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(54) Title: ADDITIVES FOR ENHANCING THE ANTISTATIC PROPERTIES OF CONDUCTIVE POLYMER-BASED COATINGS

(57) Abstract: The present invention relates to a curable composition, providing, upon curing, a transparent, antistatic coating, comprising at least one conductive polymer, at least one epoxysilane binder, at least one solvent, and at least one compound of formula $R^1-[R^2]_n-OSO_3H$ or $R^1-[R^2]_n-SO_3H$ or a salt thereof, wherein $n = 0$ or 1 , R^1 is H or a substituted or unsubstituted alkyl group, and R^2 is a substituted or unsubstituted arylene group, with the proviso that the compound of formula II is not a fluorine containing surfactant. The invention further relates to optical articles comprising a substrate at least partially coated with a transparent antistatic coating formed by depositing onto the substrate and curing the above curable composition. The obtained optical articles exhibit enhanced antistatic properties, high optical transparency with about 91% transmittance, and low haze.



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ADDITIVES FOR ENHANCING THE ANTISTATIC PROPERTIES OF CONDUCTIVE POLYMER-BASED COATINGS

BACKGROUND OF THE INVENTION

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1. Field of the invention

The present invention relates to curable compositions for preparing transparent antistatic and abrasion- and/or scratch-resistant coatings, articles exhibiting antistatic and abrasion- and/or scratch-resistance properties coated therewith, in particular optical and ophthalmic lenses for eyeglasses, and a process to prepare such articles. These inventions are based on the use of new additives for enhancing antistatic properties while maintaining excellent abrasion and scratch-resistance properties.

15 2. Description of related art

It is well known that optical articles, which are essentially composed of insulating materials, have a tendency to get charged with static electricity, especially when they are cleaned in dry conditions by rubbing their surface with a cloth or synthetic piece, for example a polyester piece (triboelectricity). The charges which are present at the surface of said optical articles create an electrostatic field capable of attracting and fixing, as long as the charge remains on optical articles, objects lying in the vicinity thereof (a few centimeters) that have a very little weight, generally small size particles such as dusts.

In order to decrease or suppress attraction of the particles, it is necessary to decrease the intensity of the electrostatic field, i.e. to decrease the number of static charges which are present at the surface of the article. This may be carried out by imparting mobility to the charges, for instance by introducing in the optical article a layer of a material inducing a high mobility of the charges. Materials inducing the highest mobility are conductive materials. Thus, a material having a high conductivity allows dissipating more rapidly charges.

It is known in the art that an optical article acquires antistatic properties owing to the incorporation at the surface thereof of at least one electrically conductive layer, which is called an antistatic layer.

By "antistatic", it is meant the property of not retaining and/or developing an appreciable electrostatic charge. An article is generally considered to have acceptable antistatic properties when it does not attract or fix dust or small particles after one of its surfaces has been rubbed with an appropriate cloth. It is capable of quickly dissipating accumulated electrostatic charges.

The ability of a glass to evacuate a static charge created by rubbing with a cloth or any other electrostatic charge generation process (charge applied by corona...) can be quantified by

measuring the time required for said charge to be dissipated (charge decay time). Thus, antistatic glasses have a discharge time in the order of 100-200 milliseconds, while static glasses have a discharge time in the order of several tens seconds, sometimes even several minutes. A static glass having just been rubbed can thus attract surrounding dusts as long as it requires time to get discharged.

Only a limited number of materials are known in the art for preparing electrically conductive inorganic or organic layers having high optical transparency, i.e. a transmittance in the visible light of at least 90%. Known optically transparent antistatic coatings include vacuum-deposited metal or metal oxide films, for example films based on optionally doped (semi-)conductive metal oxides such as tin oxide doped with indium (ITO), tin oxide doped with antimony (ATO) or vanadium pentoxide, spin-coated or self-assembled conductive polymer films.

ITO is the industry standard antistatic agent to provide optically transparent electrically conductive thin coatings, but the performance of ITO suffers when it is applied to plastics. These coatings are fragile and are readily damaged during bending or other stress inducing conditions. In addition, ITO layers need to be deposited by vacuum deposition in a controlled gas atmosphere.

Conductive polymers represent the most investigated alternative to ITO coatings. They are generally formed from a liquid coating composition, but still cannot match the optical and electrical performances of ITO and sometimes suffer from environmental stability problems in specific applications.

Poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate) (abbreviated as PEDT/PSS) is one of the most popular conductive polymers due to its excellent thermal stability and hydrolysis resistance. PEDT/PSS films can be synthesized from water dispersions. However, the conductivity of conventional PEDT/PSS films is typically insufficient for many uses.

A number of methods for enhancing the conductivity of waterborne conductive polymers consist in combining particular solvents or additives with the waterborne composition and then forming a film. It has been shown that the conductivity of polythiophene based films could be improved by the addition of compounds with polar groups such as polyols, 2-nitroethanol or high-dielectric solvents such as dimethyl sulfoxide (DMSO), N,N-dimethylformamide (DMF), pyridine, isopropanol, dimethylacetamide or N-methyl pyrrolidone (NMP), in the coating composition used to form the film. The conductivity enhancement strongly depends on the chemical structure of the additive. See e.g. US 2003/006401, US 2007/085061 or Yang et al., Adv. Funct. Mater. **2005**, 15, 203-208.

WO 03/087222 describes a conductive polymer-based composition comprising at least one aqueous conductive polymer such as poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate), an organic solvent such as N-methylpyrrolidone or ethylene glycol, at least one dendrimer (hyperbranched polymer) and optionally at least one additive. Dendrimers are used

to produce three-dimensional conjugated polymers that thereby exhibit isotropic electronic properties instead of the naturally anisotropic structure of the conductive polymer particles. The dendrimer also improves the intermolecular charge transfer properties of the conductive polymer particles and stabilizes the dispersion of hydrophilic conductive polymer particles in polar organic solvents. The only dendrimers disclosed contain one or more primary, secondary or tertiary amine groups. These groups are capable of interacting with sulfonic acid groups of polystyrenesulfonate polyanions to form ammonium bonds, which improves the electronic properties of the coating. This feature is described as being essential.

The additives that may be incorporated into the composition are used to control particle size and further dope the conductive polymer. They are used in an amount ranging from 0 to 20 % by weight, preferably from 1 to 10 %. Additives are small molecules comprising groups such as sulfonic acid, amine and hydroxyl, preferably sulfonic groups, for example functionalized alkyl or aromatic sulfonic acid. Preferred additives are benzene sulfonic acid, camphor sulfonic acid and 4-hydroxybenzenesulfonic acid. The sulfonic acid additives are capable of doping poly(3,4-ethylenedioxythiophene) structures while stabilizing the particle size and enhancing adhesion to a substrate.

The compositions, with or without additives, are used to form improved coatings in terms of film uniformity, surface resistance, transparency, adhesion to substrates and environmental stability. WO 03/087222 does not contemplate the use of sulfate additives.

US Pat. Appl. 2006/0035070 discloses an antistatic film comprising, as a conductive polymer, a polymer having polymerized units bearing a quaternary ammonium group. The counter-ions of this polycation are chosen from halogen, nitrate, sulfate, alkyl sulfate, sulfonate, alkyl sulfonate and halogenated alkyl ions, preferably from alkyl sulfonate ions having 1 to 5 carbon atoms. The film is obtained from an aqueous coating composition comprising said conductive polymer, and optionally a polyester or acrylic resin as a binder. The optical performances of the final antistatic films are doubtful, since their visible light transmittance is only disclosed to be higher than or equal to 70%, and the haze is preferably 4% or lower.

JP 2008-066064 discloses a transparent conductive film obtained from a composition comprising a polythiophene conductive polymer, a water miscible solvent such as isopropanol, and a fluorochemical surfactant, such as a fluoro alkyl carboxylate, a perfluoroalkyl benzenesulfonic acid salt, a quaternary perfluoroalkyl ammonium salt, a perfluoroalkyl / ether / alcoholic copolymer, or a perfluoroalkyl polyoxyethylene ethanol. The composition may also comprise a trialkoxysilane bearing a glycidoxy group for enhancing the film strength.

It is still desirable to produce new conductive polymer-based antistatic compositions having improved mechanical and antistatic properties, higher transparency, and lower haze values. The use of conductive polymers is often associated with optical transmission loss, which prevents conductive polymer-based antistatic compositions from being employed in some specific applications, especially in ophthalmic lens application.

SUMMARY OF THE INVENTION

An object of the invention is to provide novel curable coating compositions capable of imparting antistatic properties to an optical article, without concurrently decreasing its optical transparency in the visible range.

Another object of the invention is to provide a cured coating capable of imparting antistatic properties to an optical article, despite the fact that it comprises low amounts of conductive polymers, typically less than 1 wt%, preferably 0.7 or less and better 0.6wt% or less of conductive polymer relative to the weight of the cured coating (dry coating).

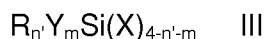
A further object of the invention is to provide electrically conductive coatings providing antistatic properties, having low haze, excellent scratch and/or abrasion resistance and decreased charge decay times at the same time.

