand if the composition comprises resin more than 10% by weight of the total weight of the composition this may lead to poor conductivity, which is not ideal for the metal mesh application.

Preferably the volume ratio of the conductive particles and the resin is from 1.5 to 3.5, preferably from 2.0 to 3.0.

The volume ratio is calculated based on the weight of the resin and conductive particles added into the composition. As the density of the particles and resin is known, $\text{volume} = \text{weight}/\text{density}$.

This volume ratio range is ideal, and it meets the conductivity requirements ($< 5\text{E-}05$ ohm.cm).

Solvent

The electrically conductive composition according to the present invention comprises at least one organic solvent. A wide variety of known organic solvents can be used in the present invention. As the solvent to be used in the present invention, it is not specifically limited as long as it has good compatibility with both the resin and the conductive particles used in the composition according to the present invention. The preferred solvents should have relatively low evaporation rate at room temperature to ensure adequate processing time and relatively high evaporation rate at cure temperature to ensure sufficient curing and adequate binder shrinkage during drying.

Suitable organic solvent to be used in the present invention is preferably selected from the group consisting of dipropylene glycol methyl ether (DPM), 3-methoxy-3-methyl-1-butanol (MMB), butyl glycol acetate (BGA), diethylene glycol, ethylene glycol mono butyl ether, DBE, mixture of dimethyl glutarate and dimethyl succinate (DBE-9), mixture of dimethyl adipate and dimethyl glutarate (DBE-3), succinic acid dimethyl ester (DBE-4), glutaric acid dimethyl ester (DBE-5), dimethyl adipate (DBE-6), propylene glycol methyl acetate (PMA), butyl

carbitol (BC), butyl carbitol acetate (BCA) and mixtures thereof, more preferably selected from the group consisting of DBE-9, DPM, PMA, BC, BGA and mixtures thereof.

The electrically conductive composition according to the present invention comprises at least one organic solvent from 10 % to 50 % by weight of the total weight of the composition, preferably from 15 % to 40 %, more preferably from 20 % to 35 %. The solvent quantity is meant herein to cover total sum of the solvent and possible the co-solvent.

By the term co-solvent is meant additional solvent what is coming into the composition with other reagents, or a solvent what is for example used to provide particle dispersion.

If the quantity of the solvent and co-solvent is too high in the composition, the effective solid content will decrease in the composition, which leads to a thinner film after the cure, and therefore, providing poorer conductivity. On the other hand, if there is not enough solvent in the composition, the composition may have too high viscosity and this may lead to workability issues during the manufacturing process.

Additives

In addition to above mentioned ingredients an electrically conductive composition according to the present invention may further comprise additives from 0.01 % to 5 % by weight of the total weight of the composition, preferably from 0.05 % to 2 %.

The additives may be selected from the group consisting of a rheology modifier, a conductivity modifier, pigments and mixtures thereof.

Conductivity modifiers are highly preferred additives, especially when the composition according to the present invention only comprises the first particles. High quantity of first particles in the composition according to the present invention may in some occasions decrease the conductivity of the composition. Therefore, it is preferred to use additional conductivity modifier to improve the conductivity of the composition.

The conductivity modifier is different from the electrically conductive particles (different from first and second particles). Examples for suitable conductivity modifiers for use in the present invention are acid containing compounds such as organic diacids e.g. glutaric acid; phosphate containing organic compounds such as phosphoric acid 2-hydroxyethyl methacrylate ester; metal containing complexes and organometallic compounds such as silver acetylacetonate, palladium methacrylate.

Examples of pigments suitable for use in the present invention are pigment materials such as dyes e.g. Clariant RLSN, Clariant GLX; inorganic materials e.g. carbon black, nickel oxide,

cobalt oxide, silver oxide; organometallic compounds such as silver acetylacetonate and palladium methacrylate.

Rheology modifiers are highly preferred additives, especially, when the composition according to the present invention only comprises the first particles. Because the use of first particles in the composition increases the adhesion and/or adhesiveness of the composition, and therefore, decreases its rheology profile. Thus, adjustment of the rheology of the composition is desired.

