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(54) **COLLOIDAL COATING DISPERSION**

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(57) **ABSTRACT**

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Disclosed are a colloidal coating dispersion containing electrochromic polymer particles, a method for manufacturing the colloidal coating dispersion, the use of the colloidal coating dispersion for depositing at least one electrochromic layer on a substrate, and an article including a layer deposited from the colloidal coating dispersion.

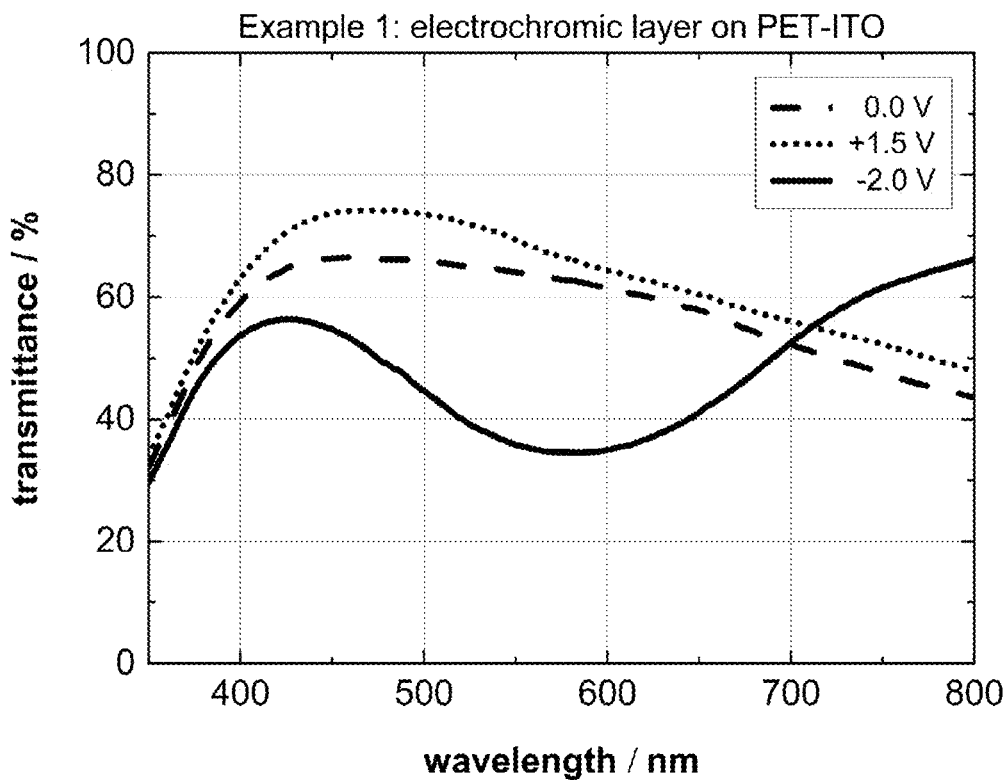