The present inventors have found that the improvement of the conductivity and also abrasion resistance of a conductive-polymer-based coating could be achieved by adding a specific organic compound or a salt thereof to its precursor coating composition.

The invention relates to a curable composition providing, upon curing, a transparent, antistatic coating, comprising:

a) at least one conductive polymer,

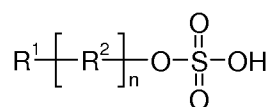
b) at least one binder chosen from compounds of formula:



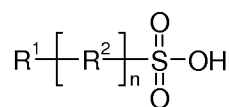
or hydrolyzates thereof, in which the R groups are identical or different and represent monovalent organic groups linked to the silicon atom through a carbon atom, the Y groups are identical or different and represent monovalent organic groups linked to the silicon atom through a carbon atom and containing at least one epoxy function, the X groups are identical or different and represent hydrolyzable groups or hydrogen atoms, m and n' are integers such that m is equal to 1 or 2 and n' + m = 1 or 2.

c) at least one solvent, and

d) at least one additive of formula I or II:



I

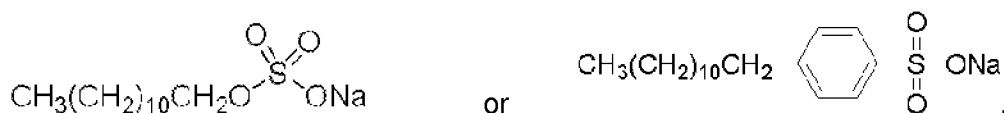


II

or a salt thereof, wherein n = 0 or 1, R¹ is H or a substituted or unsubstituted alkyl group, and R² is a substituted or unsubstituted arylene group, with the proviso that:

- the compound of formula II is not a fluorine containing surfactant,
- R¹ is not H when n = 0.

One embodiment of the invention is directed to a curable composition which provides, upon curing, an abrasion-resistant, transparent, antistatic coating, comprising at least one additive of formula:



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The invention also relates to an optical article comprising a substrate, wherein the substrate is at least partially coated with a transparent antistatic coating formed by depositing onto the substrate and curing the above described curable composition.

The invention further relates to a process for preparing said transparent antistatic optical article by a wet method.

Other objects, features and advantages of the present invention will become apparent from the following detailed description. It should be understood, however, that the detailed description and the specific examples, while indicating specific embodiments of the invention, are given by way of illustration only, since various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art from this detailed description.

DETAILED DESCRIPTION OF THE INVENTION AND PREFERRED EMBODIMENTS

The terms "comprise" (and any grammatical variation thereof, such as "comprises" and "comprising"), "have" (and any grammatical variation thereof, such as "has" and "having"), "contain" (and any grammatical variation thereof, such as "contains" and "containing"), and "include" (and any grammatical variation thereof, such as "includes" and "including") are open-ended linking verbs. They are used to specify the presence of stated features, integers, steps or components or groups thereof, but do not preclude the presence or addition of one or more other features, integers, steps or components or groups thereof. As a result, a method, or a step in a method, that "comprises," "has," "contains," or "includes" one or more steps or elements possesses those one or more steps or elements, but is not limited to possessing only those one or more steps or elements.

Unless otherwise indicated, all numbers or expressions referring to quantities of ingredients, ranges, reaction conditions, etc. used herein are to be understood as modified in all instances by the term "about."

When an optical article comprises one or more surface coatings, the phrase "to deposit a coating or layer onto the optical article" means that a coating or layer is deposited onto the outermost coating of the optical article, i.e. the coating which is the closest to the air.

A coating that is "on" a side of a lens is defined as a coating that (a) is positioned over that side, (b) need not be in contact with that side, i.e., one or more intervening coatings may be

disposed between that side and the coating in question, and (c) need not cover that side completely.

The optical article prepared according to the present invention is a transparent optical article, preferably a lens or lens blank, and more preferably an ophthalmic lens or lens blank.

5 The optical article may be coated on its convex main side (front side), concave main side (back side), or both sides with the antistatic coating according to the invention.

Herein, the term "lens" means an organic or inorganic glass lens, comprising a lens substrate which may be coated with one or more coatings of various natures.

10 The lens substrate may be made of mineral glass or organic glass, preferably organic glass. The organic glasses can be either thermoplastic materials such as polycarbonates and thermoplastic polyurethanes or thermosetting (cross-linked) materials such as diethylene glycol bis(allylcarbonate) polymers and copolymers (in particular CR-39[®] from PPG Industries), thermosetting polyurethanes, polythiourethanes, polyepoxides, polyepisulfides, poly(meth)acrylates and copolymers based substrates, such as substrates comprising
15 (meth)acrylic polymers and copolymers derived from bisphenol-A, polythio(meth)acrylates, as well as copolymers thereof and blends thereof. Preferred materials for the lens substrate are polycarbonates (PC) and diethylene glycol bis(allylcarbonate) polymers, in particular substrates made of polycarbonate.

The optical article comprising a substrate used herein may also be a carrier onto which
20 the antistatic coating is stored. It can be transferred later from the carrier onto the substrate of e.g. an optical lens.

The surface of the article onto which the transparent antistatic coating will be applied may optionally be subjected to a pre-treatment step intended to improve adhesion, for example a high-frequency discharge plasma treatment, a glow discharge plasma treatment, a corona
25 treatment, an electron beam treatment, an ion beam treatment, an acid or base treatment.

The antistatic coating according to the invention may be deposited onto a naked substrate or onto the outermost coating layer of the substrate if the substrate is coated with at least one surface coating. Said at least one surface coating may be, without limitation, an impact-resistant coating (impact resistant primer), an abrasion and/or scratch resistant coating,
30 a polarized coating, a photochromic coating or a dyed coating.

The impact-resistant coating which may be used in the present invention can be any coating typically used for improving impact resistance of a finished optical article. This coating generally enhances adhesion of the abrasion and/or scratch-resistant coating on the substrate of the finished optical article. By definition, an impact-resistant primer coating is a coating which
35 improves the impact resistance of the finished optical article as compared with the same optical article but without the impact-resistant primer coating.

Typical impact-resistance primer coatings are (meth)acrylic based coatings and polyurethane based coatings, in particular coatings made from a latex composition such as a poly(meth)acrylic latex, a polyurethane latex or a polyester latex.

5 The abrasion- and/or scratch-resistant coating which may be used in the present invention can be any coating typically used for improving abrasion- and/or scratch-resistance of a finished optical article as compared to a same optical article but without the abrasion- and/or scratch-resistant coating.

Preferred abrasion- and/or scratch-resistant coatings are (meth)acrylate based coatings and silicon-containing coatings. The latter are more preferred and are disclosed, for example, in
10 French patent application FR 2702486, which is incorporated herein by reference.

The inventive curable coating composition applied onto the substrate provides, upon curing, a functional transparent coating having antistatic properties and abrasion and/or scratch resistance. It will be sometimes referred to in this patent application as the "antistatic composition".

15 The antistatic coating composition may be a solution or dispersion, both terms being merged in the present patent application. These terms refer to a mixture of components which generally is uniform at the macroscopic scale (visually) and are not related to a particular solubility state or particle size of said components.

Said curable composition comprises at least one conductive polymer, at least one binder
20 of formula III, at least one solvent, and at least one compound of formula I or II.

As will be said later, most of the conductive polymers are available in solution or dispersion in solvent(s). In the context of this patent application, the expression "conductive polymer" is intended to mean the conductive molecular entity (without solvent).

Among conductive polymers, those leading to thin transparent layers are preferred. As
25 examples of transparent, organic, conductive polymers may be cited polyanilines, such as those disclosed in US Patents 5,716,550 and 5,093,439, polypyrroles, such as those disclosed in US Patents 5,665,498 and 5,674,654, polythiophenes, such as those disclosed in US Patents 5,575,898, 5,403,467 and 5,300,575, poly(thienothiophenes) such as those disclosed in US 2007/085061, polyethylene-imines, polyselenophenes, compounds based on allylamine such as
30 poly(allylamine), polyazines, polyvinylphenylene, polyacetylenes, poly(phenylene sulfides), copolymers thereof, derivatives of those polymers and mixtures thereof. They may be employed as mixtures. Other examples of conductive polymers can be found in "Conjugated Polymeric Materials: Opportunities in Electronics, Optoelectronics, and Molecular Engineering", J. L. Bredas and B. Silbey, Eds., Kluwer, Dordrecht, **1991**, which is incorporated herein by reference.

35 Those conductive polymers are generally employed under a polycationic form (polyaniline cation, polypyrrole cation, polythiophene cation, poly(allylamine) cation...), generally in combination with one or more polyanions. The polyionic compounds may be

compounds including a charge in their main chain or compounds including ionizable side groups.