Examples for suitable rheology modifiers for use in the present invention are for example Disperbyk-111, Disperbyk-180, Disperbyk-145, and BYK-W980 from BYK-Chemie.

In one preferred embodiment the electrically conductive composition according to the present invention contains first electrically conductive particles having an aspect ratio equal to or greater than 1 and less than 2.0, wherein said first particles are selected from spherical particles, faceted particles, pyramidal particles and mixtures thereof, a resin, and at least one organic solvent.

In another preferred embodiment the electrically conductive composition according to the present invention contains electrically conductive particles being a mixture of first particles and second particles, wherein said first particles have an aspect ratio equal to or greater than 1 and less than 2.0, wherein said first particles are selected from spherical particles, faceted particles, pyramidal particles and mixtures thereof, and said second particles are non-spherical particles having an aspect ratio of greater than 2.0 and particles, a resin, and at least one organic solvent.

In one preferred embodiment the electrically conductive composition according to the present invention contains first electrically conductive particles having an aspect ratio equal to or greater than 1 and less than 2.0, wherein said first particles are selected from spherical particles, faceted particles, pyramidal particles and mixtures thereof; a resin; and at least one organic solvent and at least one conductivity modifier.

In one preferred embodiment the electrically conductive composition according to the present invention contains first electrically conductive particles having an aspect ratio equal to or greater than 1 and less than 2.0, wherein said first particles are selected from spherical particles, faceted particles, pyramidal particles and mixtures thereof; a resin; and at least one organic solvent and at least one rheology modifier.

In one preferred embodiment the electrically conductive composition according to the present invention contains first electrically conductive particles having an aspect ratio equal to or greater than 1 and less than 2.0, wherein said first particles are selected from spherical

particles, faceted particles, pyramidal particles and mixtures thereof, a resin, at least one organic solvent, at least one conductivity modifier and at least one rheology modifier.

In another preferred embodiment the electrically conductive composition according to the present invention contains electrically conductive particles being a mixture of first particles and second particles, wherein said first particles have an aspect ratio equal to or greater than 1 and less than 2.0, wherein said first particles are selected from spherical particles, faceted particles, pyramidal particles and mixtures thereof, and said second particles are non-spherical particles having an aspect ratio of greater than 2.0 and particles, a resin, at least one organic solvent and at least one conductivity modifier.

In another preferred embodiment the electrically conductive composition according to the present invention contains electrically conductive particles being a mixture of first particles and second particles, wherein said first particles have an aspect ratio equal to or greater than 1 and less than 2.0, wherein said first particles are selected from spherical particles, faceted particles, pyramidal particles and mixtures thereof, and said second particles are non-spherical particles having an aspect ratio of greater than 2.0 and particles, a resin, at least one organic solvent, at least one conductivity modifier and at least one rheology modifier.

The electrically conductive composition according to the present invention can be prepared in several ways by mixing all ingredients together.

In one embodiment the composition is made by mixing all particles, resin, organic solvent(s) and any necessary additives using a high shear mixer until the composition is homogeneous.

The electrically conductive composition according to the present invention can be cured and/or sintered.

Normal temperature for sintering the silver particles is above 180°C. However, due to plastic substrates used in the touch sceens, sintering temperature cannot be too high because of the properties of the plastic substrate material. Therefore, low cure temperature is required. The process according to the present invention enables the cure at 150°C via selecting suitable conductive particles. The temperature can be lowered even more, if conductivity modifier is used in the composition. Standard curing or sintering profile according to the present invention is 30 minutes at 150°C.

Alternatively or in addition UV radiation can also be used in the curing process.

In another aspect, the present invention relates to a method to prepare a transparent electrically conductive mesh, comprising steps of

- forming a mesh pattern consisting of grooves having a width of greater than 0 μm and less than 5 μm on a substrate surface,

- filling the grooves with the conductive composition according to present invention,
- cleaning residue composition from the substrate surface, and
- curing or sintering said composition.