Fig. 1

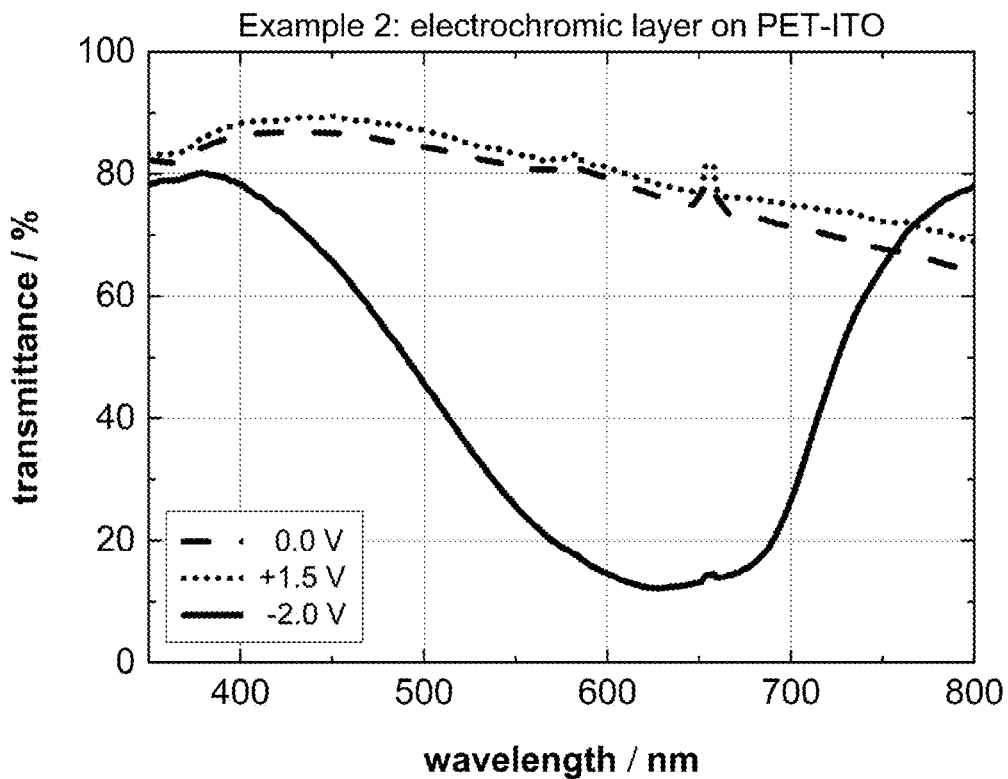


Fig. 2

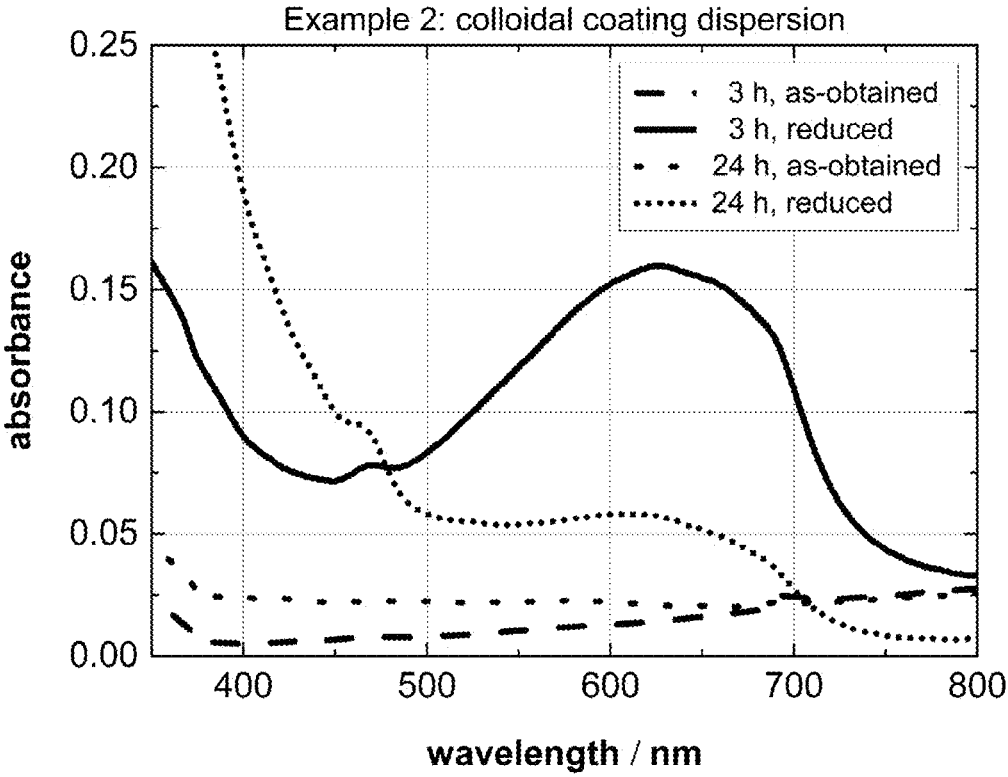


Fig. 3

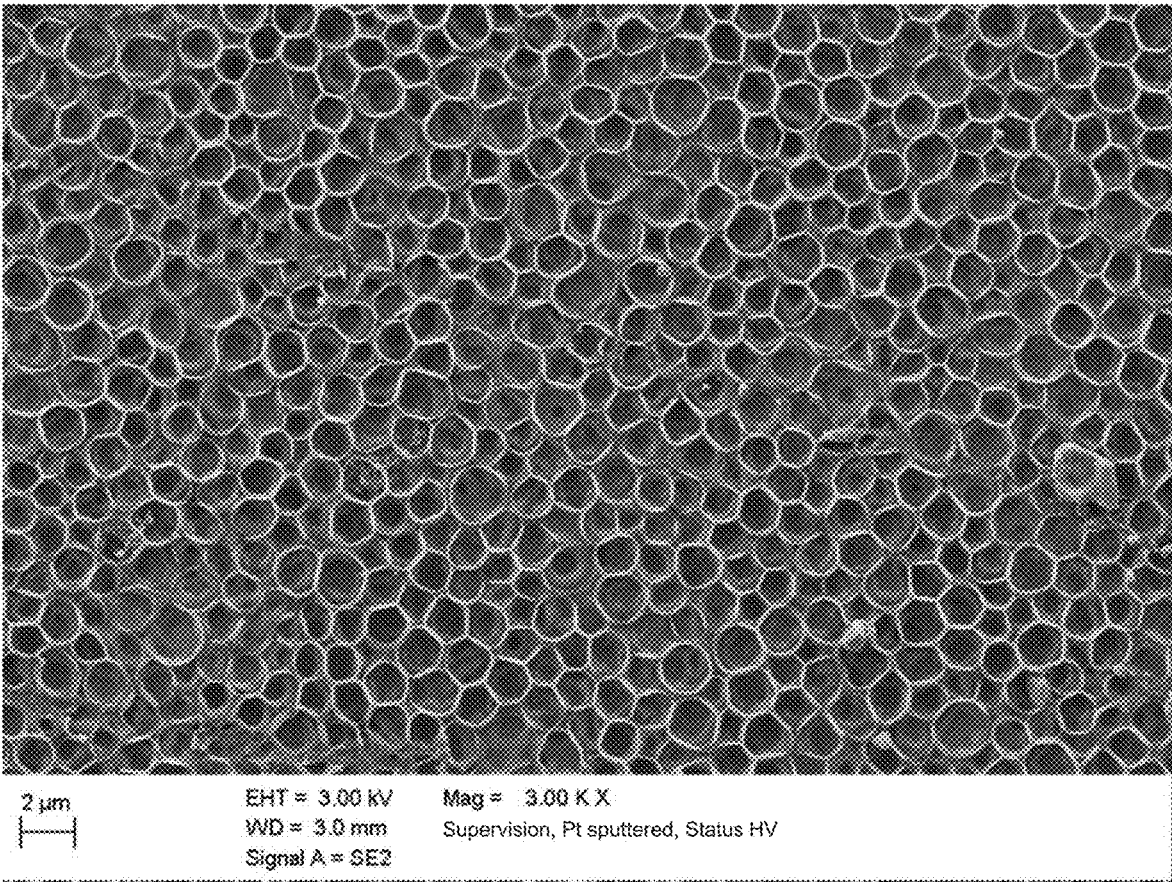


Fig. 4

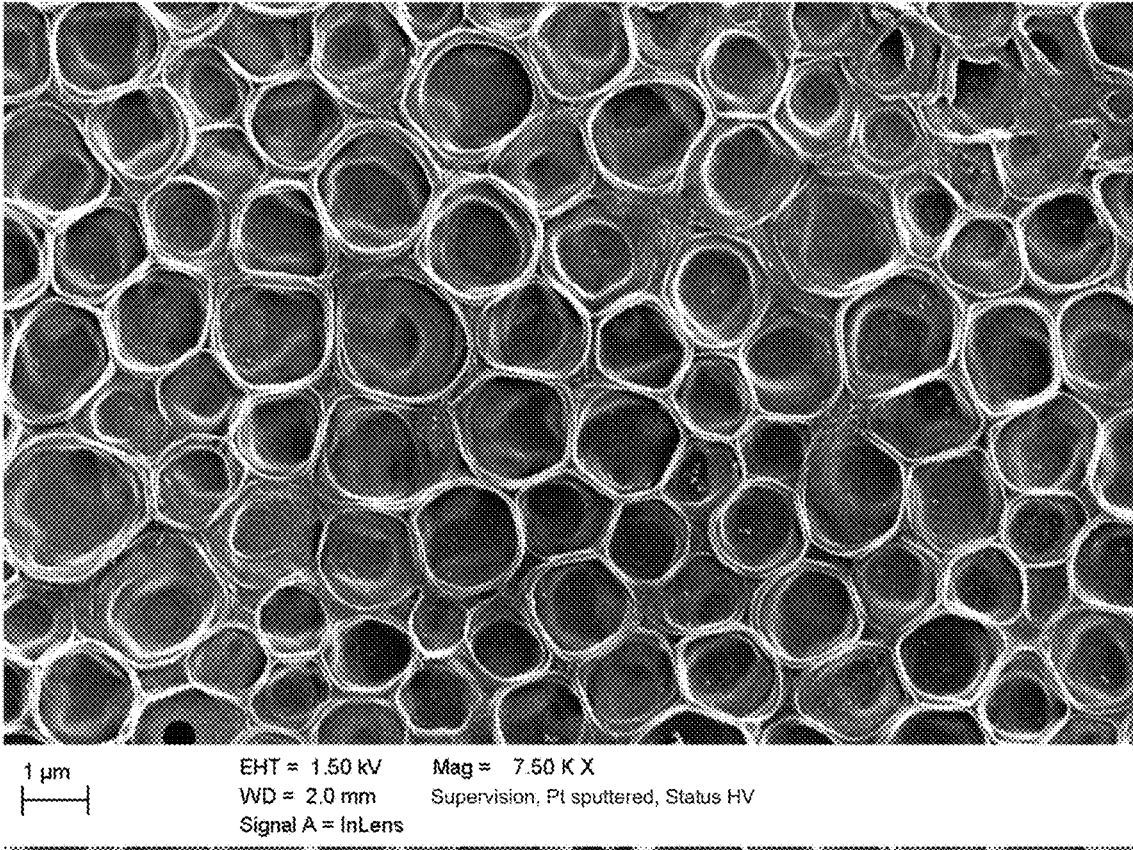


Fig. 5

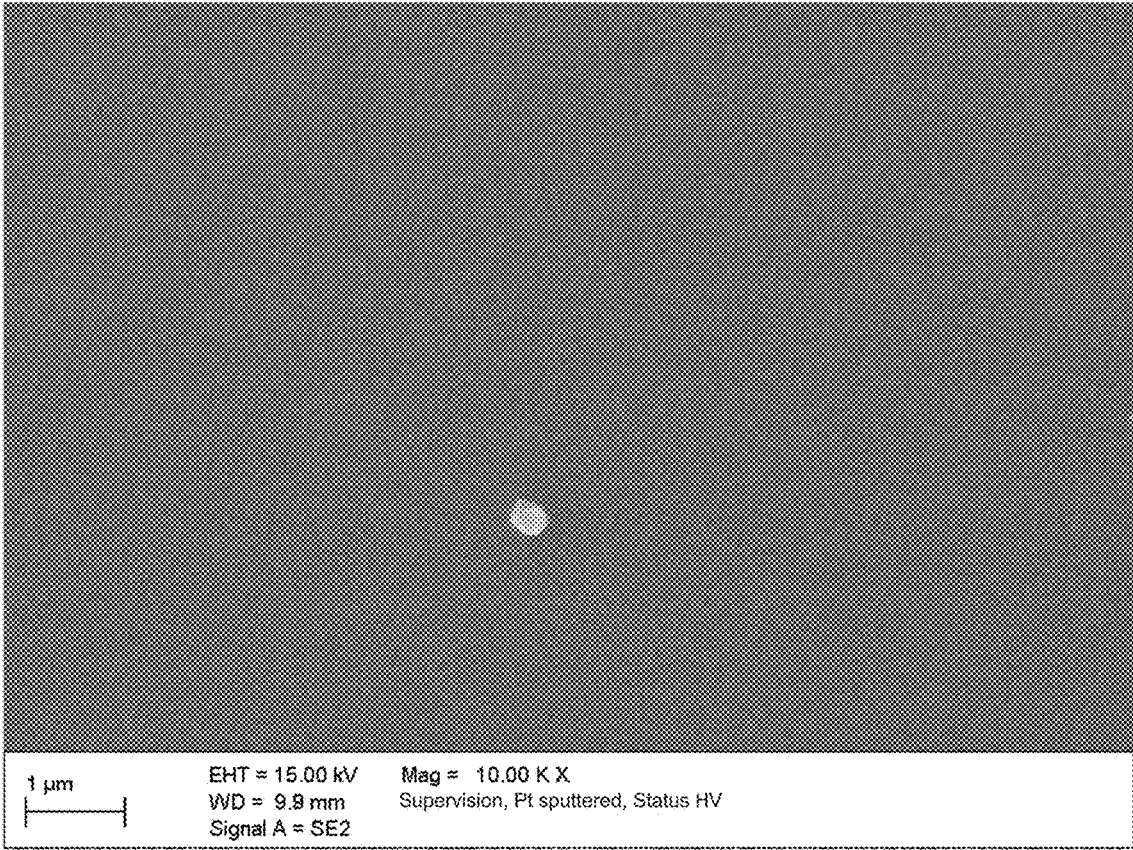


Fig. 6

**COLLOIDAL COATING DISPERSION****CROSS-REFERENCE TO A RELATED APPLICATION**

**[0001]** This patent application claims the benefit of European Patent Application No. 18 206 384.2, filed on Nov. 15, 2018, the disclosure of which is incorporated herein by reference in its entirety for all purposes.