Polyanions, either conjugated or not, represent any type of polymer fitted with ionizable groups, typically within the repeat unit, that are capable of supporting negative charges when ionized. They may be chosen, without limitation, from polymeric carboxylic or sulfonic acids anions (polyacids), and mixtures thereof. For example, polystyrene sulfonate, polyaniline sulfonate, polyvinyl sulfonate, polyacrylate, polymethacrylate, polymaleate, poly(thiophene-3-acetate), fluoropolymeric acids anions such as perfluorosulfonic acid polymer anions (e.g. Nafion[®]) as well as anions of copolymers obtained by copolymerizing at least one acidic monomer such as acrylic, methacrylic, maleic, styrene sulfonic, or vinyl sulfonic acid with at least another monomer, either acidic or not, may be cited. Among said non acidic monomers, styrene or acrylic esters may be cited. Other examples of polyanions can be found in "Coulombic interactions in Macromolecular Systems" ACS Symposium Series No.302, A. Eisenberg and F. Bailey Eds., **1986**, which is hereby incorporated by reference. The preferred polyanion is polystyrene sulfonate.

The number average molecular weight of polyanion precursor polyacids generally ranges from 1000 to $2 \cdot 10^6$ g/mol, preferably from 2000 to 500000.

Polyacids can be prepared by known methods or are commercially available, optionally under a metallic salt form.

Conductive polymers can be substituted with very diverse functional groups, notably hydrophilic groups, preferably ionic or ionizable, such as the following groups: COOH, SO₃H, NH₂, ammonium, phosphate, sulfate, imine, hydrazino, OH, SH or salts thereof. Presence of these functional groups make easier the preparation of an aqueous antistatic coating composition, since they make conductive polymers more compatible with water and thus more soluble in the composition. This may improve the quality of the deposit.

Preferred conductive polymers are polypyrroles derivatives, in particular the 3,4-dialkoxy substituted polypyrroles derivatives, and polythiophenes derivatives, in particular the 3,4-dialkoxy substituted polythiophenes derivatives such as polydioxithiophenes disclosed in US 2003/006401 (e.g. poly(3,4-alkylenedioxythiophenes), preferably poly(3,4-ethylenedioxythiophene)), poly(3-alkylthiophenes), poly(3,4-dialkylthiophenes) or poly(thieno[3,4-b]thiophenes), and mixtures thereof. They are preferably used under their polystyrene sulfonate (PSS) form, e.g. polypyrroles-PSS or polythiophenes-PSS.

Specific examples of preferred conductive polymers are poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate) and poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate).

Conductive polymers are commercially available or may be prepared according to known methods. Polypyrroles polystyrene sulfonate, for example, can be synthesized by oxidation polymerization of pyrroles in aqueous medium, in the presence of poly(styrene

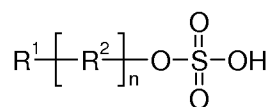
sulfonic) acid and ammonium persulfate as an oxidant. Procedures for converting the 3,4-ethylenedioxythiophene monomer to its polymeric form have been disclosed by the Bayer Corporation.

Preferred conductive polymers are water soluble or water dispersible, or soluble or dispersible in an alcohol or a mixture water/alcohol, so as to be able to be applied through a composition onto the surface of an optical article.

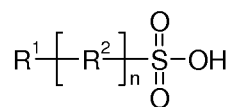
Conductive polymers are generally introduced in the antistatic coating composition under the form of a dispersion (or solution) of at least one conductive polymer in an aqueous or organic solvent, or a mixture of these solvents, preferably water, more preferably deionized water.

As examples of commercially available antistatic coating compositions which are conductive polymer dispersions may be cited Baytron® P or Baytron® PH 500 or Baytron P HC V 4, based on polythiophene, developed by Bayer and commercialized by H. C. Starck. They are aqueous dispersions of the polymer complex poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate), abbreviated as PEDT/PSS, which contain 1.2 to 1.3 % by weight of conductive polymer-PSS. Said composition leads to antistatic films which are inexpensive to produce, have a very good temperature resistance and are compatible with many material systems.

The additive responsible for the improvement of the antistatic properties of the film obtained from the inventive coating composition will now be described. Said additive is a compound of formula I or II:



I



II

or a salt thereof, wherein $n = 0$ or 1 , R^1 is H or a substituted or unsubstituted alkyl group, and R^2 is a substituted or unsubstituted arylene group, with the proviso that:

- the compound of formula II is not a fluorine containing surfactant,
- R^1 is not H when $n = 0$.

Preferably, the compound of formula II is not para-toluenesulfonic acid, and preferably not a salt thereof.

All compounds of formula I and II can be used under a salt form, such as, without limitation, a lithium salt, a potassium salt, a sodium salt, a cesium salt, a phosphonium salt, an ammonium (NH_4^+) salt, a substituted ammonium salt such as $\text{NH}_3^+\text{C}(\text{CH}_2\text{OH})_3$ or a quaternary ammonium salt.

In a preferred embodiment, n is 0 when the additive is a compound of formula I.

R^1 is preferably a substituted or unsubstituted alkyl group, more preferably an unsubstituted alkyl group. The R^1 alkyl group may be linear or branched, preferably linear. The R^1 alkyl group may be cyclic, polycyclic or acyclic, preferably acyclic. The R^1 alkyl group may

also comprise one or more C=C double bonds. Preferred compounds of formula I and II are those having a R¹ hydrophobic chain.

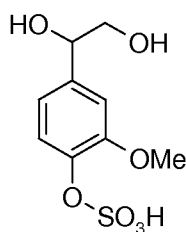
Non limiting examples of R¹ groups are CH₃, ethyl, n-propyl, n-butyl, n-hexyl, n-C₈H₁₇, n-decyl, n-C₁₂H₂₅, 2-ethylhexyl, 2-octyl, 7-ethyl-2-methyl-4-undecyl, 4-hydroxybi(cyclohexane)-4-yl, 2-hydroxy-3-(3-methoxy-phenoxy)-propane-1-yl, 1-heptene-2-yl. The R¹ group of compounds I and/or II preferably has more than 5 carbon atoms.

R², when present (n = 1), is preferably branched with the sulfate or sulfonate group and the R¹ group in para configuration. R² is preferably an unsubstituted arylene group. Non limiting examples of R² groups are phenylene, in particular 1-4-phenylene, biphenylene such as 1,4'-biphenylene or a substituted phenylene or biphenylene group such as tolylene and methoxyphenylene groups. R² is preferably a phenylene group, more preferably a para-disubstituted phenylene group.

Non limiting examples of substituents that may be borne by the R¹ and/or R² groups are hydroxyl, alkyloxy such as methoxy, and aryloxy groups.

Preferred sulfate compounds of formula I are those wherein n = 0 and R¹ is a C4-C25 alkyl chain, preferably a C4-C20 alkyl chain, more preferably a C5-C15 alkyl chain, even better a C6-C15 alkyl chain, ideally a C6-C12 alkyl chain. Preferably, R¹ is an unsubstituted linear alkyl chain.

Specific examples of compounds of formula I are 7-ethyl-2-methyl-4-undecyl sulfate sodium salt, Trizma[®] dodecyl sulfate, sodium octyl sulfate, sodium dodecyl sulfate, lithium dodecyl sulfate, ammonium dodecyl sulfate, sodium 2-ethylhexyl sulfate, hexyl sulfate sodium salt, methyl sulfate sodium salt and 4-hydroxy-3-methoxyphenylglycol sulfate having the following formula:



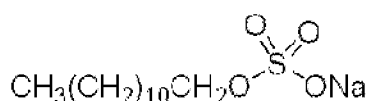
Preferred sulfonate compounds of formula II are those wherein n = 1, R² is a substituted or unsubstituted phenylene group, in particular a 1-4-phenylene group, and R¹ is a C4-C25 alkyl chain, preferably a C4-C20 alkyl chain, more preferably a C5-C15 alkyl chain, even better a C6-C15 alkyl chain, ideally a C6-C12 alkyl chain. Preferably, R¹ is an unsubstituted linear alkyl chain. Preferably, the compound of formula II is not a perfluoroalkyl benzenesulfonic acid salt, and also preferably not a perfluoroalkyl benzenesulfonic acid.

Specific examples of compounds of formula II are sodium 1-butanesulfonate, sodium 1-decanesulfonate, potassium [1,1'-biphenyl]-4-sulfonate, potassium octane-2-sulfonate, sodium

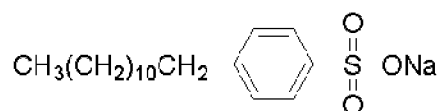
4-hydroxybi(cyclohexane)-4-sulfonate, sodium 1-heptene-2-sulfonate, sodium 2-hydroxy-3-(3-methoxy-phenoxy)-propane-1-sulfonate, sodium dodecyl benzene sulfonate.

Compounds of formula I or II can be readily synthesized according to known methods, but most of them are commercially available from Fluka® or Sigma-Aldrich® under a dry form or as a solution in e.g. water.

The preferred compound of formula I is sodium dodecyl sulfate (SDS) of formula:



The preferred compound of formula II is sodium dodecyl benzene sulfonate (SDBS) of formula:



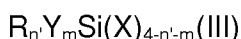
Compounds of formula I and II are small organic compounds of low molecular weight. They are preferably not polymeric compounds. Preferably, the molecular weight of the neutral form of compounds I and II (i.e. the sulfuric and sulfonic forms, respectively) is lower than or equal to 500 g/mol, more preferably lower than or equal to 450 g/mol, most preferably lower than or equal to 400 g/mol, even better lower than or equal to 350 g/mol, and ideally lower than or equal to 300 g/mol.

