

TRANSPARENT CONDUCTIVE GLASS SUBSTRATE

DESCRIPTION

TECHNICAL FIELD

[0001]

The present invention relates to a transparent conductive glass substrate.

BACKGROUND ART

[0002]

A transparent conductive film obtained by sputtering conductive ceramics such as ITO (in abbreviated form of Indium Tin Oxide) on a glass substrate has been used in many electronic members now. However, since there are problems of depletion and rise in price of indium as raw material with regard to ITO, substitutes to other conductive materials have been required. In addition, a flexible substrate with flexibility has been technically craved instead of conventional solid substrates in terms of design and functionality.

[0003]

Therefore, an attempt has been made to coat a dispersion of metal nanoparticles on a film substrate or to coat a transparent conductive polymer and the like on various plastics (for example, see Patent Literature 1). ITO conventionally used in a glass substrate has no flexibility, and thus, as a substitute for this, the above conductive compositions have been recently considered. In case of plastic sheet such as a polyethylene terephthalate resin widely used, for example, "an easy adhesion layer" is generally provided for coating these conductive compositions in many cases. This layer is provided to facilitate coating, and to improve the quality and the performance as a product so as to improve adhesion between the plastic sheet and the conductive materials and to inhibit bubbles from being included.

[0004]

On the other hand, sputtering of ITO or coating of dispersion has been performed generally as a transparent conductive material on a glass substrate, and glasses in these cases are thick and molded products with no flexibility. Disclosed is a technique of coating in which a conductive polymer is coated on a glass using a slit coater (for example, see Patent Literature 2). A glass used herein has no flexibility and not be used in a curved surface. Further, this conductive polymer is used by applying on ITO as a hole-injecting layer of organic EL, and is not so much considered on the degree of adhesion with the glass substrate.

CITATION LIST

Patent Literature

[0005]

Patent Literature 1: Japanese Unexamined Patent Application Publication No. 2008-288067

Patent Literature 2: Japanese Unexamined Patent Application Publication No. 2004-139814

SUMMARY OF INVENTION

Technical Problem

[0006]

However, in the plastic substrate as disclosed in Patent Literature 1, it is needed to coat a hard coat material as a base material of a conductive layer, since there is such problem that warp, hardness, excoriation resistance and optical transmission are deteriorated contrary to bending performance and flexibility held as they are.

[0007]

The glass as disclosed in Patent Literature 2 has no flexibility and is not used in curved surface, and the conductive polymer is used by applying on ITO as a hole-injecting layer of organic EL, and is not so much considered on the degree of adhesion with the glass substrate.

[0008]

The present invention is achieved in view of the above problems, it is an objective to provide a transparent conductive glass substrate which has flexibility similar to a plastic substrate, has hardness and transparency not existing in plastics, and has adhesion capable of withstanding a use on a curved surface.

Solution to Problem

[0009]

The objective as above is performed by the following aspects (1) to (15) according to the present invention.

[0010]

(1) A transparent conductive glass substrate comprises a glass substrate and a conductive polymer layer on at least one surface of the glass substrate, wherein the glass

substrate has a thickness in the range of 0.03 to 0.7 mm and a water contact angle of the glass surface in the range of 5 to 40 degrees, wherein the conductive polymer layer has surface resistance of $1.8 \text{ G}\Omega/\text{sq.}$ or less, total light transmittance of 85 % or more, and surface pencil hardness of H or more, and wherein the transparent conductive glass has flexibility as a whole enough not to be damaged in bending test with the radius R25 mm.

[0011]

(2) In the transparent conductive glass substrate according to the above (1), the conductive polymer layer may be formed from a conductive polymer paint, the conductive polymer paint comprising a conductive polymer, a polyanion and further one or more selected from the group consisting of binders, curing agents, high conductive agent, surfactant, catalyst, and agent for improving adhesion.

[0012]

(3) In the transparent conductive glass substrate according to the above (2), the conductive polymer may comprise one or more polymer belonging one or more selected from the group consisting of polypyrroles, polythiophenes, polyacetylenes, polyphenylenes, polyphenylene vinylene, polyanilines, polyacene, polythiophene vinylene and copolymers thereof, in which an organic polymer main chain is composed of a π conjugated system.

[0013]

(4) In the transparent conductive glass substrate according to the above (2) or (3), the conductive polymer may comprise at least an anionic polymer and a polymer of thiophene or a derivative thereof.

[0014]

(5) In the transparent conductive glass substrate according to the above (4), the anionic polymer may be a polystyrene sulfonic acid and the polymer of thiophene or a derivative thereof is poly-3,4-ethylene dioxythiophene.

[0015]

(6) In the transparent conductive glass substrate according to the above (2), the polyanion may comprise one or more polymer having one or more anionic group selected from the group consisting of sulfate ester group monosubstituted, phosphoric

ester group monosubstituted, phosphoric acid group, a carboxyl group and a sulfo group.

[0016]

(7) In the transparent conductive glass substrate according to the above (2), the binder may be a binder resin, and the binder resin may be one or more thermoplastic resin and/or thermosetting resin capable of being dissolvable or mixable and dispersible with the conductive polymer.

[0017]

(8) In the transparent conductive glass substrate according to the above (2), the high conductive agent may be one or more compound selected from the group consisting of a compound having a hydroxy group, a cyclic compound containing aromatic nitrogen, a compound having two or more hydroxy groups, a compound having two or more carboxyl groups, a compound having one or more hydroxy group(s) and one or more carboxyl group(s), a compound having an amide group, a compound having an imide group, lactam compounds, a compound having glycidyl group, a silane coupling agent, DMSO (in abbreviated form of Dimethyl sulfoxide) and a water-soluble organic solvent.

[0018]

(9) In the transparent conductive glass substrate according to any one of the above (2) to (8), the conductive polymer layer may have the boiling point in the range of 50 to 200 °C and comprises 5 to 95 % by weight solvent soluble in water.

[0019]

(10) In the transparent conductive glass substrate according to any one of the above (1) to (9), the conductive polymer layer may be obtained by applying the conductive polymer paint and subsequently drying and heating and/or irradiating with infrared or ultraviolet.

[0020]

(11) In the transparent conductive glass substrate according to the above (10), the conductive polymer paint may be applied in one method selected from the group consisting of a screen printing method, a gravure printing method, a flexographic printing method, an offset printing method, inkjet printing method, a spin coating

method, a die coating method including a slit coater method, a curtain coating method, and a cap coating method.

[0021]

(Deleted)

[0022]

(13) In the transparent conductive glass substrate according to the above (1), a surface having at least the conductive polymer layer on the glass substrate may include a portion formed by etching with a mixed solution containing hydrofluoric acid.

[0023]

(14) In the transparent conductive glass substrate according to any one of the above (1) to (11) and (13), the conductive polymer layer may be cured by heating and/or irradiating infrared or ultraviolet.

[0024]

(15) In the transparent conductive glass substrate according to any one of the above (1) to (11), (13) and (14), the conductive polymer layer may be cured at a temperature of 160 °C or below.

Advantageous Effects of Invention

[0025]

According to the present invention, it is possible to provide a transparent conductive glass substrate which has flexibility similar to plastic substrate, materialize hardness and transparency not in plastics, and has adhesion to withstand use on a curved surface.

DESCRIPTION OF EMBODIMENTS

[0026]

Embodiments for carrying out the present invention (hereinafter referred to as embodiments) will be described in detail below.

[0027]

The inventors have found that, as a result of various investigations in order to achieve the above objective, by forming a conductive polymer layer on a glass substrate having a thickness of 0.03 to 0.7 mm and an arithmetic mean roughness Ra of 0.2 μm or less, a flexible transparent conductive glass substrate can be obtained to have flexibility similar to a plastic substrate and adhesion useful in a curved surface by achieving transparency and hardness not included in plastics.

[0028]

In order to achieve the objective of the present invention, first, a flexible and strong glass substrate is needed. Preferably, the thickness of the glass substrate is in the range of 0.03 to 0.7 mm and the arithmetic mean roughness Ra is 0.2 μm or less. Sufficient flexibility can not be obtained when the thickness is more than 0.7 mm, and the strength can not be exerted when the thickness is less than 0.03mm. An alkali glass, a nonionic glass, a quartz glass and the like can be employed as a material for the glass substrate, of which, a nonionic glass can be preferably used from the viewpoint of environmental load.

[0029]

Chemical etching using a fluoric acid or the like is known for a method of manufacturing a thin film glass. A mixture of at least two of fluoric acid, hydrochloric acid, sulfuric acid, nitric acid and phosphoric acid may be employed as a chemical in use for chemical etching. Among these, fluoric acid is preferably used from the viewpoint of a glass slimming. As a condition of chemical etching, desirable is a liquid temperature 25 to 55 $^{\circ}\text{C}$ for reason of the slimming accuracy.