**[0002]** The present invention relates to a colloidal coating dispersion comprising electrochromic polymer particles, a method for manufacturing the colloidal coating dispersion, the use of the colloidal coating dispersion for depositing at least one electrochromic layer on a substrate and an article comprising a layer deposited from the colloidal coating dispersion.

**[0003]** The manufacturing method according to the present invention allows manufacturing colloidal coating dispersions for depositing electrochromic polymer layers. With these colloidal dispersions of nanoparticles of conductive polymers electrochromic layers can be produced by a continuous roll-to-roll process. The colloidal coating dispersion is suitable for coatings on large-area, flexible film substrates. Due to favorable mechanical and optical properties, the resulting thin films can be used for smart shading applications in the architectural and automotive sectors. In addition, the colloid is suitable for printing processes (inkjet, etc.) after appropriate formulation. This also opens up application possibilities in display (wearables, nearables), packaging and (interior) design areas. The process according to the invention combines a greatly simplified process with easy scalability and thus has great potential for cost savings. High costs have so far been the main obstacle to the wider use of smart shading systems beyond small series scale.

**[0004]** Coating dispersions based on polythiophenes are already known from the state of the art.

**[0005]** U.S. Pat. No. 4,959,430 A refers to polythiophenes containing structural units of formula (I) in which A denotes an optionally substituted C1-C4-alkylene radical, their preparation by oxidative polymerization of the corresponding thiophenes and the use of the polythiophenes for imparting antistatic properties on substrates which only conduct electrical current poorly or not at all, in particular on plastic mouldings, and as electrode material for rechargeable batteries.

**[0006]** EP 0 440 957 A2 relates to dispersions of polythiophenes which are built up from structural units of the formula in which R1 and R2, independently of one another, are hydrogen or C1-C4-alkyl or together form an optionally substituted C1-C4-alkylene radical, in the presence of poly-anions, to the preparation of these dispersions, and to their use for the antistatic finishing of plastic mouldings.

**[0007]** DE 10 2012 018 978 A1 describes processes for the production of a capacitor, comprising the process steps: a) the provision of an electrode body of an electrode material, wherein a dielectric covers one surface of this electrode material at least partly to form an anode body; b) the introduction of a dispersion comprising a dispersing agent and complexes of polythiophenes and polyanions, wherein the weight ratio of polythiophenes:polyanions in the dispersion is greater than 0.5, into at least a part of the anode body; c) the at least partial removal of the dispersing agent to obtain a solid electrolyte in a capacitor body. Also described are capacitors, electronic circuits, uses of these capacitors, processes for the preparation of dispersions, dispersions

obtainable by these processes, organic solar cells, processes for the production of these organic solar cells, and the use of dispersion for the production of organic solar cells.

**[0008]** EP 2 831 183 A1 refers to a composite particle including a spheroidal core having a polymeric layer disposed thereon. In one embodiment, the polymeric layer includes a cationic surfactant and at least one of a nonionic polymer or an anionic polymer. In another embodiment, the polymeric layer includes a cationic polymer and an anionic polymer. Methods of making the composite particles, composite materials, and articles including them are also disclosed.

**[0009]** US 2016/064672 A1 refers to a method for fabricating a PEDOT:PSS-based electrode, comprising the steps of: preparing a PEDOT:PSS thin film formed on a substrate; treating the thin film with a solution containing 75-100 vol % of sulphuric acid or a sulphuric acid derivative; separating the thin film from the solution and rinsing the separated thin film; and drying the rinsed thin film at a temperature between 60° C. and 160° C.

**[0010]** US 2013/270537 A1 describes a complex comprising a polythiophene and a sulphonated synthetic rubber. Also described is a process for producing complexes, the complexes obtained by this process, a composition, a layer structure, a process for producing the layer structure, the layer structure obtained by this process, electronic components, and the use of a composition.

**[0011]** DE 20 2012 007 001 U1 discloses a complex of poly(3,4-alkylenedioxythiophene) and polystyrene sulphonic acid, wherein the polystyrene sulphonic acid is a copolymer of styrene sulphonic acid and styrene and wherein for the degree of sulphation of the polystyrene sulphonic acid SGPSS: 50%>=SGPSS<80%.

**[0012]** DE 10 2013 004 526 A1 relates to a process for preparing a dispersion which comprises complexes of a polythiophene and a surfactant, wherein thiophene monomers are oxidatively polymerized in an aqueous phase in the presence of a surfactant by means of an organic peroxide. Also disclosed are dispersions obtainable by this process, a dispersion comprising complexes of a polythiophene and a surfactant, a process for producing an electrically conductive layer, by this obtainable electrically conductive layer and the use of the novel dispersions.

**[0013]** WO 2013/112777 A1 discloses a process for preparing a conductive polymer dispersion and a method for making capacitors using the conductive polymer. The process includes providing a monomer solution and shearing the monomer solution with a rotor-stator mixing system comprising a perforated stator screen having perforations thereby forming droplets of said monomer. The droplets of monomer are then polymerized during shearing to form the conductive polymer dispersion.

**[0014]** EP 2 438 120 A1 relates to an aqueous dispersion and a method for making an aqueous dispersion. The dispersion including at least one conductive polymer, such as a polythienothiophene, at least one hyperbranched polymer and optionally at least one colloid-forming polymeric acid and one non-fluorinated polymeric acid. Devices utilizing layers formed of the aqueous dispersions are also disclosed.

**[0015]** US 2005/224765 A1 refers to compositions, and methods of making non-aqueous dispersions of at least one doped conductive polymer and at least one colloid-forming polymeric acid, wherein the conductive polymer is selected from a polythiophene, a polypyrrole, a polyaniline, and

combinations thereof. Electronic devices and other applications having at least one layer made from at least one of such compositions are further described.

**[0016]** US 2010/189918 A1 relates to a method for the preparation of a hybrid electrochromic coating material with superior performance in terms of transparency, electrochromic contrast, coloration efficiency, and adhesion, for a use in electrochromic devices for applications where a high transparency is required in the bleached state.

**[0017]** US 2014/226201 A1 refers to a flexible transparent electrochromic device, which includes the following components, each of which is a flexible film: a working electrode comprising a transparent conducting substrate supporting a working electrode active material; a counter electrode including a transparent conducting substrate supporting a counter electrode active material; a solid polymer electrolyte (SPE) including a solution of a lithium salt in a polymer solvent.

**[0018]** Starting herefrom, one object of the present invention is to avoid the known in-situ-polymerization processes for depositing layers of electrochromic polymers on a substrate and to allow depositing these layers by technically less demanding, less solvent consuming and more economic continuous roll-to-roll processes.

**[0019]** Another object of the present invention is to overcome the disadvantages of the coating dispersion for depositing electrochromic polymer layers known from the prior art and the provision of a colloidal coating dispersion based on at least one organic solvent as liquid phase allowing to use polymers based on water-insoluble monomers, preferably alcohol-soluble monomers, allowing to deposit thin films consisting solely of electronically conductive and electrochromic polymers, allowing to deposit layers that are free of water and thus lead to significantly higher stability in electrochemical cells, allowing to deposit a doped, electronically conductive and electrochromic colloid by wet-chemical standard processes on any substrate. Furthermore, it is one object of the present invention to provide a coating dispersion that can be prepared on a kilogram scale, that can be easily scaled up and that is stable for several months. An additional object of the present invention is the provision of a colloidal coating solution allowing a better film formation, having a homogenous, smooth surface and better wetting and adhesion properties compared to films deposited from aqueous dispersions or by in-situ oxidative polymerization.