The compounds of formula I or II are used at very low concentrations and can represent from 0.01 to 2 % by weight, relative to the weight of the coating composition, preferably from 0.02 to 1 %, more preferably from 0.05 to 0.5 %, even better from 0.05 to 0.3 %, and optimally 0.05 to 0.2%. Using an excessive amount of compounds of formula I or II may lead to a loss of transmittance of the resulting coating, and/or an increase of the haze value.

The antistatic coating composition comprises at least one silicon containing binder of formula III. The binder is defined as a film-forming material, which is capable of improving adhesion of the antistatic coating to the underlying layer and/or the upper layer, and/or integrity of the antistatic coating. The binder generally allows strengthening abrasion and/or scratch resistance of the final optical article, depending on the binder nature.

The binder has to be compatible with the conductive polymer, i.e. not be detrimental to its antistatic properties, form a stable solution by avoiding precipitation of said polymer or aggregation thereof in more or less big particles, which would generate optical flaws.

The binder comprises at least one compound of formula:



or a hydrolyzate thereof, in which the R groups are identical or different and represent monovalent organic groups linked to the silicon atom through a carbon atom, the Y groups are

identical or different and represent monovalent organic groups linked to the silicon atom through a carbon atom and containing at least one epoxy function, the X groups are identical or different and represent hydrolyzable groups or hydrogen atoms, m and n' are integers such that m is equal to 1 or 2 and $n' + m = 1$ or 2.

5 The X groups may independently and without limitation represent H, alkoxy groups -O-R¹, wherein R¹ preferably represents a linear or branched alkyl or alkoxyalkyl group, preferably a C₁-C₄ alkyl group, acyloxy groups -O-C(O)R³, wherein R³ preferably represents an alkyl group, preferably a C₁-C₆ alkyl group, and more preferably a methyl or ethyl group, halogen groups such as Cl and Br, amino groups optionally substituted with one or two functional groups
10 such as an alkyl or silane group, for example the NHSiMe₃ group, alkyleneoxy groups such as the isopropenoxy group, trialkylsiloxy groups, for example the trimethylsiloxy group.

The X groups are preferably alkoxy groups, in particular methoxy, ethoxy, propoxy or butoxy, more preferably methoxy or ethoxy. In this case, compounds of formula III are alkoxysilanes.

15 The integers n' and m define three groups of compounds III: compounds of formula RYSi(X)₂, compounds of formula Y₂Si(X)₂, and compounds of formula YSi(X)₃. Among these compounds, epoxysilanes having the formula YSi(X)₃ are preferred.

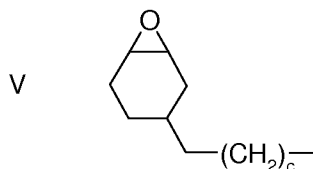
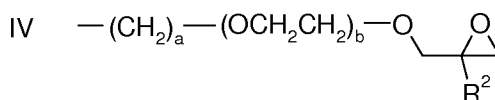
The monovalent R groups linked to the silicon atom through a Si-C bond are organic groups. These groups may be, without limitation, hydrocarbon groups, either saturated or
20 unsaturated, preferably C₁-C₁₀ groups and better C₁-C₄ groups, for example an alkyl group, preferably a C₁-C₄ alkyl group such as methyl or ethyl, an aminoalkyl group, an alkenyl group, such as a vinyl group, a C₆-C₁₀ aryl group, for example an optionally substituted phenyl group, in particular a phenyl group substituted with one or more C₁-C₄ alkyl groups, a benzyl group, a (meth)acryloxyalkyl group, or a fluorinated or perfluorinated group corresponding to the above
25 cited hydrocarbon groups, for example a fluoroalkyl or perfluoroalkyl group, or a (poly)fluoro or perfluoro alkoxy[(poly)alkyloxy]alkyl group.

The most preferred R groups are alkyl groups, in particular C₁-C₄ alkyl groups, and ideally methyl groups.

The monovalent Y groups linked to the silicon atom through a Si-C bond are organic
30 groups since they contain at least one epoxy function, preferably one epoxy function. By epoxy function, it is meant a group of atoms, in which an oxygen atom is directly linked to two adjacent carbon atoms or non adjacent carbon atoms comprised in a carbon containing chain or a cyclic carbon containing system. Among epoxy functions, oxirane functions are preferred, i.e. saturated three-membered cyclic ether groups.

35 Epoxysilanes compounds of formula (III) provide a highly cross-linked matrix. The preferred epoxysilanes have an organic link between the Si atom and the epoxy function that provides a certain level of flexibility.

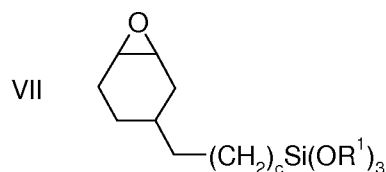
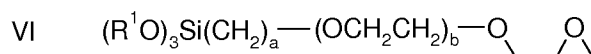
The preferred Y groups are groups of formulae IV and V:



in which R^2 is an alkyl group, preferably a methyl group, or a hydrogen atom, ideally a hydrogen atom, a and c are integers ranging from 1 to 6, and b is 0, 1 or 2.

The preferred group having formula IV is the γ -glycidoxypropyl group ($\text{R}^2 = \text{H}$, $a = 3$, $b = 0$) and the preferred (3,4-epoxycyclohexyl)alkyl group of formula V is the β -(3,4-epoxycyclohexyl)ethyl group ($c = 1$). The γ -glycidoxyethoxypropyl group may also be employed ($\text{R}^2 = \text{H}$, $a = 3$, $b = 1$).

Preferred epoxysilanes of formula III are epoxyalkoxysilanes, and most preferred are those having one Y group and three alkoxy X groups. Particularly preferred epoxytrialkoxysilanes are those of formulae VI and VII:



in which R^1 is an alkyl group having 1 to 6 carbon atoms, preferably a methyl or ethyl group, and a , b and c are such as defined above.

Examples of such epoxysilanes include but are not limited to glycidoxy methyl trimethoxysilane, glycidoxy methyl triethoxysilane, glycidoxy methyl tripropoxysilane, α -glycidoxy ethyl trimethoxysilane, α -glycidoxy ethyl triethoxysilane, β -glycidoxy ethyl trimethoxysilane, β -glycidoxy ethyl triethoxysilane, β -glycidoxy ethyl tripropoxysilane, α -glycidoxy propyl trimethoxysilane, α -glycidoxy propyl triethoxysilane, α -glycidoxy propyl tripropoxysilane, β -glycidoxy propyl trimethoxysilane, β -glycidoxy propyl triethoxysilane, β -glycidoxy propyl tripropoxysilane, γ -glycidoxy propyl trimethoxysilane, γ -glycidoxy propyl triethoxysilane, γ -glycidoxy propyl tripropoxysilane, 2-(3,4-epoxycyclohexyl) ethyltrimethoxysilane, 2-(3,4-epoxycyclohexyl) ethyltriethoxysilane. Other useful epoxytrialkoxysilanes are described in Patents US 4,294,950, US 4,211,823, US 5,015,523, EP 0614957 and WO 94/10230, which are hereby incorporated by reference. Among those silanes, γ -glycidoxypropyltrimethoxysilane (GLYMO) is preferred.

Preferred epoxysilanes of formula III having one Y group and two X groups include, but are not limited to, epoxydialkoxysilanes such as γ -glycidoxypropyl-methyl-dimethoxysilane, γ -glycidoxypropyl bis(trimethylsiloxy) methylsilane, γ -glycidoxypropyl-methyl-diethoxysilane, γ -

glycidoxypropyl-methyl-diisopropenoxysilane, and γ -glycidoxyethoxypropyl-methyl-dimethoxysilane. When epoxy dialkoxysilanes are used, they are preferably combined with epoxytrialkoxysilanes such as those described above, and are preferably employed in lower amounts than said epoxytrialkoxysilanes.

The choice of the binder is generally determined by the employed system of solvents in the coating composition, for it has to be soluble or dispersible in said system of solvents. Binders from different categories may be employed.

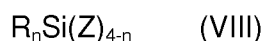
Binders according to the invention are soluble or dispersible in water or in an aqueous composition such as a hydro-alcoholic composition.

Preferably, the binder employed in the inventive antistatic coating composition does not contain any primary, secondary or tertiary amine groups. Preferably, the inventive antistatic coating composition does not contain any dendrimer, in particular a dendrimer containing one or more primary, secondary or tertiary amine groups.

The above described organofunctional binders form silica organosols. After having been subjected to hydrolysis, they generate interpenetrated networks by forming silanol groups, which are capable of establishing bonds with the underlying layer. They may act as adhesion promoters toward organic or mineral glass substrates. They may also act as cross-linking agents toward conductive polymers used under the form of polystyrene sulfonate salts and the like.

Antistatic coatings prepared from compositions according to the invention comprising at least one compound of formula (III) as a binder exhibit abrasion resistance properties, which are generally similar to or higher than those obtained from the corresponding compositions without any compound of formula I or II. Such coatings can therefore be used as transparent, antistatic hard coats.