[0030]

Since bending strength is inferior when there is a grinding mark on a surface, the glass substrate of the present invention is preferably thinned by chemical etching. In addition, a usable product can be obtained by increasing strength with conductive polymer coat when a glass grinded and thinned has an arithmetic mean roughness Ra of 0.2 μm or less, in which the wettability against conductive polymer is improved by treating the surface with fluoric acid and the like.

[0031]

In case of applying a conductive polymer, the conductive polymer is selected from among polyaniline system, polypyrrole system and polythiophene system. Polythiophene system is preferred from the viewpoints of transparency and color conductivity, and a complex made of polyethylenedioxythiophene and polystyrene sulfonic acid is most preferred.

[0032]

In this case, since conductive polymer dispersing element is dispersed in water

or disperse solvent containing water, a glass substrate of the present invention has a contact angle with water preferably in the range of 5 to 40 degrees, more preferably in the range of 5 to 7 degrees. The conductive polymer dispersion does not form clean coating film and fails to obtain adhesion strength when the contact angle exceeds 40 degrees due to crawling.

[0033]

Following examples can be given for a method of applying a conductive polymer coating on a glass substrate, namely, a screen printing method, a gravure printing method, a flexographic printing method, an offset printing method, an inkjet printing method, a spin coating method, a die coating method including a slit coater method, a curtain coating method, a cap coating method and the like.

[0034]

Since it is necessary to form a low resistance and high transparent thin film such as 10 to 1000 nm, it is preferred to apply a conductive polymer using a gravure printing method, a flexographic printing method, an inkjet printing method, a spin coating method, a die coating method and the like. Among these, since it is easy also to support a large area, a gravure printing method, a flexographic printing method, a die coating method are preferred. Furthermore, since it is easy to supply ink in a closed system such that, in a fast-drying disperse solvent contained in the conductive polymer coating, solid contents do not move and foreign substances do not occur in applying. In particular, by using a slit coater among die coating methods, it is possible to achieve coating, in which a thin film is uniformly made, disperse solvent slightly dries or variation of ink slightly occurs while applying, and loss of expensive conductive polymer paint is slightly brought.

[0035]

A slit coater is a device for applying a thin film with a slot die to move in non-contact on the substrate, and has advantages, as compared with a spin coater, such as less consumption of materials, possibly reduced cycle time, and no wraparound to a rear surface of a fringe.

[0036]

It is necessary, as described below, that a material of a wetted part is resistant to corrosion because the conductive polymer dispersion does often have strong acidic. For example, SUS metal can be employed, in particular, SUS304 is preferred in view of acid resistance.

[0037]

On coating condition of a slit coater, it is important to control a nozzle gap, a coating speed, a working distance, a discharge rate, etc. From the viewpoint of precision coating, the nozzle gap is preferably 80 to 150 μm . This range is appropriate

because the entire coated surface becomes thin when less than 80 μm , and the entire coated surface becomes thick when more than 150 μm .

[0038]

From the viewpoint of coating precision, coating speed is preferably 10 to 60 mm/sec, and desirably 20 to 50mm/sec. This range is appropriate because the entire coated surface becomes thick when less than 10 mm/sec, the entire coated surface becomes thin when more than 60 mm/sec.

[0039]

From the viewpoint of the coating precision, working distance is preferably 80 to 150 μm . This range is appropriate because the entire coated surface becomes thin when less than 80 μm , the entire coated surface becomes thick when more than 150 μm .

[0040]

From the viewpoint of thickness precision, discharge flow rate is preferably 0.05 to 0.7 ml, and desirably 0.1 to 0.55 ml. This range is appropriate from the fact that the central coating place of head becomes thick when less than 0.05 ml, coating places at both ends of the head becomes thin when more than 0.7 ml.

[0041]

Conductive polymer used in the present invention may include, in addition to polyanion for dispersing the conductive polymer in a dopant doubling as a solvent, a binder or a curing agent for solidifying or curing the conductive polymer composition, a high electrically conductive agent, a surfactant, a catalyst or an adhesion improving agent for improving conductivity.

[0042]

The conductive polymers, the polyanions, the binder resins and the high conductive agents are explained in detail below.

[0043]

(Conductive polymer)

Any conductive polymer can be employed, provided that it is an organic polymer in which a main chain thereof is comprised of a π -conjugated system. Examples include polypyrroles, polythiophenes, polyacetylenes, polyphenylenes, polyphenylene vinylenes, polyanilines, polyacenes, polythiophene vinylenes, and copolymers thereof. Polypyrroles, polythiophenes and polyanilines are preferable in view of ease of polymerization and stability in the air.

[0044]

Specific examples of such conductive polymers include polypyrrole, poly(3-methylpyrrole), poly(3-ethylpyrrole), poly(3-n-propylpyrrole), poly(3-butylpyrrole), poly(3-octylpyrrole), poly(3-decylpyrrole), poly(3-dodecylpyrrole), poly(3,4-dimethylpyrrole), poly(3,4-dibutylpyrrole),

poly(3-carboxypyrrole), poly(3-methyl-4-carboxypyrrole),
poly(3-methyl-4-carboxyethylpyrrole), poly(3-methyl-4-carboxybutylpyrrole),
poly(3-hydroxypyrrole), poly(3-methoxypyrrole), poly(3-ethoxypyrrole),
poly(3-butoxypyrrole), poly(3-hexyloxypyrrole), poly(3-methyl-4-hexyloxypyrrole),
poly(3-methyl-4-hexyloxypyrrole), poly(thiophene), poly(3-methylthiophene),
poly(3-ethylthiophene), poly(3-propylthiophene), poly(3-butylthiophene),
poly(3-hexylthiophene), poly(3-heptylthiophene), poly(3-octylthiophene),
poly(3-decylthiophene), poly(3-dodecylthiophene), poly(3-octadecylthiophene),
poly(3-bromothiophene), poly(3-chlorothiophene), poly(3-iodothiophene),
poly(3-cyanothiophene), poly(3-phenylthiophene), poly(3,4-dimethylthiophene),
poly(3,4-dibutylthiophene), poly(3-hydroxythiophene), poly(3-methoxythiophene),
poly(3-ethoxythiophene), poly(3-butoxythiophene), poly(3-hexyloxythiophene),
poly(3-heptyloxythiophene), poly(3-octyloxythiophene), poly(3-oxydecylthiophene),
poly(3-dodecyloxythiophene), poly(3-octadecyloxythiophene),
poly(3,4-dihydroxythiophene), poly(3,4-dimethoxythiophene),
poly(3,4-diethoxythiophene), poly(3,4-dipropoxythiophene),
poly(3,4-dibutoxyanthracenethiophene), poly(3,4-dihexyloxythiophene),
poly(3,4-diheptyloxythiophene), poly(3,4-dioctyloxythiophene),
poly(3,4-didecyloxythiophene), poly(3,4-didodecyloxythiophene),
poly(3,4-ethylenedioxythiophene), poly(3,4-propylenedioxythiophene),
poly(3,4-butenedioxythiophene), poly(3-methyl-4-methoxythiophene),
poly(3-methyl-4-ethoxythiophene), poly(3-carboxythiophene),
poly(3-methyl-4-carboxythiophene), poly(3-methyl-4-carboxyethylthiophene),
poly(3-methyl-4-carboxybutylthiophene), polyaniline, poly(2-methylaniline),
poly(3-isobutylaniline), poly(2-anilinesulfonic acid), poly(3-anilinesulfonic acid), and
the like.

[0045]

Among these polymers, a (co)polymer composed of one or two compound(s) selected from polypyrrole, polythiophene, poly(N-methylpyrrole), poly(3-methylthiophene), poly(3-methoxythiophene), poly(3,4-ethylenedioxythiophene) is preferably used in view of resistance value and reactivity. Further, polypyrrole and poly(3,4-ethylenedioxythiophene) are more preferable in view of increasing conductivity and improving heat resistance.

[0046]

(Polyanion)

Polyanion is a polymer which solubilizes the conductive polymer. Examples of the polyanion include a polymer having an anion group.

[0047]

Any anion group of the polyanion may be employed, provided that it is a functional group which dopes by chemical oxidation to the conductive polymers. In particular, mono-substituted sulfate ester group, mono-substituted phosphate ester group, phosphate group, carboxy group, sulfo group and the like are preferable in view of ease of manufacturing and stability. Further, sulfo group, mono-substituted sulfate ester group and carboxy group are more preferable in view of doped effects of functional groups to the conductive polymers.

[0048]

Specific examples of the polyanion include polyvinyl sulfonic acid, polystyrene sulfonic acid, polyallyl sulfonic acid, polyacryl sulfonic acid, polymethacryl sulfonic acid, poly-2-acrylamide-2-methylpropane sulfonic acid, polyisoprene sulfonic acid, polyvinyl carboxylic acid, polystyrene carboxylic acid, polyallyl carboxylic acid, polyacryl carboxylic acid, polymethacryl carboxylic acid, poly-2-acrylamide-2-methylpropane carboxylic acid, polyisoprene carboxylic acid, polyacrylic acid, and the like. These polyanions may be homopolymers or copolymers of two or more of them.