**[0020]** This object is achieved by the features of the colloidal coating dispersion described herein, comprising electrochromic polymer particles having an average particle size  $d_{50}$  in the range from 1 to 200 nm as solid phase and at least one organic solvent as liquid phase; wherein the solids content of the colloidal coating dispersion is from 0.1 to 20 wt.-% based on the total mass of the colloidal coating dispersion; the electrochromic polymer particles are derived from a water-insoluble monomer; and the colloidal coating solution contains a maximum of 5 wt.-% of stabilizers and dispersing agents.

**[0021]** The advantageous embodiments of the colloidal coating dispersion according to the invention are also described.

**[0022]** In addition, a method for manufacturing a colloidal coating dispersion and preferred embodiments of the method according to the invention are also described.

**[0023]** Furthermore, use of the colloidal coating solution according to the invention for depositing at least one elec-

trochromic layer on a substrate and advantageous embodiments according to said use are also described.

**[0024]** In addition, an article comprising at least one layer deposited from the colloidal coating solution according to the invention and preferred embodiments of said article are also described.

#### Average Particle Size, $d_{50}$ Value

**[0025]** For the purpose of the present invention the “average particle size” is expressed by the “ $d_{50}$  value”. The “ $d_{50}$  value” means that 50 wt.-% of all particles are bigger than this particle size, whereas the remaining 50 wt.-% are smaller than this particle size. For the purpose of the present invention the particle size is specified as weight median particle size “ $d_{50}$ ” unless indicated otherwise. For determining the “ $d_{50}$  value” dynamic light scattering technology may be used. For determining the “ $d_{50}$  value” of the polymer particles preferably a Zetasizer Nano ZS from Malvern Instruments GmbH is used.

#### Absorption Maximum and Visual Transmission Hub

**[0026]** For the purpose of the present invention the absorption maximum is determined on the reduced (“dedoped” or neutral) polymer by UV-Vis-spectroscopy as described in the Experimental Section. The analysis is carried out on the reduced form of the polymer, due to the fact that the visible light absorption is maximally pronounced in this form. The reduction may be carried out as follows. A small sample is taken from the reaction mixture and transferred into n-heptanol in a separating funnel and washed three times with distilled water for removing the oxidant. After dilution with an alcohol a reducing agent is added for converting the polymer from an intermediate state in the completely reduced or neutral form.

**[0027]** Transmission spectra may be recorded on a AvaSpec-2048 Standard Fibre Optic Spectrometer with vaLight-DH—S-BAL Balanced deuterium-halogen lamp combination from Avantes. Photometric characteristics were calculated according to DIN EN 410.

#### Layer Adhesion

**[0028]** The layer adhesion may be determined according to DIN EN ISO 2409.

**[0029]** Where the term “comprising” is used in the present description and claims, it does not exclude other elements. For the purposes of the present invention, the term “consisting of” is considered to be a preferred embodiment of the term “comprising of”. If hereinafter a group is defined to comprise at least a certain number of embodiments, this is also to be understood to disclose a group, which preferably consists only of these embodiments.

#### Colloidal Coating Dispersion

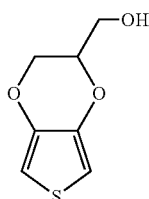
**[0030]** According to a preferred embodiment of the present invention the average particle size  $d_{50}$  of the electrochromic polymer particles is in the range from 10 to 200 nm, preferably from 10 to 100 nm and more preferably from 10 to 50 nm.

**[0031]** According to another preferred embodiment of the present invention, the solids content of the colloidal dispersion is from 0.5 to 10 wt.-%, preferably from 1 to 7.5 wt.-% and more preferably from 1 to 5 wt.-% based on the total mass of the colloidal coating dispersion.

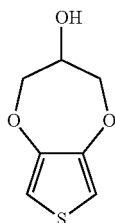
[0032] A further preferred embodiment of the present invention provides that the average particle size  $d_{50}$  of the electrochromic polymer particles is in the range from 10 to 200 nm, preferably from 10 to 100 nm and more preferably from 10 to 50 nm and the solids content of the colloidal dispersion is from 0.5 to 10 wt.-%, preferably from 1 to 7.5 wt.-% and more preferably from 1 to 5 wt.-% based on the total mass of the colloidal coating dispersion.

[0033] According to another preferred embodiment of the present invention the water-insoluble monomer is selected from the group consisting of pyrrole and pyrrole derivatives, thiophene and thiophene derivatives, preferably poly(3-hexylthiophene-2,5-diyl), or sidechain-modified alkylene-3,4-dioxythiophenes, preferably ethylene-3,4-dioxythiophene or propylene-3,4-dioxythiophene or their mixtures, more preferably naphthalenediimide-functionalized ethylene-3,4-dioxythiophenes; or sidechain-modified alkylene-3,4-dioxythiophenes, preferably ethylene-3,4-dioxythiophene or propylene 3,4-dioxythiophenes or their mixtures obtained by subsequently performing the following steps:

[0034] a) reaction of a solution comprising a mixture of a compound having the general formula (I) and a compound having the general formula (II) in a molar ratio of (I):(II) which is equal to  $m:(100-m)$  wherein  $m$  has a value in the range from 60 to 99

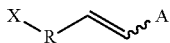


(I)



(II)

[0035] with a compound of the general formula (III)



(III)

[0036] wherein X is selected from the group consisting of Y—, Y—C(O), —OCN— or Y—CH<sub>2</sub>C(O)O—

[0037] in which Y is selected from the groups of halides, mesylates and or triflates,

[0038] R is a linear and/or branched alkylene chain with 1 to 16 carbon atoms, and

[0039] A is a linear and/or branched alkyl chain with 1 to 16 carbon atoms or hydrogen

[0040] b) optionally reacting the mixture of compounds derived from step a) by either

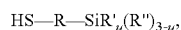
[0041] b1) a vinyl copolymerization

[0042] b2) a hydrosilylation of the vinyl moiety with a silane of the general formula  $\text{HSiR}'_u(\text{R}'')_{3-u}$ , wherein

[0043] R' is selected from the group consisting of linear or branched alkyl or alkenyl chains with 1 to 12 carbon atoms in the main-chain, wherein the chains can be substituted with acryloxy-, methacryloxy-, succinyl-, amino-, hydroxyl-, mercapto-, and/or glycidyloxy groups and/or interrupted by O- and/or S-atoms and/or a NR group,

[0044] R'' is selected from the group consisting of halogens, hydroxyl groups, alkoxy groups and/or acyl groups with 1 to 4 carbon atoms, and  $u=0, 1, 2, 3$ ; and further

[0045] b3) a thiol-ene addition to the vinyl moiety with a compound of the general formula

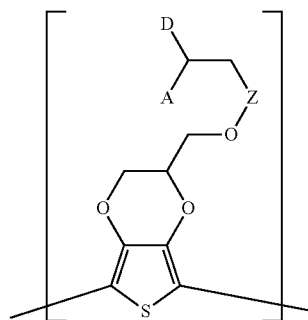


[0046] wherein R, R', R'' and  $u$  have the same meaning as indicated above;

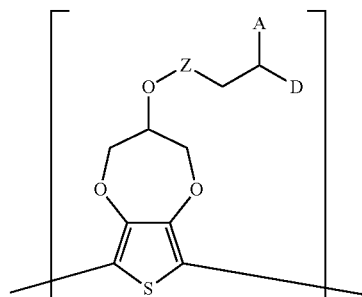
[0047] c) chemical oxidative polymerization of a solution of the compound and/or the compounds derived from step b); and/or

[0048] naphthalenediimide-functionalized ethylene-3,4-dioxythiophenes.