In one embodiment of the invention, the binder of the antistatic composition further comprises at least one compound of formula:



or a hydrolyzate thereof, in which the R groups are identical or different and represent monovalent alkyl groups, the Z groups are identical or different and represent hydrolyzable groups or hydrogen atoms, and n is an integer equal to 0, 1 or 2, preferably 0, with the proviso that the Z groups do not all represent a hydrogen atom when n = 0, and preferably do not all represent a hydrogen atom.

Compounds of formula VIII or their hydrolyzates may be used to improve the cross-linking of the coating obtained from the curable composition of the invention, thereby providing higher hardness and abrasion-resistance.

Silanes of formula VIII bear three to four Z groups directly linked to the silicon atom, each leading to an OH group upon hydrolysis and one or two monovalent organic R groups linked to the silicon atom. It is worth noting that SiOH bonds may be initially present in the

compounds of formula VIII, which are considered in this case as hydrolyzates. Hydrolyzates also encompass siloxane salts.

The Z groups may represent hydrolyzable groups independently chosen from the hydrolyzable groups which have been previously cited when describing the X groups.

5 Preferably, the Z groups are hydrolyzable groups which are identical or different.

The most preferred R groups are C₁-C₄ alkyl groups, such as methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl, preferably methyl groups.

Most preferred compounds of formula II are those having formula Si(Z)₄. Examples of such compounds are tetraalkoxysilanes such as tetraethoxysilane Si(OC₂H₅)₄ (TEOS),
10 tetramethoxysilane Si(OCH₃)₄ (TMOS), tetra(n-propoxy)silane, tetra(i-propoxy)silane, tetra(n-butoxy)silane, tetra(sec-butoxy)silane or tetra(t-butoxy)silane, preferably TEOS.

Compounds of formula VIII may also be chosen from compounds of formula RSi(Z)₃, for example methyl triethoxysilane (MTEOS).

Silanes present in the curable antistatic composition may be hydrolyzed partially or
15 totally, preferably totally. Hydrolyzates can be prepared in a known manner, e.g. such as disclosed in FR 2702486 and US 4,211,823. Hydrolysis catalysts such as hydrochloric acid or acetic acid may be used to promote the hydrolysis reaction over the condensation reaction.

Some antistatic coating compositions comprising a binder of formula III and a conductive polymer are commercially available and can be used in the invention, such as for example
20 compositions based on the Baytron[®] P dispersion, all commercialized by H. C. Starck: CPP 105D (GLYMO binder), CPP 116.6D and CPP 134.18D (polyurethane + GLYMO binders). A preferred coating composition is composition CPP 105D, which dry extract is around 1.5% by weight. It leads to antistatic coatings having good adhesion properties to organic or mineral glass substrates.

25 The antistatic coating composition may also comprise other binders in addition to the binder of formula III, for example homopolymers or copolymers of the following monomers: styrene, vinylidene chloride, vinyl chloride, alkyl acrylates, alkyl methacrylates, (meth)acrylamides, polyester homopolymers or copolymers, poly(urethane-acrylate), poly(ester-urethane), polyether, vinyl polyacetate, polyepoxyde, polybutadiene, polyacrylonitrile,
30 polyamide, melamine, polyurethane, polyvinyl alcohol, copolymers thereof, and mixtures thereof. Other non limiting examples of additional binders are polyurethane latexes optionally comprising polyester moieties (e.g. Witcobond[®] 240 or 234), poly(meth)acrylic latexes, polyester latexes, ureidoalkyl alkoxysilanes, vinylsilanes, allylsilanes, (meth)acrylic silanes, carboxylic silanes. Some antistatic coating compositions comprising an additional binder (i.e. a binder
35 different from formula III) and a conductive polymer are commercially available and can be used in the invention, such as for example compositions CPUD-2 (polyurethane binder) and CPP 103D (aliphatic polyester-polyurethane binder) commercialized by H. C. Starck.

The binder, which includes compounds of formula III and VIII but not fillers, is generally comprised in the antistatic coating composition in an amount ranging from 1 to 20% by weight based on the total weight of the antistatic composition, preferably from 2 to 15%.

In some embodiments, the antistatic composition does not comprise any compound of formula VIII. Preferably, the antistatic composition does not comprise any compounds of formula VIII when fillers are present in said composition.

Since the antistatic coating composition comprises a binder of formula III, it may be cross-linked or cured owing to the presence of at least one cross-linking agent which preferably is soluble or dispersible in water. These cross-linking agents are well known and react with functional groups of the binder, such as carboxyl or hydroxyl groups. They may be chosen from polyfunctional aziridines, methoxyalkylated melamine or urea resins, for example methoxyalkylated melamine/formaldehyde and urea/formaldehyde resins, epoxy resins, carbodiimides, polyisocyanates, triazines and blocked polyisocyanates. Preferred cross-linking agents are aziridines, in particular trifunctional aziridines.

The antistatic composition optionally comprises a catalytic amount of at least one curing catalyst, so as to accelerate the curing step. Examples of curing catalysts are photo-initiators that generate free radicals upon exposure to ultraviolet light or heat such as organic peroxides, azo compounds, quinones, nitroso compounds, acyl halides, hydrazones, mercapto compounds, pyrylium compounds, imidazoles, chlorotriazines, benzoin, benzoin alkyl ethers, diketones, acetophenones, and mixtures thereof.

The antistatic composition may also comprise a curing catalyst such as aluminum acetylacetonate $\text{Al}(\text{AcAc})_3$, a hydrolyzate thereof or carboxylates of metals such as zinc, titanium, zirconium, tin or magnesium. Condensation catalysts such as saturated or unsaturated polyfunctional acids or acid anhydrides may also be used, in particular maleic acid, itaconic acid, trimellitic acid or trimellitic anhydride. Numerous examples of curing and/or condensation catalysts are given in "Chemistry and Technology of the Epoxy Resins", B. Ellis (Ed.) Chapman Hall, New York, **1993** and "Epoxy Resins Chemistry and Technology" 2^{ème} edition, C. A. May (Ed.), Marcel Dekker, New York, **1988**.

In general, the catalysts described above are used according to the invention in an amount ranging from 0.01 to 10%, preferably from 0.1 to 5% by weight based on the total weight of the curable antistatic composition.

In some embodiments, the antistatic composition comprises fillers, generally nanoparticles (or nanocrystals), for increasing the hardness and/or the refractive index of the cured coating. The nanoparticles may be organic or inorganic. A mixture of both can also be used. Preferably, inorganic nanoparticles are used, especially metallic or metalloid oxide, nitride or fluoride nanoparticles, or mixtures thereof. The nanoparticles (fillers) are preferably not electrically conductive.

By "nanoparticles", it is meant particles which diameter (or longest dimension) is lower than 1 μm , preferably lower than 150 nm and still better lower than 100 nm. In the present invention, fillers or nanoparticles preferably have a diameter ranging from 2 to 100 nm, more preferably from 2 to 50 nm, and even better from 5 to 50 nm.

5 Suitable inorganic nanoparticles are for example nanoparticles of aluminum oxide Al_2O_3 , silicon oxide SiO_2 , zirconium oxide ZrO_2 , titanium oxide TiO_2 , antimony oxide Sb_2O_5 , tantalum oxide Ta_2O_5 , zinc oxide, tin oxide SnO_2 , indium oxide, cerium oxide, Si_3N_4 , MgF_2 or their mixtures.

10 It is also possible to use particles of mixed oxides or composite particles, for example those having a core/shell structure. Using different types of nanoparticles allows making hetero-structured nanoparticles layers.

15 Preferably, the nanoparticles are particles of aluminum oxide, tin oxide, zirconium oxide or silicon oxide SiO_2 , more preferably SiO_2 nanoparticles. Mineral fillers are preferably used under colloidal form, i.e. under the form of fine particles dispersed in a dispersing medium such as water, an alcohol, a ketone, an ester or mixtures thereof, preferably an alcohol.

When fillers are present, they are generally used in an amount ranging from 0.5 to 10% by weight based on the total weight of the antistatic composition, preferably from 1 to 8%. In some embodiments, the antistatic composition does not comprise any filler such as nanoparticles.

20 The antistatic coating composition comprises at least one solvent, preferably a polar solvent, like water, an alcohol, or mixtures thereof, preferably a mixture of water and a water-miscible alcohol, e.g. methanol, ethanol, n-propanol, isopropanol, n-butanol, isobutanol, sec-butanol, tert-butanol, n-amylic alcohol, isoamylic alcohol, sec-amylic alcohol, tert-amylic alcohol, 1-ethyl-1-propanol, 2-methyl-1-butanol, 1-methoxy-2-propanol n-hexanol, cyclohexanol, ethyl
25 cellosolve (monoethoxy ethylene glycol), and ethylene glycol.

It is also possible to add an appropriate amount of another hydrophilic organic solvent in said composition in order to improve the dissolution of the conductive polymer, or increase compatibility of the binder with the composition. To this end, organic solvents such as NMP, acetone, tetrahydrofuran, DMSO, DMAc, triethylamine or DMF may be employed, without being
30 limited to this solvent list. However, the antistatic coating composition preferably only comprises environmentally benign solvents, such as water and/or $\text{C}_1\text{-C}_4$ alcohols.