[0049]

Among these polyanions, polyvinyl sulfonic acid, polyacryl sulfonic acid, polymethacryl sulfonic acid and polystyrene sulfonic acid are preferable since they are superior in heat stability and dispersibility. In particular, polystyrene sulfonic acid is most preferable since good conductivity can be obtained.

[0050]

The degree of polymerization of polyanion is preferably in the range of 10 to 100,000 monomer units, and more preferably in the range of 50 to 10,000 monomer units in view of solubility in a solvent and conductivity.

[0051]

The content of polyanions is preferably in the range of 0.1 to 10 mol relative to the conductive polymer of 1 mol, and more preferably in the range of 1 to 7 mol. When the content of polyanions is less than 0.1 mol, the doped effects to the conductive polymers tends to weaken, and conductivity may be insufficient. In addition, dispersebility and solubility in a solvent are deteriorated and thereby it makes difficult to obtain uniform dispersion. When the content of polyanions is more than 10 mol, the content ratio of the conductive polymers is reduced and thereby it makes still difficult to obtain sufficient conductivity.

[0052]

In preparing a conductive polymer coating material, first, a polyanion component is dissolved in a solvent for dissolving it, and the solvent is sufficiently stirred and mixed after adding a precursor monomer of a conductive polymer and, as

needed, a dopant. Next, an oxidant is added dropwise into the obtained mixture to advance polymerization and obtain complexes of the polyanion and the conductive polymer. Subsequently, the oxidant, residual monomer and by-products are removed from the complexes, and the complexes after purified are dissolved in an appropriate solvent, by adding, as needed, a dopant and a binder resin, to obtain a conductive polymer coating material.

[0053]

Solvents of conductive polymer coating material are not specifically limited. Examples include polar solvents such as water, N-methyl-2-pyrrolidone, N,N-dimethylformamide, N,N-dimethylacetamide, dimethylsulfoxide, hexamethylenephosphotriamide, acetonitrile, benzonitrile and the like; phenols such as cresol, phenol, xylene and the like; alcohols such as methanol, ethanol, propanol, butanol and the like; ketones such as acetone, methyl ethyl ketone, methyl isobutyl ketone and the like; esters such as methyl acetate, ethyl acetate, propyl acetate and the like; hydrocarbons such as hexane, benzene, toluene, xylene and the like; carboxylic acids such as formic acid, acetic acid and the like; carbonate compounds such as ethylene carbonate, propylene carbonate and the like; ether compounds such as dioxane, diethylether and the like; chain ethers such as ethylene glycol alkyl ether, propylene glycol alkyl ether, polyethylene glycol alkyl ether and polypropylene glycol alkyl ether, and the like; heterocyclic compounds such as 3-methyl-2-oxazolidinone and the like; nitrile compounds such as acetonitrile, glutaronitrile, methoxyacetonitrile, propionitrile, benzonitrile and the like.

[0054]

As described below, since a transparent conductive glass substrate of the present invention is formed with a surface molded by desirably etching with hydrofluoric acid, it is preferable to contain 5 % by weight or more of a solvent soluble in water in order to improve the wettability to the surface, and it is more desirable to contain 10 % by weight or more thereof. Here, "soluble in water" means dissolving 1 g or more in 100 g of water at 25 °C.

[0055]

A complex with a conductive polymer and a polyanion as described above is mostly stable in the state of solution since the polyanion indicates water-soluble, and thus it is to select a solvent soluble in water is desirable. However, the conductive polymer can no longer be dispersed in the solution and the complex can not preserve the form of a coating when the solvent other than water becomes too much. So, solvent soluble is preferably 99 % by weight or less and desirably 95 % by weight or less.

[0056]

As described further below, it is desirable that the boiling point of the solvent is

preferably not more than 200 °C from the necessity of performing drying and curing of conductive polymer coating at a low temperature, and desirably not more than 180 °C. However, from the viewpoints of workability, leveling performance and prevention of brushing at the time of coating using a coater in a slit type, the boiling point of the solvent is preferably not less than 50 °C, and more preferably not less than 70 °C.

[0057]

(Binder)

Since the transparent conductive glass substrate of the present invention may be used for an electrode and the like of a liquid crystal display and the like, it is necessary to cure it in the presence of various organic compounds such as liquid crystal material. Therefore, the transparent conductive glass substrate must be cured at temperature of 120 °C or less taking into account evaporation of water or an organic solvent. As examples of such cross-linking, heating by irradiation of infrared rays, ultraviolet rays or the like is effective in curing. When cured by irradiating ultraviolet rays, curing can be achieved by adding a compound having a polyfunctional acrylic group, a sensitizer or a photoinitiator. When cured by heating, it is possible to immobilize the conductive polymer and also to crosslink the polyanion by adding and curing the binder. To be cured at temperatures of 120 °C or less in a relatively short time, it is recommended to use crosslinking agents such as polyfunctional epoxy compounds, polyfunctional oxetane compounds, polyfunctional aziridine compounds and the like, and further polymeric carboxylic acids or curing catalysts highly reactive with these compounds. A water soluble or emulsified polyfunctional carbodiimide can be also used.

[0058]

[Binder resin]

It is preferable that the conductive polymer coating material contains a binder resin since the environmental durability and the scratch resistance of a coating are increased and the adhesion with a substrate is improved. When the conductive polymer coating material contains a binder resin, the pencil hardness (JIS K 5400) of the conductive polymer coating formed of the conductive polymer coating material is easily made to HB or harder. Namely, the binder resin functions as a hard coat component.

[0059]

As the binder resins, they may be thermosetting resins or thermoplastic resins if they are compatible with or mixable/dispersible in the conductive polymer coating material. Examples include polyesters such as polyethylene terephthalate, polybutylene terephthalate, polyethylene naphthalate, and the like; polyimides such as polyimide, polyamideimide, and the like; polyamides such as polyamide 6, polyamide

6,6, polyamide 12, polyamide 11, and the like; fluororesins such as polyvinylidene fluoride, polyvinyl fluoride, polytetrafluoroethylene, ethylenetetrafluoroethylene copolymer, polychlorotrifluoroethylene, and the like; vinyl resins such as polyvinyl alcohol, polyvinyl ether, polyvinyl butyral, polyvinyl acetate, polyvinyl chloride, and the like; epoxy resin; oxetane resin; aziridine resin; oxazoline resin; xylene resin; aramid resin; polyimide silicone; polyurethane; polyurea; melamine resin; phenolic resin; polyether; acrylic resin; and copolymers thereof.

[0060]

These binder resins may be dissolved in organic solvents, made into solutions by imparting functional groups such as a sulfo group or carboxyl group to the resins, or dispersed in water by emulsification and the like.

[0061]

If necessary, curing agents such as a crosslinking agent, a polymerization initiator, and the like, a polymerization accelerator, a solvent, a viscosity modifier, or the like can be used in addition to the binder resins.

[0062]

Among these binder resins, any one or more of polyurethane, polyesters, acrylic resins, polyamide, polyimide, epoxy resin, oxetane resin, aziridine resin, melamine resin, and polyimide silicone is/are preferably used in view of easy mixing. Moreover, acrylic resins are suited to use for a glass substrate in view of high hardness and excellent transparency.

[0063]

Furthermore, it is preferable that the binder resin contains a liquid polymer which is cured by heat energy and/or light energy.

[0064]

Here, as the liquid polymer which is cured by heat energy, a reactive polymer and a self-crosslinkable polymer.

[0065]

The reactive polymers are polymers obtained by polymerizing monomers with a substituent such as hydroxyl group, carboxyl group, anhydride, oxetane group, glycidyl group, amino group, and the like. Specific examples of the monomers include polyfunctional alcohols such as ethylene glycol, diethylene glycol, dipropylene glycol, glycerin, and the like; carboxylic acid compounds such as malonic acid, succinic acid, glutamic acid, pimelic acid, ascorbic acid, phthalic acid, acetylsalicylic acid, adipic acid, isophthalic acid, benzoic acid, m-toluic acid, and the like; acids anhydrides such as maleic anhydride, phthalic anhydride, dodecylsuccinic anhydride, dichloromaleic anhydride, tetrachlorophthalic anhydride, tetrahydrophthalic anhydride, pyromellitic anhydride, and the like; oxetane compounds such as 3,3-dimethyloxetane,