[0049] More preferably the sidechain-modified ethylene-3,4-dioxythiophene comprises the units according to the following general formulae (IV) and (V)



(IV)



(V)

wherein Z is selected from the group consisting of the structural elements —R—, —C(O)—R—, —C(O)—NH—R— and —CH<sub>2</sub>C(O)O—R—, wherein R is a linear and/or branched alkylene chain with 1 to 16 carbon atoms,

[0050] D is selected from the group consisting of H, —SiR'<sub>u</sub>(R'')<sub>3-u</sub>—, —S—R—SiR'<sub>u</sub>(R'')<sub>3-u</sub>—, and R has the same meaning as indicated above, preferably D=H,

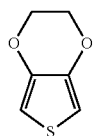
[0051] R' is selected from the group consisting of linear or branched alkyl or alkenyl chains with 1 to 12 carbon atoms in the main chain, wherein the chains can be substituted with acryloxy-, methacryloxy-, succinyl-, amino-, hydroxyl-, mercapto-, and/or glycidyloxy groups and/or interrupted by O- and/or S-atoms and/or a NR'-group, wherein R' has the same meaning as indicated above,

[0052] R'' is selected from the group consisting of halogens, hydroxyl groups, alkoxy groups and/or acyl groups with 1 to 4 carbon atoms, and u=0, 1, 2, 3; or alternatively represents a chemical bonding to corresponding positions D of neighbored monomers of the formulae (IV) and/or (V),

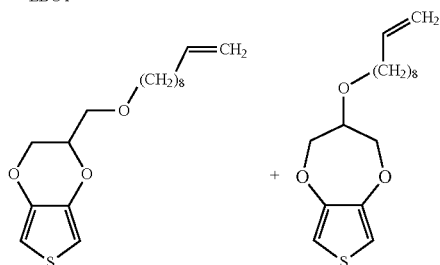
[0053] A is a linear and/or branched alkyl chain with 1 to 16 carbon atoms or hydrogen, and the compounds of the general formulae (IV) and (V) are comprised in a molar ratio of (IV):(V)=m/(100-m), wherein m has a value in the range from 1 to 99 and preferably from 60 to 99.

[0054] Particularly preferred sidechain-modified ethylene-3,4-dioxythiophene are summarized in the table below and their structure is shown below the table.

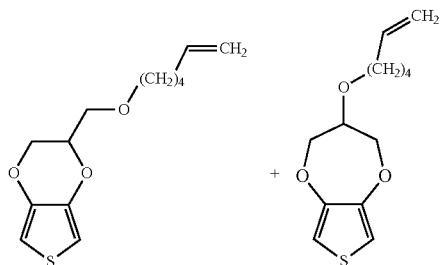
IUPAC-name	abbreviation	molecular formula	molecular weight [g/mol]
3,4-(2-(6-decenyloxy)propylene) dioxothiophene	EDOT-C10	C <sub>17</sub> H <sub>26</sub> O <sub>3</sub> S	310,45
3,4-(2-(6-hexenyloxy)propylene) dioxothiophene	EDOT-C6	C <sub>13</sub> H <sub>18</sub> O <sub>3</sub> S	254,35
3,4-(1-(hydroxypropylene) dioxothiophene	EDOT-MeOH	C <sub>7</sub> H <sub>8</sub> O <sub>3</sub> S	172,20
3,4-(2-(6-decenoate)propylene) dioxothiophene	EDOT-C11	C <sub>18</sub> H <sub>26</sub> O <sub>4</sub> S	338,46
Naphthalenediimide-functionalized ethylene-3,4-dioxothiophene	EDOT-NTCI	C <sub>42</sub> H <sub>38</sub> O <sub>16</sub> S <sub>2</sub> N <sub>2</sub>	890,89



EDOT



EDOT-C10



EDOT-C6

-continued

IUPAC-name	abbreviation	molecular formula	molecular weight [g/mol]
	EDOT-MeOH		
	EDOT-C11		
	EDOT-NTCI		

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[0055] According to another preferred embodiment of the present invention the organic solvent for the colloidal coating solution is an alcohol, preferably selected from the group consisting of ethanol, n-butanol, n-heptanol and mixtures thereof.

[0056] A further preferred embodiment of the present invention provides that the colloidal coating dispersion comprises additives. These additives are selected from the group consisting of

[0057] non-polymeric binder materials, preferably SiO<sub>2</sub> or Indium-Tin oxide,

[0058] surfactants, preferably stearates, dodecylbenzenesulphonates, sulphate esters, sulphonate esters, phosphate esters, ethoxylates (e.g. Triton X-100), fatty acid esters (e.g. Spans, Tweens), amines, amine oxides, Solsperse Hyperdispersants,

[0059] polymeric binders, preferably inorganic-organic hybrid polymers, more preferably producible from a prepolymer (a) having groups, which are bonded to silicon via carbon, with organically crosslinkable or organically crosslinked moieties, more preferably (meth)acrylic groups, norbornenyl groups or epoxy groups, and/or wherein the crosslinkable organic monomer or a prepolymer (b) that contains at least one group per molecule that has one or more COC double

bonds, more preferably vinyl-, acrylate-, methacrylate groups, or at least one epoxy group; and mixtures thereof.

**[0060]** It is furthermore preferred that the additives are contained in 1 to 50 wt.-% based on the total mass of the colloidal coating dispersion.

**[0061]** The additives in the gist of present invention are added for improving film formation and improvement of the adhesive properties, but do not have a stabilizing or dispersing effect.

**[0062]** According to another preferred embodiment of the present invention after 12 months of storage of the colloidal coating dispersion no agglomeration, precipitation or phase separation is observed.

**[0071]** Another preferred embodiment of the method according to the present invention provides that the molar ratio between the at least one oxidizing agent provided in step (iv) and the at least one water-insoluble monomer provided in step (i) is from 1:1.50 to 1:3.00, preferably from 1:1.75 to 1:2.5 and more preferably is 1:2.25.

**[0072]** According to another preferred embodiment of the present invention step (v) is carried out for a period of time from 1 to 72 h, preferably from 1 to 6 h and more preferably for 3 h in a temperature range from  $-12$  to  $25^{\circ}$  C., most preferably step (v) is carried out until the absorption maximum of the reduced polymer is in the range from 350 to 650 nm.

**[0073]** Below table summarizes the preferred absorption wavelength of some polymers as well as preferred ranges.

IUPAC-name	abbreviation	molecular formula	molecular weight [g/mol]	absorption wavelength [nm] of the polymer
Poly(3-hexylthiophene)	P3HT	$(C_{10}H_{14}S)_n$	166.28n	$480 \pm 50$
Poly(3-decylpyrrole)	P3DP	$(C_{14}H_{24}N)_n$	206.35n	$400 \pm 50$
3,4-(1-(hydroxypropylene)dioxythiophene	EDOT-MeOH	$C_7H_8O_3S$	172.20	$600 \pm 50$
3,4-(2-(6-decenoate)propylene dioxythiophene	EDOT-C11	$C_{18}H_{26}O_4S$	338.46	$600 \pm 50$
Poly(3,4-(2-(6-hexenyloxy)propylene)dioxythiophene	PEDOT-C6	$(C_{13}H_{18}O_3S)_n$	254.35n	$600 \pm 50$
3,4-(2-(6-decenyloxy)propylene)dioxythiophene	EDOT-C10	$C_{17}H_{26}O_3S$	310.45	$600 \pm 50$
Naphthalenediimide-functionalized poly(ethylene-3,4-dioxythiophene) <sup>a</sup>	PEDOT-NTCI	$(C_{42}H_{38}O_{16}S_2N_2)_n$	890.89n	$400 \pm 50$ $600 \pm 50$

<sup>a</sup>has two characteristic absorption bands.

#### Method for Manufacturing a Colloidal Coating Dispersion

**[0063]** The inventive method for manufacturing a colloidal coating dispersion as described above comprises the following steps:

**[0064]** (i) provision of at least one water-insoluble monomer;

**[0065]** (ii) provision of at least one organic solvent;

**[0066]** (iii) solving the water-insoluble monomer from step (i) in the organic solvent from step (ii);

**[0067]** (iv) addition of at least one oxidizing agent before, during or after step (iii) to initiate the polymerization of the water-insoluble monomer;

**[0068]** (v) polymerizing the water-insoluble monomer;

**[0069]** (vi) removing the oxidizing agent added in step (iv) to stop the polymerization and to obtain a colloidal coating dispersion.

**[0070]** According to a preferred embodiment of the method according to the present invention the molar ratio between the at least one water-insoluble monomer provided in step (i) and the at least one organic solvent provided in step (ii) is from 1:25 to 1:510, preferably from 1:255 to 1:510 and more preferably is 1:255 or 1:25.