The solvent or mixture of solvents may represent from 50 to 99 % by weight, relative to the weight of the coating composition, preferably from 50 to 90 %, more preferably from 60 to 90 %.

35 The antistatic coating composition may also comprise at least one non ionic or ionic surfactant, i.e. anionic, cationic or amphoteric surfactant, to improve the wettability of the coating solution or the optical quality of the deposit. A particularly preferred class of surfactants

comprises fluorinated surfactants, preferably anionic fluorinated surfactants. Said at least one surfactant is different from compounds of formula I and II.

Fluorinated surfactants are known and described generally in "Fluorinated Surfactants" by E. Kissa, Surfactants Science Series, Vol. 50 (Marcel Dekker, New York 1994). Fluorinated surfactants include perfluoroalkanoic acids and salts thereof, in particular perfluorooctanoic acids and salts thereof, such as ammonium perfluorooctanoic acid, fluorinated polyethers or perfluoropolyether surfactants such as disclosed in EP 1059342, EP 712882, EP 752432, EP 816397, US 6,025,307, US 6,103,843 and US 6,126,849. Further fluorinated surfactants are disclosed in US 5,229,480, US 5,763,552, US 5,688,884, US 5,700,859, US 5,804,650, US 5,895,799, WO 00/22002 and WO 00/71590. Fluorinated polyethers derived from hexafluoropropyleneoxide have been described in US 2005/096244. Another class of fluorinated surfactants includes fluorocarbon modified polysiloxane surfactants, e.g. polyalkyleneoxide-modified heptamethyltrisiloxane allyloxypolyethyleneglycol surfactant.

The surfactant or mixture of surfactants may represent from 0.001 % to 5 % by weight, relative to the weight of the coating composition, preferably from 0.02 to 1 %, more preferably from 0.05 to 0.5 %, even better from 0.05 to 0.3 %, and optimally 0.05 to 0.2%.

The combination of at least one compound of formula I or II and at least one non ionic or ionic surfactant (preferably a fluorinated surfactant, more preferably an anionic fluorinated surfactant) in the inventive antistatic composition is particularly interesting, as it increases the abrasion resistance of the resulting coating. This surprising effect is evidenced in the experimental part.

The antistatic composition may also contain various additives conventionally used in polymerizable compositions, in conventional proportions. These additives include stabilizers such as antioxidants, UV light absorbers, light stabilizers, anti-yellowing agents, adhesion promoters, dyes, photochromic agents, pigments, rheology modifiers, lubricants, cross-linking agents, photo-initiators fragrances, deodorants and pH regulators (particularly in the case of antistatic agents such as polypyrroles or polyanilines). They should neither decrease the effectiveness of the antistatic agent nor deteriorate optical properties of the article.

The antistatic coating composition according to the invention generally has a theoretical dry extract weight which represents less than 50 % of the total weight of the composition, and preferably ranging from 0.2 to 30 %, even better from 0.2 to 20 %, which includes both required compounds (antistatic agent, binder...) and optional compounds.

By "theoretical dry extract weight of a component in a composition," it is meant the theoretical weight of solid matter of this component in said composition. The theoretical dry extract weight of a composition is defined as the sum of the theoretical dry extract weights of each of its components. As used herein, the theoretical dry extract weight of compounds of formula III or VIII is the calculated weight in $R_{n'}Y_mSi(O)_{(4-n'-m)/2}$ or $R_nSi(O)_{(4-n)/2}$ units, wherein R, Y, n, n' and m are such as defined previously.

Although the weight content of conductive polymers in the coating composition is not particularly limited, it preferably ranges from 0.04 to 15 % by weight relative to the total weight of the composition, more preferably from 0.05 to 5 %, better from 0.05 to 0.5% and even better from 0.05 to 0.35%. Beyond 15-20 % by weight, the antistatic coating composition is generally too viscous and the resulting antistatic coating may show transmittance lower than 85%, while below 0.05 %, the composition may be too diluted and the resulting coating may not exhibit antistatic properties.

Preferably, the binder III is used in such an amount that the ratio of total weight of solid binder components (dry extract weight of binder) / total weight of the composition ranges from 2 to 15%, preferably from 3 to 12%.

Preferably, the ratio of conductive polymers weight/dry extract weight of solid binder components in the coating composition ranges from 0.4 to 10%, more preferably from 0.4 to 5%, even better from 0.4 to 3%, the best range being from 0.4 to 2%. The use such a low content of conductive polymer is made possible by the addition of the inventive compound of formula I or II, which allows to obtain elevated antistatic properties.

The antistatic coating composition allows to achieve a sufficient electrical conduction, so that it is not necessary to add additional conductive compounds.

In a preferred embodiment, the antistatic composition according to the invention comprises less than 1% by weight based on the total weight of the antistatic composition, of carbon nanotubes or other electrically conductive fillers, which are generally oxides such as ITO (tin oxide doped with indium), ATO (tin oxide doped with antimony), zinc antimonate (ZnSb_2O_6), indium antimonate (InSbO_4), or SrTiO_3 , preferably less than 0.5% by weight and even better 0%. Within the meaning of the invention, oxides such as SiO_2 , Al_2O_3 , ZrO_2 , SnO_2 and mixtures thereof are not considered to be electrically conductive oxides (fillers). Preferably, the antistatic composition does not contain any carbon nanotubes or electrically conductive fillers.

The inventive antistatic coating is formed at the surface of an optical article by liquid phase deposition or lamination according to any appropriate method, starting from the above described liquid antistatic coating composition. Application of said composition may be carried out, without limitation, by spin coating, dip coating, spray coating, brush coating, roller coating. Spin coating and dip coating are preferred.

After application of the antistatic coating composition onto the surface of the optical article, the composition may be dried or cured, if necessary, according to any appropriate method, for example drying with air, in an oven or by using a drier, so as to provide a conductive transparent film. Generally, a temperature of 50-130°C is employed. A higher temperature and/or a longer drying/curing step sometimes allow to improve abrasion resistance of the antistatic coating to the underlying coating or article. The drying/curing step comprises evaporation of the solvents and solidification of the binder. In the case of cross-linkable binders,

the deposited composition is exposed to an appropriate energy source so as to initiate polymerization and curing of the binder.

Thickness of the antistatic coating in the final optical article preferably ranges from 5 to 5000 nm, more preferably from 5 to 3000 nm, even more preferably from 50 to 2000 nm.

5 The compositions according to the invention provide coatings with better antistatic properties than those with the same thickness obtained from compositions without any additive. This also allows to prepare antistatic coatings having less thickness than conventional antistatic coatings but the same or a higher level of antistatic performance, thereby increasing the optical transmittance of the coating, or to prepare antistatic coatings having a higher thickness than
10 conventional antistatic coatings and consequently a higher level of antistatic performance, but that still remain optically transparent.

Most conductive polymers absorb in the visible range, but the conductive polymer content is low in the present antistatic coating. As a consequence, thicknesses as high as a few micrometers can be used for said coating without significantly decreasing the optical
15 transparency of the coated article. However, if the thickness of the antistatic coating becomes too high ($> 5\text{-}10\text{ }\mu\text{m}$), the relative transmission factor of light in the visible range of the optical article may significantly drop. The PEDT/PSS polymer, for example, absorbs high wavelengths of the visible range (near IR). A too thick film made of this polymer will consequently have a bluish color. On the contrary, if thickness of the AS coating is too thin, it does not exhibit
20 antistatic properties.

The present coating composition can be used in the ophthalmic lens industry to prepare antistatic lenses, but also for general antistatic purpose in the field of photographic films, electronics or food packaging and imaging materials. Particular non limiting uses include electromagnetic windows, optically transparent conductors for display devices and
25 electromagnetic radiation shielding.

Its advantages are numerous and include applicability to most of substrates with good adhesion, in particular plastic substrates, and the production of optical articles having high transmittance, low haze, high electrical conductivity, excellent antistatic properties while maintaining excellent adhesion of the coatings.

30 The present invention provides optical articles having charge decay times ≤ 500 milliseconds, preferably ≤ 200 milliseconds, more preferably ≤ 150 milliseconds and better ≤ 100 milliseconds, when coated on one main surface with the above described antistatic coating or the two main faces of the optical article. The examples that will be described later only show the convex side of coatings.

35 The final optical articles do preferably not absorb light in the visible range (or little), which means herein that when coated on one side with the inventive antistatic coating, the optical article has a luminous absorption in the visible range due to the antistatic coating of preferably 1% or less, more preferably less than 1%, and/or a relative light transmission factor in the

visible spectrum, Tv, preferably higher than 90%, more preferably higher than 91%, and even more preferably higher than 91.5%. Preferably, both features are simultaneously satisfied and can be reached by carefully controlling thicknesses of the coatings and the content of conductive polymers. As used herein, a "transparent" optical article is an optical article having a Tv higher than 90%, more preferably higher than 91%, and even more preferably higher than 91.5%. The Tv factor is such as defined in the standard NF EN 1836 and corresponds to the 380-780 nm wavelength range.