3,3-dichloromethyloxetane, 3-methyl-3-hydroxymethyloxetane, azidomethylmethyloxetane, and the like; glycidyl ether compounds such as bisphenol A diglycidyl ether, bisphenol F diglycidyl ether, phenol novolac polyglycidyl ether, N,N-diglycidyl-p-aminophenol glycidyl ether, tetrabromobisphenol A diglycidyl ether, hydrogenated bisphenol A diglycidyl ether (i.e., 2,2-bis(4-glycidyloxycyclohexyl)propane), neopentylglycol diglycidyl ether, 1,6-hexanediol diglycidyl ether, trimethylolpropane polyglycidyl ether, diglycidyl hexahydrophthalate, propyleneglycol diglycidyl ether, tripropyleneglycol diglycidyl ether, polypropyleneglycol diglycidyl ether, epoxy-modified fatty acid, diethyleneglycol diglycidyl ether, polyethyleneglycol diglycidyl ether, glycerol polyglycidyl ether, diglycerol polyglycidyl ether, polyglycerol polyglycidyl ether, sorbitol-based polyglycidyl ether, ethyleneoxidelauryl alcohol glycidyl ether, ethyleneoxidephenol glycidyl ether, glycidyl ether adipate, and the like; glycidyl amine compounds such as N,N-diglycidylaniline, tetraglycidyl-diaminodiphenylmethane, N,N,N,N-tetraglycidyl-m-xylylenediamine, triglycidyl isocyanurate, N,N-diglycidyl-5,5-dialkylhydantoin, and the like; amine compounds such as diethylenetriamine, triethylenetetramine, dimethylaminopropylamine, N-aminoethylpiperazine, benzyldimethylamine, tris(dimethylaminomethyl)phenol, DHP(in abbreviated form of Dihydropyran)30-tri(2-ethylhexoate), metaphenylenediamine, diaminodiphenylmethane, diaminodiphenyl sulfone, dicyandiamide, boron trifluoride, monoethylamine, methanedianiline, xylenediamine, ethylmethyylimidazole and the like; and glycidyl compounds based on epichlorohydrin of bisphenol A among compounds containing two or more oxirane rings in one molecule, or analogs thereof.

[0066]

In the reactive polymers, crosslinking agents, catalysts, cationic polymerization initiators as described later may be used together with. The crosslinking agents include melamine resin, epoxy resin, metal oxides, and the like. Examples of the metal oxides, basic metal compounds such as $\text{Al}(\text{OH})_3$, $\text{Al}(\text{OOC}-\text{CH}_3)_2(\text{OOCH})$, $\text{Al}(\text{OOC}-\text{CH}_3)_3$, $\text{ZrO}(\text{OCH}_3)_2$, $\text{Mg}(\text{OOC}-\text{CH}_3)_2$, $\text{Ca}(\text{OH})_2$, $\text{Ba}(\text{OH})_2$, and the like can be properly used.

[0067]

The self-crosslinkable polymers are polymers that self-crosslink with each other via functional groups due to heating, and include, for example, those containing glycidyl and carboxy groups or those containing both N-methylol and carboxy groups, and the like.

[0068]

The liquid polymer which is cured by optical energy include oligomers or

prepolymers such as polyester, epoxy resin, oxetane resin, polyacryl, polyurethane, polyimide, polyamide, polyamideimide, polyimide silicone, and the like.

[0069]

Examples of monomer units constituting the liquid polymer which is cured by optical energy include monofunctional monomers and polyfunctional monomers of acrylates such as bisphenol A ethylene oxide-modified diacrylate, dipentaerythritol hexa(penta) acrylate, dipentaerythritol monohydroxy pentaacrylate, dipropylene glycol diacrylate, trimethylolpropane triacrylate, glycerin propoxytriacylate, 4-hydroxybutyl acrylate, 1,6-hexanediol diacrylate, 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate, isobornyl acrylate, polyethylene glycol diacrylate, pentaerythritol triacrylate, tetrahydrofurfuryl acrylate, trimethylolpropane triacrylate, tripropylene glycol diacrylate, and the like; methacrylates such as tetraethylene glycol dimethacrylate, alkyl methacrylate, allyl methacrylate, 1,3-butylene glycol dimethacrylate, n-butyl methacrylate, benzyl methacrylate, cyclohexyl methacrylate, diethylene glycol dimethacrylate, 2-ethylhexyl methacrylate, glycidyl methacrylate, 1,6-hexanediol dimethacrylate, 2-hydroxyethyl methacrylate, isobornyl methacrylate, lauryl methacrylate, phenoxyethyl methacrylate, t-butyl methacrylate, tetrahydrofurfuryl methacrylate, trimethylolpropane trimethacrylate, and the like; glycidyl ethers such as allylglycidyl ether, butylglycidyl ether, higher alcohol glycidyl ether, 1,6-hexanediolglycidyl ether, phenylglycidyl ether, stearyl glycidyl ether, and the like; acryl(methacryl)amides such as diacetoneacrylamide, N,N-dimethylacrylamide, dimethylaminopropylacrylamide, dimethylaminopropylmethacrylamide, methacrylamide, N-methylolacrylamide, N,N-dimethylacrylamide, acryloylmorpholine, N-vinylformamide, N-methylacrylamide, N-isopropylacrylamide, N-t-butylacrylamide, N-phenylacrylamide, acryloylpiperidine, 2-hydroxyethyl acrylamide, and the like; vinyl ethers such as 2-chloroethylvinyl ether, cyclohexylvinyl ether, ethylvinyl ether, hydroxybutylvinyl ether, isobutylvinyl ether, triethyleneglycol vinyl ether, and the like; vinyl carboxylates such as vinyl butyrate, vinyl monochloroacetate, vinyl pivalate, and the like.

[0070]

The liquid polymer which is cured by optical energy is cured with a photo polymerization initiator. The photo polymerization initiators include acetophenones, benzophenones, Michler's benzoylbenzoates, α -amiloxim esters, tetramethylthiuram monosulphides, thioxanthenes, and the like. In addition, photosensitizers such as n-butylamine, triethylamine, tri-n-butylphosphine, and the like may be mixed.

[0071]

Cationic polymerization initiators include aryl diazonium salts, diaryl halonium salts, triphenyl sulfonium salts, silanol/aluminum chelate, α -sulfonyloxyketones, and the

like.

[0072]

The content of the binder resin is 1 to 1000 % by weight relative to 100 % by weight in total of the conductive polymer and the polyanion, and preferably 10 to 400 % by weight. When the content of the binder resin is less than 1 % by weight, the durability of the conductive polymer layer is sometimes insufficient. When it is more than 1000 % by weight, the conductivity can not be sufficiently obtained due to the amount of conductive polymer decreased in the conductive polymer layer.

[0073]

(High conductive agent)

High conductive agent is a component to improve the conductivity of the conductive coating film formed of a conductive polymer solution.

[0074]

Specifically, the high conductive agent is at least one compound selected from the group consisting of nitrogen-containing aromatic cyclic compound, hydroxy group-containing compound with two or more hydroxy groups, compound with two or more carboxy groups, compound with one or more hydroxy group(s) and one or more carboxy group(s), compound with amide group, compound with imide group, lactam compound, compound with glycidyl group, silane coupling agent, DMSO (in abbreviated form of Dimethyl Sulfoxide), and water-soluble organic solvent.

[0075]

[Nitrogen-containing aromatic cyclic compound]

Nitrogen-containing aromatic cyclic compounds include pyridines containing one nitrogen atom and derivatives thereof, imidazoles containing two nitrogen atoms and derivative thereof, pyrimidines and derivatives thereof, pyrazines and derivatives thereof, triazines containing three nitrogen atoms and derivatives thereof, and the like. Pyridines and derivatives thereof, imidazoles and derivatives thereof, and pyrimidines and derivatives thereof are preferably used in view of solvent solubility and the like.

[0076]

Specific examples of pyridines and derivatives thereof include pyridine, 2-methylpyridine, 3-methylpyridine, 4-methylpyridine, 4-ethylpyridine, N-vinylpyridine, 2,4-dimethylpyridine, 2,4,6-trimethylpyridine, 3-cyano-5-methylpyridine, 2-pyridinecarboxylic acid, 6-methyl-2-pyridinecarboxylic acid, 4-pyridinecarboxaldehyde, 4-aminopyridine, 2,3-diaminopyridine, 2,6-diaminopyridine, 2,6-diamino-4-methylpyridine, 4-hydroxypyridine, 4-pyridinemethanol, 2,6-dihydroxypyridine, 2,6-pyridinedimethanol, 6-hydroxynicotinic acid methyl, 2-hydroxy-5-pyridinemethanol, 6-hydroxynicotinic acid ethyl, 4-pyridinemethanol, 4-pyridinethanol, 2-phenylpyridine, 3-methylquinoline,

3-ethylquinoline, quinolinol, 2,3-cyclopentenopyridine, 2,3-cyclohexanopyridine, 1,2-di(4-pyridyl)ethane, 1,2-di(4-pyridyl)propane, 2-pyridinecarboxaldehyde, 2-pyridinecarboxylic acid, 2-pyridinecarbonitrile, 2,3-pyridinedicarboxylic acid, 2,4-pyridinedicarboxylic acid, 2,5-pyridinedicarboxylic acid, 2,6-pyridinedicarboxylic acid, 3-pyridinesulfonic acid, and the like.