**[0074]** Another preferred embodiment of the method according to the present invention provides that the molar ratio between the at least one water-insoluble monomer provided in step (i) and the at least one organic solvent provided in step (ii) is from 1:25 to 1:510, preferably from 1:255 to 1:510 and more preferably is 1:255 and that the molar ratio between the at least one oxidizing agent provided in step (iv) and the at least one water-insoluble monomer provided in step (i) is from 1:1.50 to 1:3.00, preferably from 1:1.75 to 1:2.5 and more preferably is 1:2.25 and that step (v) is carried out for a period of time from 1 to 72 h, preferably from 1 to 6 h and more preferably for 3 h in a temperature range from  $-12$  to  $25^{\circ}$  C., most preferably step (v) is carried out until the absorption maximum of the reduced polymer is in the range from 350 to 650 nm, preferably in the range from 380 to 650 and more preferably from 400 to 650 nm.

**[0075]** The water-insoluble monomer is preferably selected from the group consisting of pyrrole and pyrrole derivatives, thiophene and thiophene derivatives, preferably poly(3-hexylthiophene), or sidechain-modified alkylene-3,4-dioxythiophenes, preferably ethylene-3,4-dioxythiophenes or propylene-3,4-dioxythiophenes and more preferably naphthalenediimide-functionalized alkylene-3,4-

dioxythiophenes; or sidechain-modified alkylene-3,4-dioxythiophene as defined above in section "colloidal coating dispersion".

**[0076]** According to another preferred embodiment of the method of the present invention the organic solvent is an alcohol, preferably selected from the group consisting of ethanol, n-butanol, n-heptanol and mixtures thereof.

**[0077]** Another preferred embodiment of the method according to the present invention provides that the oxidizing agent is selected from the group consisting of iron(III)-salts, preferably iron(III)-chloride, iron-(III)-sulphate, iron-(III)-perchlorate, iron(III) butylnaphthalenesulphonate, iron-(III)-alkylsulphonates, iron-(III)-carboxylate, iron(III) camphorsulphonate, iron-(III)-dodecylsulphonate, iron-(III)-salts of aromatic sulphonic acids, preferably iron-(III)-benzenesulphonate, iron(III) dodecylbenzenesulphonate, iron(III)-p-toluenesulphonates and/or mixtures thereof, hydrogenperoxide, dichromates, peroxydisulphates, perchlorates, persulphates, perborates, permanganates and/or mixtures thereof.

**[0078]** According to another preferred embodiment of the method of the present invention the water-insoluble monomer is preferably at least one sidechain-modified alkylene-3,4-dioxythiophene, more preferably at least one sidechain-modified alkylene-3,4-dioxythiophene as defined above and the organic solvent is selected from the group consisting of alcohols, preferably ethanol, n-butanol, n-heptanol and mixtures thereof and the oxidizing agent is selected from the group consisting of iron(III)-salts, preferably iron(III)-chloride, iron-(III)-sulphate, iron-(III)-perchlorate, iron(III) butylnaphthalenesulphonate, iron-(III)-alkylsulphonates, iron-(III)-carboxylate, iron(III) camphorsulphonate, iron-(III)-dodecylsulphonate, iron-(III)-salts of aromatic sulphonic acids, preferably iron-(III)-benzenesulphonate, iron(III) dodecylbenzenesulphonate, iron(III)-p-toluenesulphonates and/or mixtures thereof, hydrogenperoxide, dichromates, peroxidisulphates, perchlorates, persulphates, perborates, permanganates and/or mixtures thereof.

**[0079]** Another preferred embodiment of the method according to the present invention provides that step (vi) is carried out by diluting the mixture with an organic solvent, preferably n-heptanol, and stirring this mixture, addition of water to obtain an aqueous phase and an organic phase, and separation of the aqueous phase containing the oxidizing agent, more preferably the sequence: addition of water and separating the aqueous phase is repeated at least three times.

**[0080]** According to another preferred embodiment of the method of the present invention after step (vi) at least one organic solvent, preferably n-butanol, is added to adjust the solids content in the range from 0.1 to 20 wt.-% and preferably from 1 to 20 wt.-% based on the total weight of the colloidal coating dispersion, preferably the colloidal coating dispersion is stirred vigorously after addition of the at least one organic solvent and subsequently agglomerates having an average particle size >5 nm are removed by filtration.

**[0081]** Another preferred embodiment of the method according to the present invention provides that water is added before or during step (iii) and the organic solvent provided in step (ii) is preferably acetonitrile.

**[0082]** According to another preferred embodiment of the method of the present invention additives are added before, after or during step (v). These additives are preferably

selected from the group consisting of non-polymeric binder materials, surfactants, polymeric binders, inorganic-organic hybrid polymers and mixtures thereof, more preferably the additives are contained in 1 to 50 wt.-% based on the total mass of the colloidal coating dispersion.

**[0083]** According to a further preferred embodiment of the method of the present invention water is added before or during step (iii) and the organic solvent provided in step (ii) is preferably acetonitrile or steps (ii) to (v) are conducted in a temperature range from -5 to -15° C. or step (v) is conducted over a period of time from 1.5 to 4.5 hours.

**[0084]** According to another preferred embodiment of the method of the present invention water is added before or during step (iii) and the organic solvent provided in step (ii) is acetonitrile and steps (ii) to (v) are conducted in a temperature range from -5 to -15° C. and step (v) is conducted over a period of time from 1.5 to 4.5 hours. By applying these conditions the absorption maximum of the reduced polymer is in the range from 350 to 650 nm.

**[0085]** According to a further preferred embodiment of the method of the present invention the organic solvent provided in step (ii) is n-butanol or steps (ii) to (v) are conducted in a temperature range from 15 to 25° C. or step (v) is conducted over a period of time from 60 to 80 hours.

**[0086]** According to another preferred embodiment of the method of the present invention the organic solvent provided in step (ii) is n-butanol and steps (ii) to (v) are conducted in a temperature range from 15 to 25° C. and step (v) is conducted over a period of time from 60 to 80 hours. By applying these conditions the absorption maximum of the reduced polymer is in the range from 350 to 650 nm.

#### Use of the Colloidal Coating Solution

**[0087]** Another aspect of the present invention relates to the use of the colloidal coating solution as described above for depositing at least one electrochromic layer on a substrate.

**[0088]** According to one preferred embodiment of the use of present invention the deposition is conducted by spin coating, slot-die coating or printing processes.

**[0089]** Another preferred embodiment of the use according to the present invention provides that the substrate is selected from the group consisting of

**[0090]** Transparent conducting plastic films, more preferably polyesters such as polyethylene terephthalate, coated with a transparent conducting oxide selected from the group consisting of tin-doped indium oxide, fluorine-doped tin oxide, aluminium-doped zinc oxide, aluminium-doped zirconium oxide, antimony-doped tin oxide, antimony/tin-doped zinc oxide, indium/tin-doped zinc oxide, and/or mixtures thereof,

**[0091]** Glass coated with a transparent conducting oxide selected from the group given above,

**[0092]** Metal (mirrors) selected from the group Al, Ni, Ag, Au, Pd, Pt, Cu and alloys thereof, coated with a transparent conducting oxide selected from the group given above,

**[0093]** Textiles and fabrics comprising conductive components, e.g. metal wires, or a conducting oxide selected from the group given above,

**[0094]** Plastic film, glass, metal, and fabrics coated with an intrinsically conducting polymer such as PEDOT: PSS and combinations.

**[0095]** Plastic film, glass, metal, and fabrics coated with a transparent conducting oxide selected from the group given above and an intrinsically conducting polymer such as PEDOT:PSS and combinations. Plastic film, glass and metal coated with a transparent layer stack comprising insulator/metal/insulator, semi-conductor/metal/insulator or semi-conductor/metal/semi-conductor or multiples thereof.

**[0096]** Plastic film, glass and metal optionally over- or under-coated with a metal mesh or grid, an optionally over- or undercoated metal or carbon nanowire deposit, carbon nanotubes, graphene and mixtures thereof.

**[0097]** Another preferred embodiment of the use according to the present invention provides that the deposited layer is used in an application selected from the group consisting of electrochromic devices, an electron acceptor (or hole conductor) layer for organic photovoltaics, a conductive finishing of surfaces and fabrics, an active layer of a battery component/electrode, a hole conductor layer in OLEDs, a cathode layer or deposit in electrolytic capacitors or a layer or deposit in a sensor.

Article Comprising at Least One Layer Deposited from the Colloidal Coating Solution

**[0098]** Another aspect of the present invention relates to an article comprising at least one layer deposited from the colloidal coating solution as defined above.