According to the present invention the mesh pattern can be formed on a substrate surface by various techniques. Suitable techniques for use herein are for example imprinting process, soft lithography method and laser patterning method. Imprinting process is the most preferred method.

Suitable substrate for use in the present invention is preferably selected from the group consisting of polyethylene terephthalate (PET), polymethyl methacrylate, polyethylene, polypropylene, polycarbonate, an epoxy resin, polyimide, polyamide, polyester or glass, preferably substrate is polyethylene terephthalate.

In the cleaning step the residue composition is removed from the substrate by wiping with a wiper and a solvent. It is important that as little residue as possible remains on the surface of the substrate after the filling and cleaning steps. Spherical and/or faceted and/or pyramidal particles are preferred over the non-spherical/flake like particles because flake particles tend to adhere more to the surface of the substrate and are more difficult to remove.

According to the present invention it is preferred to carry out said curing or sintering at a temperature less than 150 °C, or even less than 130 °C.

The composition according to the present invention improves efficacy of the cleaning step, while the excess adhesive outside the grooves is removed.

In a further aspect, the present invention relates to an electrically conductive mesh prepared by the method described above.

The electrically conductive composition according to the present invention has a volume resistivity less than 5E-5 Ohms.cm after drying and curing, preferably less than 3E-5 Ohms.cm. The volume resistivity is measured by using the standard four-wire resistance measurement method using an Agilent 34401A multimeter. Once resistance value of the sample is measured and dimension of the sample is measured, the volume resistivity of the sample can be calculated accordingly.

The electrically conductive composition according to the present invention has a reflective lightness value L^* of less than 65%, preferably less than 60%, after drying and curing as determined by CIELAB colour space measurements using Datacolor 650 instrument. L^*

stands for the lightness of the colour. For the present invention the reflected lightness from the sample surface is preferably as low as possible.

The electrically conductive mesh according to the present invention has an adhesion of at least level 5B between said mesh and the substrate, as determined by ASTM standard cross-cut tape test according to the test method D 3359-97.

An electrically conductive mesh according to the present invention is suitable for use in flexible or rigid touch panels or OLED displays or smart windows or transparent heaters or thin film photovoltaics or dye sensitized photovoltaics or organic photovoltaics or electromagnetic interference shielding or electrostatic discharge or membrane switches.

Thus it is a further aspect of the present invention to provide a touch panel display comprising an electrically conductive mesh on a substrate, wherein said mesh comprises cured or sintered composition according to the present invention.

Examples

The example compositions were prepared by mixing particles, resin, organic solvent(s) and any necessary additives using a high shear mixer until the composition is substantially homogeneous.

In all the compositions resin PVDC copolymer (Saran F-310 from DOW) and solvent DBE-9 (Sigma-Aldrich) are used. The silver to resin volume ratio is kept constant at 2.43 (also in the comparative examples). All samples are cured at 150°C for 30 min. Volume resistivity and surface L* measurements are done according to the methods described above.

Unless otherwise defined, the additives are added at given percent by weight of the total weight of the composition.

Unless otherwise defined, the substrate used in the examples is PET substrate. Adhesion of the cured mesh structure to PET substrate is tested by standard cross hatch test (test method described above).

The quantity of the residue composition on the surface of the substrate can be done by visual inspection and/or SEM.

Example 1

Compositions 1 – 6 according to the present invention:

Compo sitions	Silver particles	Volume resistivity (ohm*cm)	L*	Adhesion level	Residue after cleaning
1	spherical particles only (faceted shape, LN300 from Tokusen)	1.27E-05	62.2	5B	Less
2	spherical particles (faceted shape LN300 from Tokusen) : spherical particles (spheroidal shape SP7000-35 from Ames Goldsmith) with weight ratio of 6:1	1.2E-5	65.6	5B	Less
3	spherical particles (faceted shape LN300 from Tokusen) : spherical particles (spheroidal shape SP7000-35 from Ames Goldsmith) with weight ratio of 3:1	2.86E-05	61.8	5B	Less
4	spherical particles (faceted shape LN300 from Tokusen) with 0.2 wt.-% conductivity promoter 1 (2-Hydroxyethyl methacrylate phosphate from Sigma-Aldrich)	7.70E-06	60.7	5B	Less
5	spherical particles (faceted shape LN300 from Tokusen) with 0.2 wt.-% black dye (Clariant RLSN from Clariant)	1.27E-05	58.8	5B	Less
6	spherical particles (faceted shape LN300 from Tokusen) : spherical particles (spheroidal shape SP7000-35 from Ames Goldsmith) with weight ratio of 3:1, with 0.5%wt palladium methacrylate (AC2753 from Henkel)	4.17E-5	56.5	5B	Less

Composition 1 comprises spherical silver particles together with faceted shape particles having an average particle size about 0.3 μm . As a result the L^* value of the cured mesh structure decreases further to about 62% with acceptable volume resistivity. Moreover, it is found that there are fewer residual silver particles in the substrate after cleaning compared to comparative example 2.

Composition 2 comprises a mixture of faceted silver particles (average particle size is about 0.3 μm) and spherical silver particles (average particle size is about 100nm) with the weight ratio of 6:1. As a result the L^* value of the cured film mesh structure decreases further to about 65% with volume resistivity slightly lower than composition 3. Moreover, it is found that there are fewer residual silver particles after cleaning compared to comparative example 2.

Composition 3 comprises a mixture of spherical silver particles with faceted silver particles (average particle size is about 0.3 μm) and spherical silver particles (average particle size is about 100nm) with the weight ratio of 3:1. As a result the L^* value of the cured mesh structure decreases further to about 62% with volume resistivity still less than $5\text{E-}5$ ohm cm. Moreover, it is found that there are fewer residual silver particles after cleaning compared to comparative example 2.

Composition 4 comprises 0.2 wt.-% (of the total composition) of conductivity promoter (2-hydroxyethyl methacrylate phosphate) in addition to basic components as in composition 3 above. It is found that there is almost no change in the L^* value but the volume resistivity decreases from $1.27\text{E-}5$ to $7.7\text{E-}6$ ohm cm. Thus, the conductivity was improved while maintaining the low reflectance of the mesh structure. Moreover, it is found that there are fewer residual silver particles after cleaning compared to comparative example 2.

Composition 5 comprises 0.2 wt.-% (of the total composition) of black dye GLX from Clariant in addition to basic components of composition 6 above. It is found that L^* value decreases from 60.74% to 58.82% while the volume resistivity increases from $7.7\text{E-}6$ to $1.27\text{E-}5$ ohm cm, which is still within the application requirement. Moreover, it is found that there are fewer residual silver particles after cleaning compared to comparative example 2.

Composition 6 comprises 0.5 wt.-% (of the total composition) of palladium methacrylate in addition to basic components of composition 5. It is found that L^* decreases from about 62% to 56% and volume resistivity still within the application requirement. Moreover, it is found that there are fewer residual silver particles after cleaning compared to comparative example 2.

Example 2

Comparative example - composition 7

The binder resin polyvinylidene chloride (PVDC) Saran F-310 from Dow Chemicals is dissolved in DBE-9 solvent with a solid weight percent of 30 % (30 wt.-% PVDC and 70wt.-%

DBE-9). Subsequently, the solution is used as the master resin solution. The silver particles used are non-spherical particles (N300 from Tokusen) with an aspect ratio greater than 30 (average particles size is about 0.3 μm). The silver dispersion contains 90 wt.-% silver particles and 10 wt.-% DBE-9. Additional solvent (DBE-9) is added to adjust the final solid weight percent and viscosity accordingly. Silver to resin volume ratio is kept constant at 2.43.