[0077]

Specific examples of imidazoles and derivatives thereof include imidazole, 2-methylimidazole, 2-propylimidazole, 2-undecylimidazole, 2-phenylimidazole, N-methylimidazole, N-vinylimidazole, N-allylimidazole, 1-(2-hydroxyethyl)imidazole(N-hydroxyethylimidazole), 2-ethyl-4-methylimidazole, 1,2-dimethylimidazole, 1-benzyl-2-methylimidazole, 1-benzyl-2-phenylimidazole, 1-cyanoethyl-2-methylimidazole, 1-cyanoethyl-2-ethyl-4-methylimidazole, 2-phenyl-4,5-dihydroxymethylimidazole, 1-acetylimidazole, 4,5-imidazoledicarboxylic acid, 4,5-imidazoledicarboxylic acid dimethyl, benzimidazole, 2-aminobenzimidazole, 2-aminobenzimidazole-2-sulfonic acid, 2-amino-1-methylbenzimidazole, 2-hydroxybenzimidazole, 2-(2-pyridyl)benzimidazole, and the like.

[0078]

Specific examples of pyrimidines and derivatives thereof include 2-amino-4-chloro-6-methylpyrimidine, 2-amino-6-chloro-4-methoxypyrimidine, 2-amino-4,6-dichloropyrimidine, 2-amino-4,6-dihydroxypyrimidine, 2-amino-4,6-dimethylpyrimidine, 2-amino-4,6-dimethoxypyrimidine, 2-aminopyrimidine, 2-amino-4-methylpyrimidine, 4,6-dihydroxypyrimidine, 2,4-dihydroxypyrimidin-5-carboxylic acid, 2,4,6-triaminopyrimidine, 2,4-dimethoxypyrimidine, 2,4,5-trihydroxypyrimidine, 2,4-pyrimidinediol, and the like.

[0079]

Specific examples of pyrazines and derivatives thereof include pyrazine, 2-methylpyrazine, 2,5-dimethylpyrazine, pyrazinecarboxylic acid, 2,3-pyrazinedicarboxylic acid, 5-methylpyrazinecarboxylic acid, pyrazinamide, 5-methylpyrazineamide, 2-cyanopyrazine, aminopyrazine, 3-aminopyrazine-2-carboxylic acid, 2-ethyl-3-methylpyrazine, 2,3-dimethylpyrazine, 2,3-diethylpyrazine, and the like

[0080]

Specific examples of triazines and derivatives thereof include 1,3,5-triazine, 2-amino-1,3,5-triazine, 3-amino-1,2,4-triazine, 2,4-diamino-6-phenyl-1,3,5-triazine, 2,4,6-triamino-1,3,5-triazine, 2,4,6-tris(trifluoromethyl)-1,3,5-triazine, 2,4,6-tri-2-pyridine-1,3,5-triazine, 3-(2-pyridine)-5,6-bis(4-phenylsulfonic acid)-1,2,4-triazine disodium, 3-(2-pyridine)-5,6-diphenyl-1,2,4-triazine, 3-(2-pyridine)-5,6-diphenyl-1,2,4-triazine-p,p'-disulfonic acid disodium, and

2-hydroxy-4,6-dichloro-1,3,5-triazine, and the like.

[0081]

The content of the nitrogen-containing aromatic cyclic compound is preferably in the range of 0.1 to 100 mol relative to 1 mol of anionic group of the polyanion, more preferably in the range of 0.5 to 30 mol, and especially preferably in the range of 1 to 10 mol in view of physical properties and conductivity of the conductive coating. When the content of the nitrogen-containing aromatic cyclic compound is less than 0.1 mol, the interaction of the nitrogen-containing aromatic cyclic compound with the polyanion and the conjugated conductive polymer tends to weaken and conductivity may be insufficient. When the content of the nitrogen-containing aromatic cyclic compound is more than 100 mol, the content of the conjugated conductive polymer decreases making it difficult to obtain sufficient conductivity.

[0082]

[Hydroxy group-containing compound with two or more hydroxy groups]

Examples of hydroxy group-containing compounds with two or more hydroxy groups include polyhydric aliphatic alcohols such as propylene glycol, 1,3-butylene glycol, 1,4-butylene glycol, D-glucose, D-glucitol, isoprene glycol, dimethylolpropionic acid, butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,9-nonanediol, neopentylglycol, trimethyloethane, trimethylolpropane, pentaerythritol, dipentaerythritol, thiodiethanol, glucose, tartaric acid, D-glucaric acid, glutamic acid, and the like; alcohol polymer such as cellulose, polysaccharide, sugar alcohol, and the like; aromatic compounds such as 1,4-dihydroxybenzene, 1,3-dihydroxybenzene, 2,3-dihydroxy-1-pentadecylbenzene, 2,4-dihydroxyacetophenone, 2,5-dihydroxyacetophenone, 2,4-dihydroxybenzophenone, 2,6-dihydroxybenzophenone, 3,4-dihydroxybenzophenone, 3,5-dihydroxybenzophenone, 2,4'-dihydroxydiphenylsulfone, 2,2',5,5'-tetrahydroxydiphenylsulfone, 3,3',5,5'-tetramethyl-4,4'-dihydroxydiphenylsulfone, hydroxyquinone carboxylic acid and salts thereof, 2,3-dihydroxy benzoic acid, 2,4-dihydroxy benzoic acid, 2,5-dihydroxy benzoic acid, 2,6-dihydroxy benzoic acid, 3,5-dihydroxy benzoic acid, 1,4-hydroquinone sulfonic acid and salts thereof, 4,5-hydroxybenzene-1,3-disulfonic acid and salts thereof, 1,5-dihydroxynaphthalene, 1,6-dihydroxynaphthalene, 2,6-dihydroxynaphthalene, 2,7-dihydroxynaphthalene, 2,3-dihydroxynaphthalene, 1,5-dihydroxynaphthalene-2,6-dicarboxylic acid, 1,6-dihydroxynaphthalene-2,5-dicarboxylic acid, 1,5-dihydroxynaphthoic acid, 1,4-dihydroxy-2-phenyl naphthoate, 4,5-dihydroxynaphthalene-2,7-disulfonic acid and salts thereof, 1,8-dihydroxy-3,6-naphthalenedisulfonic acid and salts thereof, 6,7-dihydroxy-2-naphthalenesulfonic acid and salts thereof, 1,2,3-trihydroxybenzene (pyrogallol), 1,2,4-trihydroxybenzene, 5-methyl-1,2,3-trihydroxybenzene, 5-ethyl-1,2,3-trihydroxybenzene, 5-propyl-1,2,3-trihydroxybenzene, trihydroxy benzoic

acid, trihydroxyacetophenone, trihydroxybenzophenone, trihydroxybenzaldehyde, trihydroxyanthraquinone, 2,4,6-trihydroxybenzene, tetrahydroxy-p-benzoquinone, tetrahydroxyanthraquinone, garlic acid methyl (methyl gallate), garlic acid ethyl (ethyl gallate); potassium hydroquinone sulfonate, and the like.

[0083]

The content of the hydroxy group-containing compound with two or more hydroxy groups is preferably in the range of 0.05 to 50 mol relative to 1 mol of anionic group of the polyanion, and more preferably in the range of 0.3 to 10 mol. When the content of the hydroxy group-containing compound is less than 0.05 mol relative to 1 mol of anionic group unit of the polyanion, conductivity and heat resistance may be insufficient. When the content of the hydroxy group-containing compound relative to 1 mol of anionic group of the polyanion is more than 50 mol, the content of the π conjugated conductive polymer in the conductive coating decreases making it difficult to obtain sufficient conductivity, too.

[0084]

[Carboxy group-containing compounds with two or more carboxy groups]

Examples of carboxy group-containing compounds with two or more carboxy groups include aliphaticcarboxylic acids compounds such as maleic acid, fumaric acid, itaconic acid, citraconic acid, malonic acid, 1,4-butanedicarboxylic acid, succinic acid, tartaric acid, adipic acid, D-glucaric acid, glutaconic acid, citric acid, and the like; aromaticcarboxylic acids compounds, in which at least one or more carboxy group is bonded to an aromatic ring, such as phthalic acid, terephthalic acid, isophthalic acid, tetrahydrophthalic anhydride, 5-sulfoisophthalic acid, 5-hydroxyisophthalic acid, methyltetrahydrophthalic anhydride, 4,4'-oxydiphthalic acid, biphenyltetracarboxylic acid dianhydride, benzophenonetetracarboxylic dianhydride, naphthalenedicarboxylic acid, trimellitic acid, pyromellitic acid, and the like; diglycolic acid, hydroxydibutyric acid, thiodiacetic acid (acetic thiodi), thiodibutyric acid, iminodiacetic acid, iminobutyric acid, and the like.

[0085]

The content of the carboxy group-containing compound with two or more carboxy groups is preferably in the range of 0.1 to 30 mol relative to 1 mol of anionic group of the polyanion, and more preferably in the range of 0.3 to 10 mol. When the content of the carboxy group-containing compound is less than 0.1 mol relative to 1 mol of anionic group of the polyanion, conductivity and heat resistance may be insufficient. When the content of the carboxy group-containing compound is more than 30 mol relative to 1 mol of anionic group of the polyanion, the content of the π conjugated conductive polymer in the conductive coating decreases making it difficult to obtain sufficient conductivity, too, and then the properties of the conductive coating may be

changed.