**[0099]** According to a preferred embodiment of the article of the present invention the deposited layer consists of at least one electrochromic polymer.

**[0100]** Another preferred embodiment of the article according to the present invention provides that the layer adhesion determined according to DIN EN ISO 2409 is rated with GT0.

**[0101]** According to another preferred embodiment of the article of the present invention the visual transmission  $T_v$  determined according to DIN EN 410 is in the range from 55 to 60%.

#### DESCRIPTION OF THE FIGURES

**[0102]** FIG. 1 shows the results of (in-situ) spectro-electrochemical measurements of the layer obtained from a dispersion according to Working Example 1.

**[0103]** FIG. 2 shows the results of (in-situ) spectro-electrochemical measurements of the layer obtained from a dispersion according to Working Example 2.

**[0104]** FIG. 3 shows UV-Vis-NIR spectra measured during the polymerization according to Working Example 2.

**[0105]** FIG. 4 shows scanning electron microscopy image (field emission scanning electron microscope Ultra 55 from Carls Zeiss NTS GmbH) of electrochromic polymer layers. FIG. 4 (magnification: 3.00 KX) and 5 (magnification: 7.50 KX) shows layers obtained by in-situ polymerization of the electrochromic polymer on the surface of a substrate, respectively. An alveolar surface structure is observed.

**[0106]** FIG. 5 shows another scanning electron microscopy image (field emission scanning electron microscope Ultra 55 from Carls Zeiss NTS GmbH) of electrochromic polymer layers.

**[0107]** FIG. 6 (magnification: 10.00 KX) shows a layer deposited from a colloidal coating dispersion according to the present invention. As can be gathered from this figure the surface is homogenous and smooth.

**[0108]** The subject according to the invention is intended to be explained in more detail with reference to the subse-

quent examples without wishing to restrict said subject to the specific embodiments shown here.

#### Measuring Methods

**[0109]** Within the scope of this application, the following measuring methods have been used.

#### UV-Vis-NIR-Spectroscopy

**[0110]** The UV-Vis-NIR spectra were measured on a digital CCD Avantes Ava-Spec-2048 Standard Fiber Optic Spectrometer of the company Avantes. The light source used was a deuterium-halogen lamp combination from Avantes (wave length from 200 nm to 2500 nm). The optical contribution of the substrate was taken into account by a reference measurement. The measurements were carried out at room temperature. The sample was arranged so that first the electrochromic layer and subsequently the substrate were irradiated.

#### (In-Situ) Spectroelectrochemical Measurements

**[0111]** The in-situ spectro-electrochemical measurements were also carried out with the AvaSpec-2048 Standard Fiber Optic Spectrometer from Avantes. For this purpose, the sample of the electrochromic layer to be analyzed was first arranged on a PET-ITO film (working electrode) and then installed in a special glass cuvette made for the Fraunhofer Institute for Silicate Research ISC. The area of the sample was  $1.7 \times 3.0 \text{ cm}^2$ . For better contacting, the conductive side of the sample was glued to the uncoated edge with a copper tape commercially available from 3M. The counterelectrode used consists of platinum and the electrolyte used was 1 M lithium perchlorate in propylene carbonate. The required switching voltage was generated with a Voltcraft PS 1152A laboratory power supply.

#### REM-EDX

**[0112]** The polymer layers were examined in terms of topology and composition using a field emission scanning electron microscope Ultra 55 from the company Carl Zeiss NTS GmbH under high vacuum. Acceleration voltage, working distance and magnification are each given together with the corresponding images. The samples to be examined were sputtered with platinum on the sputtering unit MED 010 from Oerlikon Balzers Coating AG.

#### Layer Adhesion

**[0113]** The adhesion quality of the electrochromic polymer layers on the PET-ITO substrate was determined by means of the cross-cut and tape test in accordance with DIN EN ISO 2409. For this purpose, 6 horizontal and 6 vertical sections were cut into the layer at a distance of 1 mm using a cutter knife and a template. Subsequently, an adhesive tape was applied to the cutting grid and pulled off after a waiting time of 1 minute.

#### Particle Size

**[0114]** To measure the particle size distribution of the dispersions, the method of dynamic light scattering was used. The measurement was carried out on the Zetasizer Nano ZS of Malvern Instruments GmbH using a red helium-neon laser emitting at a wavelength of 633 nm. Ethanol was used as the dispersing medium.

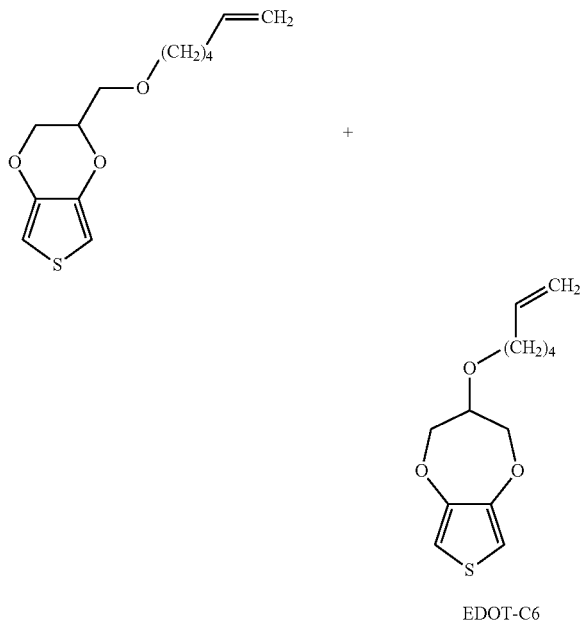
## 2 Starting Materials

[0115] The materials used for manufacturing the colloidal coating dispersion according to the invention are compiled in table 1.

TABLE 1

Components	Manufacturer
n-butanol	Sigma Aldrich
iron(III)-tosylate	Heraeus
n-heptanol	Sigma Aldrich
hydrochloric acid	Merck

[0116] Furthermore, the mixture EDOT-C6 as shown below has been used as monomer.



[0117] The monomer mixture EDOT-C6 (ratio of EDOT: ProDOT isomer=99:1) has been prepared according to the conditions and methods disclosed in WO 2008/064878 A1.

## 3 EXAMPLES

## Example 1 (Inventive)

[0118] Example 1 was carried out in a round flask equipped with a magnetic stirring bar. First, the solvent n-butanol (5 mol) was added to the round flask and then the monomer mixture EDOT-C6 (1 mol) was added at 25° C. under stirring to obtain a yellowish, but transparent solution. Subsequently, the solution has been stirred for further 10 minutes at 300 rpm. Then the oxidizing agent iron(III)-tosylate (1.75 mol solved in 20 mol n-BuOH) was added under stirring. The resulting yellow-orange mixture has been stirred and polymerized at 25° C. for 72 hours. Afterwards, the polymerization was stopped by solvent extraction. For that purpose the reaction mixture was added into n-heptanol (6.5 mol) and the solvent extraction was conducted in a separating funnel using distilled water acidified with 1 molar hydrochloric acid (pH 2-3, 5 times the volume of the organic

phase) as aqueous phase. For entirely removing the oxidizing agent from the organic phase the solvent extraction process was repeated three times with the same amount of the acidified aqueous phase. The obtained deep blue dispersion (organic phase) was filtered via a syringe filter (5 µm). Finally, the solid content of the dispersion was adjusted to 7.5 wt.-% by addition of n-butanol (30 mol).

[0119] The dispersion produced this way shows high stability of several months (at least 24 months). Therefore, no stability-improving surfactants or other additives need to be added. A binder material may be added if the subsequent coating process requires it. Likewise, the solids content, initially at 7.5%, can be reduced by adding more n-butanol. This results—in contrast to the effect of a binder additive—in a reduction of the viscosity of the coating solution. Even without a binder, the inventive coating exhibits excellent adhesion to electronically conductive plastic substrates (e.g. PET-ITO) and a temperature stability that generally exceeds that of the substrates. FIG. 1 shows the results of the (in situ) spectro-electrochemical measurements of the layers resulting from the colloidal coating dispersion according to Example 1. These measurements represent the most important properties of an electrochromic layer. The visual transmission hub for the obtained layer is 31% and has been calculated according to DIN EN 410.