Master resin solution (30%)	Additional solvent	Silver dispersion (90%wt)
14.65g	7.32g	77.67g

Compo sition	Silver particles	Volume resistivity (ohm*cm)	L*	Adhesion level	Residue after cleaning
7	non-spherical particles only	7.0 E-6	73.2	5B	a lot of residue

Though the conductivity of the cured mesh structure is sufficiently high, the reflectance is too high and makes the mesh structure greyish white and visible to the eye. It is also found that during metal mesh structure fabrication process, residual silver particles on the substrate surface need to be carefully removed and cleaned. Otherwise the residual particles will appear as visible defects and are detrimental to final product yield.

Example 3

Comparative example - compositions 8 - 11

Savinyl RLSN black dye manufactured by Clariant is added into comparative composition 7 in quantities of 0.1 wt.-%, 0.5 wt.-%, 1 wt.-% and 2 wt.-% by weight of the total weight of the composition. The measured L* and volume resistivity are listed in the following table.

Composition	% RLSN black dye	L*	Volume resistivity (ohm*cm)
8	0.1		7.0E-6
9	0.5		1.0E-5
10	1	68.8%	1.2E-5
11	2	65.5%	8.6E-5

Even though L^* value can reach about 65.5%, the volume resistivity correspondingly increases too high value $> 5E-5$ ohm.cm. Also, there is no change in the difficulty in cleaning the residue silver particles during the metal mesh structure fabrication process.

Claims

1. An electrically conductive composition comprising:
 - a) electrically conductive particles selected from
 - first particles, having an aspect ratio equal to or greater than 1 and less than 2.0, wherein said first particles are selected from spherical particles, faceted particles, pyramidal particles and mixtures thereof;
 - or
 - a mixture of said first particles and second particles, wherein said second particles are non-spherical particles having an aspect ratio of greater than 2.0;
 - b) a resin; and
 - c) at least one organic solvent.
2. The composition according to claim 1, wherein said electrically conductive particles are selected from the group consisting of metals, metal alloys, metal-containing composites, non-metallic particles and mixtures thereof; preferably selected from the group consisting of silver, gold, platinum, copper, nickel, aluminum, zinc, iron, copper-nickel, silver-copper, silver-nickel, copper-aluminum, silver plated copper, silver plated glass, silver plated graphite, silver plated fibre, graphite, carbon black, carbon nanotubes and mixtures thereof; more preferably said electrically conductive particles are silver.
3. The composition according to claim 1 or 2, wherein said spherical or faceted or pyramidal particles have an average particle size from 5 nm to 1 μm , preferably from 5 nm to 500 nm and more preferably from 5 nm to 200 nm.
4. The composition according to any one of claims 1 to 3, wherein said non-spherical particles preferably have an aspect ratio greater than 10.0.
5. The composition according to any one of claims 1 to 4, wherein said non-spherical particles have an average particle size from 10 nm to 2 μm , preferably from 10 nm to 1 μm .
6. The composition according to any one of claims 1 to 5, wherein the composition comprises

- first particles from 5 % to 85 % by weight of the total weight of the composition, preferably from 60 % to 75 %, or
 - second particles from 10% to 85 % by weight of the total weight of the composition, preferably from 30 % to 70 % and second particles from 5 % to 40 % by weight of the total weight of the composition.
7. The composition according to any one of claims 1 to 6, wherein the weight ratio of second particles to first particles is from 6:1 to 1:2, preferably from 3:1 to 1:1.
8. The composition according to any one of claims 1 to 7, wherein the resin is preferably selected from the group consisting of halogenated thermoplastic resins, phenoxy resins, polyester resins, thermoplastic polyurethanes, polyacrylates, silicones and mixtures thereof; more preferably selected from the group consisting of PVDC polymers, PVDC copolymers, phenoxy resins, polyacrylates and mixtures thereof; and most preferably selected from the group consisting of PVDC polymers and PVDC copolymers and mixtures thereof.
9. The composition according to any one of claims 1 to 8, wherein the composition comprises resin from 1 % to 10 % by weight of the total weight of the composition, preferably from 1 % to 8 % and more preferably from 2 % to 6 %.
10. The composition according to any one of claims 1 to 9, wherein a volume ratio of particles and resin is from 1.5 to 3.5, preferably from 2.0 to 3.0.
11. The composition according to any one of claims 1 to 10, wherein the at least one organic solvent is preferably selected from the group consisting of dipropylene glycol methyl ether (DPM), 3-methoxy-3-methyl-1-butanol (MMB), butyl glycol acetate (BGA), diethylene glycol, ethylene glycol mono butyl ether, DBE, DBE-9, DBE-3, DBE-4, DBE-5, DBE-6, propylene glycol methyl acetate (PMA), butyl carbitol (BC), butyl carbitol acetate (BCA) and mixtures thereof.
12. A method to prepare an electrically conductive mesh, comprising steps of
- forming a mesh pattern consisting of grooves having a width of greater than 0 μm and less than 5 μm on a substrate surface,
 - filling the grooves with the composition according to any one of claims 1 to 11,
 - cleaning residue composition from the substrate surface,