[0086]

[Hydroxy and carboxy groups-containing compounds with one or more hydroxy group(s) and one or more carboxy group(s)]

Examples of hydroxy and carboxy groups-containing compounds with one or more hydroxy group(s) and one or more carboxy group(s) include tartaric acid, glyceric acid, dimethylolbutanoic acid, dimethylolpropanoic acid, D-glucaric acid, glutaconic acid, and the like.

[0087]

The content of the hydroxy and carboxy groups-containing compound with one or more hydroxy group(s) and one or more carboxy group(s) is preferably 1 to 5000 parts by weight relative to 100 parts by weight in the total of the polyanion and the π conjugated conductive polymer, and more preferably 50 to 500 parts by weight. When the content of the hydroxy and carboxy groups-containing compound is less than 1 part by weight, conductivity and heat resistance may be insufficient. When the content of the hydroxy and carboxy groups-containing compound is more than 5000 parts by weight, the content of the π conjugated conductive polymer in the conductive coating decreases making it difficult to obtain sufficient conductivity.

[0088]

[Amide compounds]

Amide group-containing compound is a monomolecular compound containing an amide bond represented by -CO-NH- (CO is under a double bond) in molecule. That is, the amide compounds include compound containing functional groups at both ends of the above bond, compound containing cyclic compound bonded at one end of the above bond, urea containing hydrogen as functional groups at the both ends and derivatives thereof, and the like.

[0089]

Specific examples of the amide compounds include acetamide, malonamide, succinamide, maleamide, fumaramide, benzamide, naphthamide, phthalamide, isophthalamide, terephthalamide, nicotinamide, isonicotinamide, 2-fulamide, formamide, N-methylformamide, propionamide, propiolamide, butyramide, isobutyramide, methacrylamide, palmitamide, stearylamine, oleamide, oxamide, glutaramide, adipamide, chinnamamide, glycolamide, lactamide, glyceramide, tartaramide, citramide, glyoxylamide, pyruvamide, acetoacetamide, dimethylacetamide, benzylamide, anthranilamide, ethylenediaminetetraacetamide, diacetamide, triacetamide, dibenzamide, tribenzamide, rhodanine, urea, 1-acetyl-2-thiourea, biuret, butylurea, dibutylurea, 1,3-dimethylurea, 1,3-diethylurea, derivatives thereof, and the like.

[0090]

Further, acrylamide can be used for the amide compounds. Acrylamides include N-methylacrylamide, N-methylmethacrylamide, N-ethylacrylamide, N-ethylmethacrylamide, N,N-dimethylacrylamide, N,N-dimethylmethacrylamide, N,N-diethylacrylamide, N,N-diethylmethacrylamide, 2-hydroxyethylacrylamide, 2-hydroxyethylmethacrylamide, N-methylolacrylamide, N-methylolmethacrylamide, and the like.

[0091]

The molecular weight of the amide compound is preferably 46 to 10000, more preferably 46 to 5000, and especially preferably 46 to 1000.

[0092]

The content of the amide compound is preferably 1 to 5000 parts by weight relative to 100 parts by weight in the total of the polyanion and the π conjugated conductive polymer, and more preferably 50 to 500 parts by weight. When the content of the amide compound is less than 1 part by weight, conductivity and heat resistance may be insufficient. When the content of the amide compound is more than 5000 parts by weight, the content of the π conjugated conductive polymer in the conductive coating decreases making it difficult to obtain sufficient conductivity.

[0093]

[Imide compounds]

As amide compounds, monomolecular compounds containing imide bond (hereinafter, referred to imide compounds) are preferable in view of increasing conductivity. The imide compounds include phthalimide and derivatives thereof, succinimide and derivatives thereof, benzimide and derivatives thereof, maleimide and derivatives thereof, naphthalimide and derivatives thereof, and the like depending on structure.

[0094]

In addition, the imide compounds are classified into aliphatic imide, aromatic imide, and the like depending on the type of functional groups at both ends. Aliphatic imide is preferable in view of solubility.

[0095]

Moreover, the aliphatic imide compounds are classified into saturated aliphatic imide compound having unsaturated bond between carbon atoms in molecule and unsaturated aliphatic imide compound having unsaturated bond between carbon atoms in molecule.

[0096]

Saturated aliphatic imide compound is a compound represented by $R^1\text{-CO-NH-CO-R}^2$, in which each of R^1 and R^2 is saturated hydrocarbon. Specific examples include cyclohexane-1,2-dicarboximide, allantoin, hydantoin, barbituric acid,

alloxan, glutarimide, succinimide, 5-butyridhydantoin acid, 5,5-dimethylhydantoin, 1-methylhydantoin, 1,5,5-trimethylhydantoin, 5-hydantoinacetic acid, N-hydroxy-5-norbornene-2,3-dicarboximide, semicarbazide, α,α -dimethyl-6-methylsuccinimide, bis[2-(succinimideoxycarbonyloxy)ethyl]sulfone, α -methyl- α -propylsuccinimide, cyclohexylimide, and the like.

[0097]

Unsaturated aliphatic imide compound is a compound represented by $R^1\text{-CO-NH-CO-R}^2$, in which one or two of R^1 and R^2 is/are one or more unsaturated bond. Specific examples include 1,3-dipropyleneurea, maleimide, N-methylmaleimide, N-ethylmaleimide, N-hydroxymaleimide, 1,4-bis-maleimidebutane, 1,6-bismaleimidoheptane, 1,8-bismaleimideoctane, N-carboxyheptylmaleimide, and the like.

[0098]

The molecular weight of the imide compound is preferably 60 to 5000, more preferably 70 to 1000, and especially preferably 80 to 500.

[0099]

The content of the imide compound is preferably 10 to 10000 parts by weight relative to 100 parts by weight in the total of the π conjugated conductive polymer and the polyanion, and more preferably 50 to 5000 parts by weight. When the addition of the amide compound and the imide compound is less than the lower limit, it is not preferable because the effect according to the addition of the amide compound and the imide compound decreases. When the addition exceeds the upper limit, it is not preferable because the concentration of the π conjugated conductive polymer is reduced and thereby conductivity decreases.

[0100]

[Lactam compound]

Lactam compound is a cyclic amide in molecule of aminocarboxylic acid, or a compound in which its ring is in part formed of -CO-NR- (R is hydrogen or any substituent). However, one or more carbon atoms of the ring may be replaced by unsaturated or heteroatoms. Examples of the lactam compounds include pentano-4-lactam, 4-pentanelactam-5-methyl-2-pyrrolidone, 5-methyl-2-pyrrolidinone, hexano-6-lactam, 6-hexanelactam, and the like.

[0101]

The content of the lactam compound is preferably 10 to 10000 parts by weight relative to 100 parts by weight in the total of the π conjugated conductive polymer and the polyanion, and more preferably 50 to 5000 parts by weight. When the addition of the lactam compound is less than the lower limit, it is not preferable because the effect according to the addition of the lactam compound decreases. When the addition

exceeds the upper limit, it is not preferable because the concentration of the π conjugated conductive polymer is reduced and thereby conductivity decreases.

[0102]

[Glycidyl group-containing compound]

Examples of glycidyl group-containing compounds include glycidyl compounds such as ethylglycidyl ether, butylglycidyl ether, t-butylglycidyl ether, allylglycidyl ether, benzylglycidyl ether, glycidylphenyl ether, bisphenol A, diglycidyl ether, glycidyl ether acrylate, glycidyl ether methacrylate, and the like, and the like.

[0103]

The content of the glycidyl group-containing compound is preferably 10 to 10000 parts by weight relative to 100 parts by weight in the total of the π conjugated conductive polymer and the polyanion, and more preferably 50 to 5000 parts by weight. When the addition of the glycidyl group-containing compound is less than the lower limit, it is not preferable because the effect according to the addition of the glycidyl group-containing compound decreases. When the addition exceeds the upper limit, it is not preferable because the concentration of the π conjugated conductive polymer is reduced and thereby conductivity decreases.

[0104]

[Silane coupling agents]

Specific examples of silane coupling agents, vinyltrichlorosilane, vinyltrimethoxysilane, vinyltriethoxysilane, 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane, 3-glycidoxypropyltrimethoxysilane, 3-glycidoxypropylmethyldiethoxysilane, 3-glycidoxypropyltriethoxysilane, p-styryltrimethoxysilane, 3-methacryloxypropylmethyldimethoxysilane, 3-methacryloxypropyltrimethoxysilane, 3-methacryloxypropylmethyldiethoxysilanesilane, 3-methacryloxypropyltriethoxysilane, 3-acryloxypropyltrimethoxysilane, N-2-(aminoethyl)-3-aminopropylmethyldimethoxysilane, N-2-(aminoethyl)-3-aminopropyltriethoxysilane, N-2-(aminoethyl)-3-aminopropyltrimethoxysilane, 3-aminopropyltrimethoxysilane, 3-aminopropyltriethoxysilane, 3-triethoxysilyl-N-(1,3-dimethyl-butyldiene)propylamine, N-phenyl-3-aminopropyltrimethoxysilane, N-(vinylbenzyl)-2-aminoethyl-3-aminopropyltrimethoxysilane hydrochloride salt, 3-ureidopropyltriethoxysilane, 3-chloropropyltrimethoxysilane, 3-mercaptopropylmethyldimethoxysilane, 3-mercaptopropyltrimethoxysilane, bis(triethoxysilylpropyl)tetrasulfide, 3-isocyanatepropyltriethoxysilane, and the like.