In an alternative embodiment, the optical article may be tinted or dyed and absorb light in the visible range.

The final optical articles prepared according to the invention preferably have low haze characteristics. Haze is a measurement of the transmitted light scattered more than 2.5° from the axis of the incident light. The smaller the haze value, the lower the degree of cloudiness. The haze value of the present optical articles is preferably less than 0.8%, more preferably less than 0.5%, even better less than 0.4 and ideally less than 25%.

The invention also relates to a process for preparing a transparent, antistatic and abrasion- and/or scratch-resistant optical article, comprising:

- providing an optical article comprising a substrate having at least one main surface,
- applying onto at least part of said at least one main surface of the substrate a curable composition such as described previously, and curing said composition.

The present optical articles can be processed simply and at low temperature ($\leq 100^{\circ}\text{C}$), using environment friendly solvents (alcohol or water/alcohol co-solvent). The present process is flexible and allows incorporation of other functional coatings onto the substrate.

The invention further relates to the use of a compound of formula I or II in a curable composition, for improving the antistatic properties (electrical conductivity) of the coating obtained from curing said composition.

Now, the present invention will be described in more detail with reference to the following examples. These examples are provided only for illustrating the present invention and should not be construed as limiting the scope and spirit of the present invention.

EXAMPLES

1. Testing methods

The following test procedures were used to evaluate the optical articles prepared according to the present invention. Three samples for each system were prepared for measurements and the reported data were calculated in the average of three data.

a) Charge decay time

In the present patent application, charge decay times of optical articles which have been beforehand subjected to a corona discharge at 9000 volts were measured using JCI 155v5 Charge Decay Test Unit from John Chubb Instrumentation at 25.4°C and 50% relative humidity.

The unit was set up with JCI 176 Charge Measuring Sample Support, JCI 191 Controlled Humidity Test Chamber, JCI 192 Dry Air Supply Unit and Calibration of voltage sensitivity and decay time measurement performance of JCI 155 to the methods specified in British Standard and Calibration voltage measurements and resistor and capacitor values traceable to National Standards.

b) Dry Adhesion test (crosshatch test)

Dry adhesion of the transferred coatings was measured using the cross-hatch adhesion test according to ASTM D3359-93, by cutting through the coatings a series of 5 lines, spaced 1 mm apart with a razor, followed by a second series of 5 lines, spaced 1 mm apart, at right angles to the first series, forming a crosshatch pattern comprising 25 squares. After blowing off the crosshatch pattern with an air stream to remove any dust formed during scribing, clear cellophane tape (3M SCOTCH® n° 600) was then applied over the crosshatch pattern, pressed down firmly, and then rapidly pulled away from coating in a direction perpendicular to the coating surface. Application and removal of fresh tape was then repeated two additional times. Adhesion is rated as follows (0 is the best adhesion, 1-4 is in the middle, and 5 is the poorest adhesion):

Table 1

Adhesion score	Squares removed	Area % left intact
0	0	100
1	< 1	> 96
2	1 to 4	96-84
3	> 4 to 9	83-64
4	> 9 to 16	63-36
5	> 16	< 36

c) Determination of the abrasion resistance ("ISTM Bayer test" or "Bayer alumina")

The Bayer abrasion test is a standard test used to determine the abrasion resistance of curved/lens surfaces. Determination of the Bayer value was performed in accordance with the standards ASTM F735-81 (Standard Test Method for Abrasion Resistance of Transparent Plastics and Coatings Using Oscillating Sand Method), except that the sand is replaced by alumina.

Per this test, a coated lens and an uncoated lens (reference lens of similar curvature, diameter, thickness and diopter) were subjected to an oscillating abrasive box (using

approximately 500 g of aluminum oxide ZF 152412 supplied by Specialty Ceramic Grains, former Norton Materials) for 300 cycles of abrasion in 2 minutes.

The haze H of both the reference and coated sample were then measured with a Haze Guard Plus meter, in accordance with ASTM D1003-00, before and after the test has been performed. The results are expressed as a calculated ratio of the reference lens to the coated lens (Bayer value = $H_{\text{standard}} / H_{\text{sample}}$). The Bayer value is a measure of the performance of the coating, with a higher value meaning a higher abrasion resistance.

d) Scratch-resistance: Hand Steel wool test (HSW)

The HSW test was implemented on the convex side of the lens only. Waiting time of 24 hours is respected to perform the test if an antireflection coating is deposited on the lens.

The lens was manually abraded with a steel wool perpendicularly to fibers direction performing 5 back and forth (with an amplitude from 4 to 5 cm) keeping an index finger constant pressure on the steel wool. Strength pressed on the steel wool can be evaluated with a balance: fix the lens on the balance plate with adhesive tape and press down the lens with the index finger exercising normally strength on the lens. This strength is about 5 Kg during the first way and about 2.5Kg during the return way. Lenses were visually inspected and noted according to the following table. The higher is the note, the more abraded is the lens.

Number of scratches	> 50	11-50	≤ 10
Note	5	3	1
Risk level	High	Acceptable	Low

e) Haze value, Tv and thickness

The haze value of the final optical article was measured by light transmission utilizing the Haze-Guard Plus haze meter from BYK-Gardner (a color difference meter) according to the method of ASTM D1003-00, which is incorporated herein in its entirety by reference. All references to "haze" values in this application are by this standard. The instrument was first calibrated according to the manufacturer's directions. Next, the sample was placed on the transmission light beam of the pre-calibrated meter and the haze value was recorded from three different specimen locations and averaged. Tv was measured using the same device.

Thickness of the films was evaluated by ellipsometer (thickness < 1μm) equipped with M-44™, EC-270 and LPS-400 with 75W Xenon Light Source from J. A. Woollam Co. Inc. or with a Metricon Model 2010 Prism Coupler apparatus (thickness > 1μm) from Metricon Corporation.

2. Experimental details

a) General considerations

Antistatic hard coating solutions were prepared by mixing GLYMO, 0.1 N HCl and an SiO₂ nanoparticle aqueous dispersion in methanol (15 nm size, solid content (or dry extract) 33-35%), under agitation for 12 h, followed by dispersing with 2-butanol (except for examples C3 and 8-11), Al(AcAc)₃, a Baytron® PH500 (1.2 wt% of conductive polymer in the Baytron® PH500 aqueous solution) aqueous solution, optionally a fluorinated surfactant (FC-4430) and either an additive according to the invention (The additive was first dissolved in methanol, water or 1:1 w/w methanol/water before adding into the mixture to get a well-dispersed 20 wt% solution, or 5 wt% solution in examples C3 and 8-11) or no additive (comparative examples C1, C2 and C3). See Table 1 below.

Table 1

Example	Additive
1 (invention)	sodium dodecyl benzene sulfonate
2-7 (invention)	sodium dodecyl sulfate
8	sodium 1-butane sulfonate
9	sodium octyl sulfate
10-11	sodium 1-decane sulfonate
C1, C2, C3	—

The SiO₂ nanoparticles aqueous dispersion (A2034, 33-35 wt% of nanoparticles, ~15 nm diameter) was purchased from EKa Chemicals. FC-4430 surfactant was purchased from 3M.

b) Preparation of coated optical articles

The optical articles used in the examples were round lenses (plano or -2.00 with a diameter of 68 mm) comprising an ORMA® substrate (obtained by polymerizing CR-39® diethylene glycol bis(allyl carbonate) monomer).

The convex surface of the substrate was first corona treated and then spin-coated at 500/1000 rpm with an antistatic composition, which was pre-cured at 75°C for 15 minutes and post-cured at 100°C for 3 hours. The final coating had a thickness of 1.5-2.0 μm (1.7μm in average).

c) Details of coating formulations

The coating formulations used in the examples are described in Table 2. The figures in the tables are weight percentages. In examples 4-7 and comparative example 2, the amount of Baytron® PH500 was decreased to 8.4wt% for each coating formulation (9.2 wt% in examples 1-3 and C1) and the amount of additive of formula I was varied from 0.1wt% till 0.5wt%.

The coating solutions of examples C3 and 8-11 were all filtered (1 μ m pore size), except the coating solution of example 8.