- curing or sintering said composition.

13. The method according to claim 12, wherein said curing or sintering is carried out at a temperature less than 150 °C.

14. An electrically conductive mesh prepared by the method according to claim 12 or 13.

15. A touch panel display comprising an electrically conductive mesh on a substrate, wherein said mesh comprises cured or sintered composition according to any one of claims 1 to 11.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2014/093259

A. CLASSIFICATION OF SUBJECT MATTER

H01B 1/22(2006.01)i; H01B 1/24(2006.01)i; H05K 1/09(2006.01)i; G06F 3/041(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

H01B; H05K; G06F; C09D; C09J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI;EPODOC;CNKI;CNPAT: electrical+,conduct+,particle?,powder?,aspect,ratio,resin,solvent,spherical,faceted,pyramidal, non-spherical,mesh?,touch+,panel?,display

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2006197064 A1 (PAN, A. I. ET AL.) 07 September 2006 (2006-09-07) description, paragraphs [0018]-[0022],[0029], figures 1-3	1-11
Y	US 2006197064 A1 (PAN, A. I. ET AL.) 07 September 2006 (2006-09-07) description, paragraphs [0018]-[0022],[0029], figures 1-3	12-15
Y	CN 103408993 A (SHENZHEN O-FILM TECH. CO., LTD.) 27 November 2013 (2013-11-27) description, paragraphs [0002],[0087]-[0091], figure 8	12-15
A	CN 104081468 A (MURATA MANUFACTURING CO., LTD.) 01 October 2014 (2014-10-01) the whole document	1-15
A	JP 2007188845 A (MITSUI MINING & SMELTING CO., LTD.) 26 July 2007 (2007-07-26) the whole document	1-15



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

“A” document defining the general state of the art which is not considered to be of particular relevance	“T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
“E” earlier application or patent but published on or after the international filing date	“X” document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
“L” document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	“Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
“O” document referring to an oral disclosure, use, exhibition or other means	“&” document member of the same patent family
“P” document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

23 March 2015

Date of mailing of the international search report

27 April 2015

Name and mailing address of the ISA/CN

STATE INTELLECTUAL PROPERTY OFFICE OF THE
P.R.CHINA(ISA/CN)
6,Xitucheng Rd., Jimen Bridge, Haidian District, Beijing
100088, China

Facsimile No. (86-10)62019451

Authorized officer

LAI,Fengping

Telephone No. (86-10)62414005

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/CN2014/093259

Patent document cited in search report			Publication date (day/month/year)	Patent family member(s)			Publication date (day/month/year)
US	2006197064	A1	07 September 2006	US	2010288534	A1	18 November 2010
				US	7341680	B2	11 March 2008
CN	103408993	A	27 November 2013	CN	103408993	B	26 November 2014
CN	104081468	A	01 October 2014	KR	20140107473	A	04 September 2014
				WO	2013114930	A1	08 August 2013
				US	2014329105	A1	06 November 2014
JP	2007188845	A	26 July 2007	JP	4881013	B2	22 February 2012