[0105]

The content of the silane coupling agents may be added in any amount, as needed, or not particularly limited. The content is preferably 10 to 10000 parts by weight relative to 100 parts by weight in the total of the π conjugated conductive polymer and the polyanion.

Examples

[0106]

Referring to Tab. 1, Examples 1 to 4 according to the present invention and Comparative Examples 1 to 3 are described below.

[0107]

(Preparation of Material)

[1] Preparation of Polystyrene Sulfonic Acid

206 g of sodium styrene sulfonate was dissolved in 1000 ml of ion-exchanged water, 1.14 g of ammonium persulfate oxidizing agent dissolved in advance in 10 ml of water was added dropwise over 20 minutes while stirring at 80 °C, and this solution was stirred for 2 hours. 1000 ml of sulfuric acid diluted to 10 % by weight and 10000 ml of ion-exchanged water were added to the obtained solution containing sodium styrene sulfonate, about 10000 ml of the solution containing polystyrene sulfonic acid was removed using an ultrafiltration method, 10000 ml of ion-exchanged water was added to the residue, and about 10000 ml of the solution was removed using the ultrafiltration method. The above ultrafiltration operation was repeated three times. Subsequently, about 10000 ml ion-exchanged water was added to the obtained filtrate, and about 10000 ml of the solution was removed using the ultrafiltration method. This ultrafiltration operation was repeated three times. The ultrafiltration conditions were as follows:

Cutoff molecular weight of ultrafiltration membrane: 30000

Cross-flow system

Feed solution flow rate: 3000 ml/min

Membrane partial pressure: 0.12 Pa

Water in the obtained solution was removed under reduced pressure to obtain polystyrene sulfonic acid in colorless solid.

[0108]

[2] Preparation of a Solution of Polystyrene Sulfonic Acid-doped Poly(3,4-Ethylenedioxythiophene)

14.2 g of 3,4-ethylenedioxythiophene and a solution obtained by dissolving

36.7 g of polystyrene sulfonic acid obtained in [1] in 2000 ml of ion-exchanged water were mixed at 20 °C. This mixed solution was maintained at 20 °C, 29.64 g of ammonium persulfate dissolved in 200 ml of ion-exchanged water and 8.0 g of an oxidation catalyst solution of ferric sulfate were slowly added while stirring, and the mixture was stirred for 3 hours to react. 2000 ml of ion-exchanged water was added to the obtained reaction solution, and about 2000 ml of the solution was removed using the ultrafiltration method. This operation was repeated three times. Then, 200 ml of sulfuric acid diluted to 10 % by weight and 2000 ml of ion-exchanged water were added to the treatment solution filtrated as above, about 2000 ml of the treatment solution was removed using the ultrafiltration method, 2000 ml of ion-exchanged water was added thereto, and about 2000 ml of the solution was removed using the ultrafiltration method. This operation was repeated three times. Subsequently, 2000 ml of ion-exchanged water was added to the obtained treatment solution, and about 2000 ml of the treatment solution was removed using the ultrafiltration method. This operation was repeated five times, and thus about 1.5 % by weight of a blue solution of polystyrene sulfonic acid-doped poly(3,4-ethylenedioxythiophene) (PEDOT-PSS) was obtained. The ultrafiltration conditions are the same as [1].

[0109]

[3] Preparation of a glass substrate

A glass substrate was prepared by chemically etching (38 to 42 °C of solution temperature) a nonionic glass while bubbling using a mixture of hydrofluoric acid, hydrochloric acid and nitric acid. The glass substrate had 0.4 mm in thickness, 6.2 degrees in water contact angle of surface, and 0.0008 μm in arithmetic mean roughness R_a .

[0110]

[4] Preparation of a glass substrate

A glass substrate was prepared by chemically etching (38 to 42 °C of solution temperature) a nonionic glass while bubbling using a blower. The glass substrate had 0.4 mm in thickness, 6.2 degrees in water contact angle of surface, and 0.195 μm in arithmetic mean roughness R_a .

[0111]

[5] Preparation of a glass substrate

A glass substrate was prepared by chemically etching (38 to 42 °C of solution temperature) a nonionic glass while bubbling using a blower. The glass substrate had 2 mm in thickness, 6.2 degrees in water contact angle of surface, and 0.0008 μm in

arithmetic mean roughness Ra.

[0112]

(Measurement and Evaluation Method)

(Arithmetic Mean Roughness Ra)

It was measured in accordance with JIS B0601-2001.

[0113]

(Surface Resistance)

It was measured in accordance with JIS K7194 using Loresta MCP-T600 manufactured by Mitsubishi Chemical Corporation.

[0114]

(Light Transmittance)

Light transmittance was measured in accordance with JIS K7136 using Haze/Turbidimeter Instrument (NDH5000) manufactured by Nippon Denshoku Industries Co., Ltd.

[0115]

(Pencil Hardness)

Hardness that a scratch is not observed under load of 750 g was measured in accordance with JIS K5600 using test pencils as specified in JIS S6006.

[0116]

(Flexibility)

Operation of winding a transparent conductive glass substrate around a pipe of 25 mm radius (R) in 180 contact and resetting it was performed five times, and rate of change of surface resistance before and after such operation was measured.

[0117]

(Example 1)

A conductive polymer solution A was obtained by mixing 3.6 g of garlic acid methyl, 0.9 g of Irgacure 127 (manufactured by Ciba Specialty Chemicals K.K.), 20 g of dimethyl sulfoxide, 2.5 g of hydroxy acrylate, 7.2 g of pentaerythritol triacrylate and 300 g of ethanol into 600 g of the PEDOT-PSS solution obtained in [2], and stirring the mixture.

[0118]

The conductive polymer solution A was applied on one surface of the glass substrate obtained in [3] using a slit coater of serial number IS-7900IL-NSC manufactured by Innext Co., Ltd. under conditions of 150 μm in a nozzle gap, 20 mm/sec in a coating speed, 100 μm in a working distance and 0.11 ml in a discharge flow, and dried at 100 °C for 2 minutes by infrared radiation. After that, ultraviolet (120 W of high-pressure mercury lamp, 500 mJ/cm^2 , 178 mW/cm^2) was irradiated thereon for curing to form a conductive coating film. Surface resistance, light transmittance and pencil hardness of the conductive coating film, and flexibility of the transparent conductive glass substrate were measured by procedures as described later.

[0119]

(Example 2)

A conductive polymer solution B was obtained by mixing 3.6 g of garlic acid methyl, 0.9 g of Irgacure 127 (manufactured by Ciba Specialty Chemicals K.K.), 20 g of dimethyl sulfoxide, 9.2 g of diethyleneglycoldiglycidyl ether, 0.2 g of 2-methylimidazole, 250 g of ethanol, 50 g of ethyleneglycol into 600 g of the PEDOT-PSS solution obtained in [2], and stirring the mixture. The conductive polymer solution B was applied on one surface of the glass substrate obtained in [3] using the slit coater of serial number IS-7900IL-NSC manufactured by Innext Co., Ltd. under conditions of 150 μm in a nozzle gap, 40 mm/sec in a coating speed, 100 μm in a working distance and 0.3 ml in a discharge flow, and dried at 120 °C for 2 minutes by infrared radiation for curing to form a conductive coating film. Surface resistance, light transmittance and pencil hardness of the conductive coating film, and flexibility of the transparent conductive glass substrate were measured.

[0120]

(Example 3)

A conductive polymer solution C was obtained by mixing 3.6 g of garlic acid methyl, 0.9 g of Irgacure 127 (manufactured by Ciba Specialty Chemicals K.K.), 20 g of dimethyl sulfoxide, 9.2 g of diethyleneglycoldiglycidyl ether, 0.2 g of 2-methylimidazole, 0.5 g of garlic acid, 250 g of ethanol, 50 g of ethyleneglycol into 600 g of a PEDOT-PSS solution (Crevios PH1000 manufactured by H.C. Starck Ltd.), and stirring the mixture. The conductive polymer solution C was applied on one surface of the glass substrate obtained in [3] using the slit coater of serial number IS-7900IL-NSC manufactured by Innext Co., Ltd. under conditions of 130 μm in a nozzle gap, 40 mm/sec in a coating speed, 100 μm in a working distance and 0.21 ml in a discharge flow, and dried at 120 °C for 2 minutes by infrared radiation for curing to

form a conductive coating film. Surface resistance, light transmittance and pencil hardness of the conductive coating film, and flexibility of the transparent conductive glass substrate were measured.