Table 2

Example	C1	1	2	3	C2	4	5	6	7
GLYMO	13.56	13.56	13.56	13.56	13.56	13.56	13.56	13.56	13.56
0.1N HCl	3.75	3.75	3.75	3.75	3.75	3.75	3.75	3.75	3.75
SiO ₂ nanoparticles (*)	18.24	18.24	18.24	18.24	19.04	19.04	19.04	19.04	19.04
MeOH	31.9	31.9	31.9	31.82	31.9	31.9	31.9	31.9	31.9
Butanol	2.24	2.24	2.24	2.24	2.24	2.24	2.24	2.24	2.24
H ₂ O	20.1	20.1	20.1	20.1	20.10	20.00	19.90	19.80	19.60
Al(AcAc) ₃	0.91	0.91	0.91	0.91	0.91	0.91	0.91	0.91	0.91
Fluorinated surfactant	0.1	0	0	0.1	0.1	0.1	0.1	0.1	0.1
Baytron [®] PH500	9.2	9.2	9.2	9.2	8.40	8.40	8.40	8.40	8.40
Additive (**)	0	0.1	0.1	0.08	0	0.1	0.2	0.3	0.5
Total	100	100	100	100	100	100	100	100	100

5

Table 2 (continued)

Example	C3	8	9	10	11
GLYMO	13.6	13.6	13.6	13.6	13.6
0.1N HCl	3.26	3.26	3.26	3.26	3.26
SiO ₂ nanoparticles (*)	18.18	18.18	18.18	18.18	18.18
MeOH	35.93	35.93	35.93	35.95	35.93
Butanol	0	0	0	0	0
H ₂ O	19.48	19.4	19.4	19.42	19.4
Al(AcAc) ₃	0.95	0.95	0.95	0.95	0.95
Fluorinated surfactant	0.1	0.1	0.1	0.1	0.1
Baytron [®] PH500	8.5	8.5	8.5	8.5	8.5
Additive (**)	0	0.08	0.08	0.04	0.08
Total	100	100	100	100	100

(*) Aqueous dispersion

(**) weight of additive in solid form

10 d) Coating performances

The performance test data of the prepared antistatic optical articles are collected in Table 3.

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Table 3

Example	Tv (%)	Haze (%)	Dry adhesion	ISTM Bayer	HSW	Charge decay time (ms)
C1 (Ref.)	91.6	0.15	0	7.10	1	130
1	91.7	0.13	0	5.91	1	48.8
2	91.7	0.15	0	5.83	1	37.8
3	91.7	0.14	0	7.18	1	28.3
C2 (Ref.)	91.7	0.14	0	5.88	3	355
4	91.4	0.26	0	5.91	3	44.9
5	90.6	0.51	0	8.21	3	42
6	89.7	1.08	0	7.89	3	29.3
7	87.1	1.55	0	7.44	3	21.4
C3	91.9	0.18	0	6.87	3	305
8	91.4	0.98	0	7.93	3	83.9
9	92.2	0.13	0	7.66	3	127
10	92.1	0.13	0	7.65	3	135
11	92.2	0.12	0	8.76	3	208

As can be seen from examples 1-7, C1 and C2, all the additives according to the invention (SDS or SDBS) improve the antistatic properties of the coatings, leading to charge decay times of 20-50 ms as compared to the same coatings without additive (130-350 ms). The additives of examples 8-11 also improve the antistatic properties of the coatings, as compared to example C3.

The antistatic coating remains highly transparent in the visible range after modification with the additive (transmittance: 91-92%, haze generally < 0.5%), except when high amounts of additive are used: the optical articles of examples 5-7 exhibit high haze and low transmittance, despite excellent abrasion resistance. It can be concluded that increasing the amount of additive generally decreases the charge decay time but lowers transparency, while other performances are maintained or improved.

It is worth noting that the simultaneous use of an additive of formula I or II and of an additional surfactant (preferably a fluorinated surfactant) leads to a coating that exhibits high transmittance, low haze and improved antistatic and abrasion resistance.

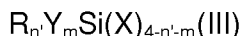
As a conclusion, the optical articles can be coated with the inventive coating so as to exhibit at the same time excellent abrasion resistance (ISTM Bayer > 5), scratch resistance, antistatic properties, high optical transparency with about 91-92% of transmittance, and low haze, while maintaining excellent adhesion to the underlying coating (crosshatch test 0).

CLAIMS

1. A curable composition, providing, upon curing, a transparent, antistatic coating, comprising:

5 a) at least one conductive polymer,

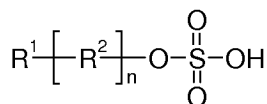
b) at least one binder chosen from compounds of formula:



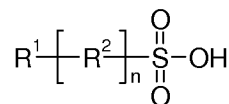
or hydrolyzates thereof, in which the R groups are identical or different and represent monovalent organic groups linked to the silicon atom through a carbon atom, the Y groups are
10 identical or different and represent monovalent organic groups linked to the silicon atom through a carbon atom and containing at least one epoxy function, the X groups are identical or different and represent hydrolyzable groups or hydrogen atoms, m and n' are integers such that m is equal to 1 or 2 and n' + m = 1 or 2.

c) at least one solvent, and

15 d) at least one additive of formula I or II:



I



II

or a salt thereof, wherein n = 0 or 1, R¹ is H or a substituted or unsubstituted alkyl group, and R² is a substituted or unsubstituted arylene group, with the proviso that:

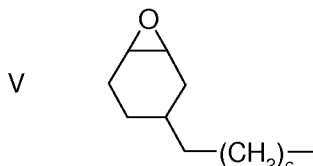
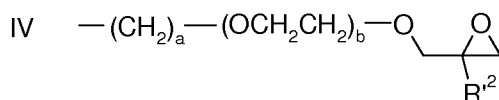
- the compound of formula II is not a fluorine containing surfactant,
 - R¹ is not H when n = 0.
- 20

2. The composition according to claim 1, wherein the at least one additive is a compound of formula I in which n = 0 and R¹ is a C4-C25 alkyl chain, preferably a C6-C15 alkyl chain.

3. The composition according to claim 1, wherein the at least one additive is a compound of formula II in which n = 1, R² is a substituted or unsubstituted phenylene group, and R¹ is a C4-
25 C25 alkyl chain, preferably a C6-C15 alkyl chain.

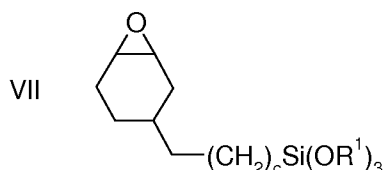
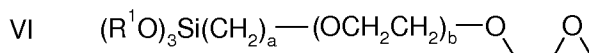
4. The composition according to claim 1, wherein the at least one additive of formula I or II is sodium dodecyl sulfate or sodium dodecyl benzene sulfonate.

5. The composition according to any one of the preceding claims, wherein the Y groups are chosen from the groups of formulae IV and V:



in which R'^2 is an alkyl group, preferably a methyl group, or a hydrogen atom, ideally a hydrogen atom, a and c are integers ranging from 1 to 6, and b is 0, 1 or 2.

6. The composition according to claim 5, wherein the compound of formula III is chosen from epoxytrialkoxysilanes of formula VI or VII:



in which R^1 is an alkyl group having 1 to 6 carbon atoms, a and c are integers ranging from 1 to 6, and b is 0, 1 or 2.

7. The composition according to any one of the preceding claims, wherein the at least one additive of formula I or II represents from 0.01 to 2 % by weight, relative to the weight of the coating composition, preferably from 0.02 to 1 %.

8. The composition according to any one of the preceding claims, wherein the molecular weight of the neutral form of said at least one additive of formula I or II is lower than or equal to 500 g/mol, more preferably lower than or equal to 400 g/mol.

9. The composition according to any one of the preceding claims, wherein the at least one conductive polymer is chosen from polyanilines, polypyrroles, polythiophenes, polythienothiophenes, polyethylene-imines, polyselenophenes, polyacetylenes, poly(allylamines), preferably from polythiophenes, more preferably polythiophenes polystyrene sulfonates.

10. The composition according to any one of the preceding claims, further comprising fillers, preferably nanoparticles of at least one metal or metalloid oxide.

11. The composition according to any one of the preceding claims, further comprising at least one non ionic or ionic surfactant, preferably at least one fluorinated surfactant, more preferably at least one anionic fluorinated surfactant.

12. An optical article comprising a substrate, wherein the substrate is at least partially coated with a transparent antistatic coating formed by depositing onto the substrate and curing a curable composition according to any one of claims 1 to 11.

13. The optical article of claim 12, further defined as having a relative light transmission factor in the visible spectrum T_v higher than 90%, preferably higher than 91%.

14. The optical article of any one of claims 12 to 13, further defined as being a lens or lens blank, preferably an ophthalmic lens or lens blank.

15. The optical article of any one of claims 12 to 14, further defined as having a charge decay time ≤ 500 milliseconds, preferably ≤ 200 milliseconds and better ≤ 100 milliseconds.

16. The optical article of any one of claims 12 to 15, wherein the thickness of the antistatic coating ranges from 5 to 5000 nm, more preferably from 5 to 3000 nm, even better from 50 to 2000 nm.

17. A process for preparing a transparent, antistatic optical article, comprising:

- 5
- providing an optical article comprising a substrate having at least one main surface,
 - applying onto at least part of said at least one main surface of the substrate a curable composition according to any one of claims 1 to 11, and curing said composition.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2009/067979

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09D5/24
ADD.

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)
C09D

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 practical, search terms used)

EPO-Internal, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2008/141981 A1 (ESSILOR INT [FR]; ZHENG HAIPENG [US]) 27 November 2008 (2008-11-27) the whole document	1-17
A	DE 42 29 192 A1 (BAYER AG [DE]) 3 March 1994 (1994-03-03) the whole document	1-17
A	EP 0 825 219 A2 (BAYER AG [DE]) 25 February 1998 (1998-02-25) the whole document	1-17



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
- "E" earlier document but published on or after the international filing date
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- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "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
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- "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.
- "&" document member of the same patent family

Date of the actual completion of the international search

29 April 2010

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2009/067979

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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