[0121]

(Example 4)

The conductive polymer solution C was applied on one surface of the glass substrate obtained in [4] using the slit coater of serial number IS-7900IL-NSC manufactured by Innex Co., Ltd. under conditions of 130 μm in a nozzle gap, 60 mm/sec in a coating speed, 80 μm in a working distance and 0.6 ml in a discharge flow, and dried at 120 °C for 2 minutes by infrared radiation for curing to form a conductive coating film. Surface resistance, light transmittance and pencil hardness of the conductive coating film, and flexibility of the transparent conductive glass substrate were measured.

[0122]

(Example 5)

A conductive polymer solution D was obtained by mixing 2 g of 2-methylimidazole, 150 g of water-dispersible polyester resin (Vylonal MD1480: solids content of 25 % by weight), 3.6 g of garlic acid, 20 g of dimethyl sulfoxide and 1500 g of methanol into 500 g of the PEDOT-PSS solution obtained in [2], and stirring the mixture. The conductive polymer solution D was applied on one surface of the glass substrate obtained in [3] using the slit coater of serial number IS-7900IL-NSC manufactured by Innex Co., Ltd. under conditions of 150 μm in a nozzle gap, 40 mm/sec in a coating speed, 100 μm in a working distance and 0.3 ml in a discharge flow, and dried at 120 °C for 2 minutes by infrared radiation to form a conductive coating film. Surface resistance, light transmittance and pencil hardness of the conductive coating film, and flexibility of the transparent conductive glass substrate were measured.

[0123]

(Comparative Example 1)

An ITO (in abbreviated form of Indium Tin Oxide) film was formed on one surface of the glass substrate obtained in [3] by sputtering to form a conductive coating film. Surface resistance, light transmittance and pencil hardness of the conductive coating film, and flexibility of the transparent conductive glass substrate were measured.

[0124]

(Comparative Example 2)

An ITO film was formed on one surface of the glass substrate obtained in [4] by sputtering to form a conductive coating film. Surface resistance, light transmittance and pencil hardness of the conductive coating film, and flexibility of the transparent conductive glass substrate were measured.

[0125]

(Comparative Example 3)

The conductive polymer solution C was applied on one surface of the glass substrate obtained in [5] using the slit coater of serial number IS-7900IL-NSC manufactured by Innext Co., Ltd. under conditions of 130 μm in a nozzle gap, 60 mm/sec in a coating speed, 80 μm in a working distance and 0.6 ml in a discharge flow. However, surface resistance, light transmittance and pencil hardness of the conductive coating film was unable to be measured, and the test piece was destructed in flexibility measurement of the transparent conductive glass substrate.

[0126]

The results of Examples 1 to 4 and Comparative Examples 1 to 3 are shown by comparison in Tab. 1.

[0127]

[Tab. 1]

	Surface Resistance ($\Omega/\text{sq.}$)	Light Transmittance (%)	Pencil Hardness	Flexibility
Example 1	300 to 600	88 to 89	2H	Rate of Change 1.2
Example 2	500 to 1000	88 to 89	3H	Rate of Change 1.2
Example 3	400 to 800	88 to 90	3H	Rate of Change 1.1
Example 4	1000 to 2000	88 to 90	2H	Rate of Change 1.3
Example 5	1.2×10^7 to 1.8×10^9	89 to 91	H	Rate of Change 1.2
Comparative Example 1	400 to 1000	85 to 88	3H	Rate of Change 1.1
Comparative Example 2	Unable to be measured	Unable to be measured	Unable to be measured	Destructed
Comparative Example 3	Unable to be measured	Unable to be measured	Unable to be measured	Destructed

[0128]

Although the present invention has been described using the embodiments, it is needless to say that the technical scope of the present invention is not limited to the range described in the above embodiments. It is apparent to those skilled in the art that the above embodiments may be modified or improved in various manners. And, it is also apparent that such modified or improved embodiments may be included in the technical scope of the present invention in view of the claims as described.

INDUSTRIAL APPLICABILITY

[0129]

A transparent conductive glass substrate of the present invention is used as a glass substrate material of liquid crystal in VA (Vertical Alignment) system, liquid crystal in TN (Twisted Nematic) system, liquid crystal in IPS (In Plane Switching) system and the like for purposes of a liquid crystal driving electrode or a material preventing from liquid crystal surface charge to cause an obstruction to viewing angle of IPS. In transparent conductive glass substrates in use for these, a conductive polymer is sometimes applied following a liquid crystal enclosed in advance because of the yield rate in production. In this case, a temperature for drying and curing the conductive polymer is preferably 200 °C or less and desirably 160 °C or less so as to prevent a liquid crystal material from being heat-denatured, since the liquid crystal material is an organic material sensitive to heat. In addition, since ITO deposition is conventionally carried out in high vacuum environment, a liquid crystal is inflated under reduced pressure and a glass is destructed when the liquid crystal is enclosed in advance of ITO deposition. Advantageously, the transparent conductive film using the conductive polymer does not bring the destruction in vacuum, since it can be achieved under ordinary pressure rather than an environment under reduced pressure such as high vacuum.

CLAIMS

1. A transparent conductive glass substrate comprising:
 - a glass substrate; and
 - a conductive polymer layer on at least one surface of the glass substrate,wherein the glass substrate has a thickness in the range of 0.03 to 0.7 mm and a water contact angle of the glass surface in the range of 5 to 40 degrees,
 - wherein the conductive polymer layer has surface resistance of $1.8 \text{ G}\Omega/\text{sq.}$ or less, total light transmittance of 85 % or more, and surface pencil hardness of H or more, and
 - wherein the transparent conductive glass has flexibility as a whole enough not to be damaged in bending test with the radius R25 mm.
2. The transparent conductive glass substrate according to claim 1, wherein the conductive polymer layer is formed from a conductive polymer paint, the conductive polymer paint comprising a conductive polymer, a polyanion and further one or more selected from the group consisting of binder, curing agent, high conductive agent, surfactant, catalyst, and agent for improving adhesion.
3. The transparent conductive glass substrate according to claim 2, wherein the conductive polymer comprises one or more polymer belonging one or more selected from the group consisting of polypyrroles, polythiophenes, polyacetylenes, polyphenylenes, polyphenylene vinylene, polyanilines, polyacene, polythiophene vinylene and copolymers thereof, in which an organic polymer main chain is composed of a π conjugated system.
4. The transparent conductive glass substrate according to claim 2 or 3, wherein the conductive polymer comprises at least an anionic polymer and a polymer of thiophene or a derivative thereof.
5. The transparent conductive glass substrate according to claim 4, wherein the anionic polymer is a polystyrene sulfonic acid and the polymer of thiophene or a derivative thereof is poly-3,4-ethylene dioxythiophene.
6. The transparent conductive glass substrate according to claim 2, wherein the polyanion comprises one or more polymer having one or more anionic group selected from the group consisting of sulfate ester group monosubstituted, phosphoric ester

group monosubstituted, phosphoric acid group, a carboxyl group and a sulfo group.

7. The transparent conductive glass substrate according to claim 2, wherein the binder is a binder resin, and the binder resin is one or more thermoplastic resin and/or thermosetting resin capable of being dissolvable or mixable and dispersable with the conductive polymer.

8. The transparent conductive glass substrate according to claim 2, wherein the high conductive agent is one or more compound selected from the group consisting of a compound having a hydroxy group cyclic compound containing aromatic nitrogen, a compound having two or more hydroxy groups, a compound having two or more carboxyl groups, a compound having one or more hydroxy group(s) and one or more carboxyl group(s), a compound having an amide group, a compound having an imide group, lactam compounds, a compound having glycidyl group, a silane coupling agent, DMSO (Dimethyl sulfoxide) and a water-soluble organic solvent.

9. The transparent conductive glass substrate according to any one of claims 2 to 8, wherein the conductive polymer layer has the boiling point in the range of 50 to 200 °C and comprises 5 to 95 % by weight solvent soluble in water.

10 The transparent conductive glass substrate according to any one of claims 1 to 9, wherein the conductive polymer layer is obtained by applying the conductive polymer paint and subsequently drying and heating and/or irradiating with infrared or ultraviolet.

11. The transparent conductive glass substrate according to claim 10, wherein the conductive polymer paint is applied in one method selected from the group consisting of a screen printing method, a gravure printing method, a flexographic printing method, an offset printing method, inkjet printing method, a spin coating method, a die coating method including a slit coater method, a curtain coating method, and a cap coating method.

12. The transparent conductive glass substrate according to claim 1, wherein a surface having at least the conductive polymer layer on the glass substrate includes a portion formed by etching with a mixed solution containing hydrofluoric acid.

13. The transparent conductive glass substrate according to any one of claims 1 to 12,

wherein the conductive polymer layer is cured by heating and/or irradiating infrared or ultraviolet.

14. The transparent conductive glass substrate according to any one of claims 1 to 13, wherein the conductive polymer layer is cured at a temperature of 160 °C or below.