## Example 2 (Inventive)

[0120] Example 2 was conducted in a double-walled reaction vessel equipped with a thermometer and a mechanical stirrer (crescent-shaped). The oxidizing agent iron(III)-tosylate (2.25 mol) was added to a laboratory bottle, acetonitrile (255 mol) and distilled water (13.7 mol) were added as solvents. Under stirring by using a magnetic stirrer the oxidizing agent was solved in the solvents at 25° C. EDOT-C6 (1 mol) was added under stirring (300 rpm) at 25° C. In the meantime the double-walled reaction vessel was cooled to -8° C. by using a cryostat. The resulting solution containing the solvents, the oxidizing agent and the monomer was added to the cooled double-walled reaction vessel and the polymerization was conducted for 3 hours at that temperature. Afterwards, the polymerization was stopped by solvent extraction. For that purpose the reaction mixture was added into n-heptanol (15 mol) and the solvent extraction was conducted in a separating funnel using distilled water, acidified with 1 molar hydrochloric acid (pH 2-3, 5 times the volume of the organic phase) as aqueous phase. For entirely removing the oxidizing agent from the organic phase the solvent extraction process was repeated three times with the same amount of the acidified aqueous phase. The obtained deep blue dispersion (organic phase) was filtered via a syringe filter (5 µm). Finally, the solid content of the dispersion was adjusted to 7.5 wt. % by addition of n-butanol (30 mol).

[0121] The dispersion prepared this way shows high storage stability. FIG. 2 shows the results of the (in situ) spectro-electrochemical measurements of the layers resulting from the colloidal coating dispersion according to Example 2. These measurements represent the most important properties of an electrochromic layer. The visual transmission hub for the obtained layer is 57% and has been calculated according to DIN EN 410.

[0122] FIG. 3 shows the development of the UV-Vis spectra as a function of the polymerization time. The spectra were recorded on a highly diluted colloidal coating disper-

sion. Surprisingly, no longer polymer chains are achieved by a longer polymerization time (bathochromic shift of the absorption band). On the contrary, an optimum results at a polymerization time of 3 h.

#### Example 3

**[0123]** Example 3 was conducted in a jacketed reaction vessel equipped with a thermometer and a magnetic stirrer. The oxidizing agent iron(III)-tosylate (2.25 mol) was added to a laboratory bottle, acetonitrile (255 mol) and distilled water (13.5 mol) were added as solvents. Under stirring by using a magnetic stirrer the oxidizing agent was solved in the solvents at 25° C. EDOT-MeOH (1 mol) was added under stirring (300 rpm) at 25° C. In the meantime the jacketed reaction vessel was cooled to -8° C. by using a cryostat. The resulting solution containing the solvents, the oxidizing agent and the monomer was added to the cooled jacketed reaction vessel and the polymerization was conducted for 3 hours at that temperature. Afterwards, the polymerization was stopped by solvent extraction. For that purpose the reaction mixture was added into n-heptanol (12 mol) and the solvent extraction was conducted in a separating funnel using distilled water, acidified with 1 molar hydrochloric acid (pH 2-3, 5 times the volume of the organic phase) as aqueous phase. For entirely removing the oxidizing agent from the organic phase the solvent extraction process was repeated three times with the same amount of the acidified aqueous phase. The obtained deep blue dispersion (organic phase) was filtered via a syringe filter (5 µm). Finally, the solid content of the dispersion was adjusted to 7.5 wt. % by addition of n-butanol (36 mol). FIG. 4 shows the results of the (in situ) spectro-electrochemical measurements of the colloidal coating dispersion according to Example 3. These measurements represent the most important properties of an electrochromic ink.

#### Example 4

**[0124]** Example 4 was conducted in a jacketed reaction vessel equipped with a thermometer and a magnetic stirrer. The oxidizing agent iron(III)-tosylate (2.25 mol) was added to a laboratory bottle, acetonitrile (255 mol) and distilled water (13.5 mol) were added as solvents. Under stirring by using a magnetic stirrer the oxidizing agent was solved in the solvents at 25° C. EDOT-MeOH (1 mol) was added under stirring (300 rpm) at 25° C. In the meantime the jacketed reaction vessel was cooled to -8° C. by using a cryostat. The resulting solution containing the solvents, the oxidizing agent and the monomer was added to the cooled jacketed reaction vessel and the polymerization was conducted for 3 hours at that temperature. Afterwards, the polymerization was stopped by solvent extraction. For that purpose the reaction mixture was added into n-heptanol (12 mol) and the solvent extraction was conducted in a separating funnel using distilled water, acidified with 1 molar hydrochloric acid (pH 2-3, 5 times the volume of the organic phase) as aqueous phase. For entirely removing the oxidizing agent from the organic phase the solvent extraction process was repeated three times with the same amount of the acidified aqueous phase. The obtained deep blue dispersion (organic phase) was filtered via a syringe filter (5 µm). Finally, the solid content of the dispersion was adjusted to 7.5 wt. % by addition of n-butanol (36 mol). FIG. 5 shows the results of the (in situ) spectro-electrochemical measurements of the

colloidal coating dispersion according to Example 3. These measurements represent the most important properties of an electrochromic ink.

#### Example 5

**[0125]** Example 4 was conducted in a laboratory bottle equipped with a magnetic stirrer. The oxidizing agent iron (III)-tosylate (2.25 mol) was added to the laboratory bottle, acetonitrile (255 mol) and distilled water (13.5 mol) were added as solvents. Under stirring by using a magnetic stirrer the oxidizing agent was solved in the solvents at 25° C. EDOT-NTCl-EtHex (1 mol) was added under stirring (300 rpm) at 25° C. The polymerization was conducted for 10 min at room temperature (25° C.). Afterwards, the polymerization was stopped by solvent extraction. For that purpose the reaction mixture was added into n-heptanol (12 mol) and the solvent extraction was conducted in a separating funnel using distilled water, acidified with 1 molar hydrochloric acid (pH 2-3, 5 times the volume of the organic phase) as aqueous phase. For entirely removing the oxidizing agent from the organic phase the solvent extraction process was repeated three times with the same amount of the acidified aqueous phase. The obtained deep blue dispersion (organic phase) was filtered via a syringe filter (5 µm). Finally, the solid content of the dispersion was adjusted to 7.5 wt. % by addition of acetonitrile (200 mol). FIG. 6 shows the results of the (in situ) spectro-electrochemical measurements of the colloidal coating dispersion according to Example 5. These measurements represent the most important properties of an electrochromic ink.

#### Example 6

**[0126]** Example 6 was conducted in a jacketed reaction vessel equipped with a thermometer and a magnetic stirrer. The oxidizing agent iron(III)-tosylate (2.25 mol) was added to a laboratory bottle, acetonitrile (255 mol) and distilled water (13.7 mol) were added as solvents. Under stirring by using a magnetic stirrer the oxidizing agent was solved in the solvents at 25° C. EDOT-C6 (1 mol) was added under stirring (300 rpm) at 25° C. In the meantime the jacketed reaction vessel was cooled to -8° C. by using a cryostat. The resulting solution containing the solvents, the oxidizing agent and the monomer was added to the cooled double-walled reaction vessel and the polymerization was conducted for 4 hours at that temperature. Afterwards, the polymerization was stopped by solvent extraction. For that purpose the reaction mixture was added into a n-heptanol/toluol (10 mol/10 mol) mixture and the solvent extraction was conducted in a separating funnel using distilled water, acidified with 1 molar hydrochloric acid (pH 2-3, 5 times the volume of the organic phase) as aqueous phase. For entirely removing the oxidizing agent from the organic phase the solvent extraction process was repeated three times with the same amount of the acidified aqueous phase. The obtained deep blue dispersion (organic phase) was filtered via a syringe filter (5 µm). FIG. 7 shows the results of the (in situ) spectro-electrochemical measurements of the colloidal coating dispersion according to Example 6. These measurements represent the most important properties of an electrochromic ink.

#### Example 7

**[0127]** Example 4 was conducted in a jacketed reaction vessel equipped with a thermometer and a magnetic stirrer.

The oxidizing agent iron(III)-tosylate (2.25 mol) was added to a laboratory bottle, acetonitrile (255 mol) and distilled water (13.5 mol) were added as solvents. Under stirring by using a magnetic stirrer the oxidizing agent was solved in the solvents at 25° C. Pyrrole (1 mol) was added under stirring (300 rpm) at 25° C. In the meantime the jacketed reaction vessel was cooled to -8° C. by using a cryostat. The resulting solution containing the solvents, the oxidizing agent and the monomer was added to the cooled jacketed reaction vessel and the polymerization was conducted for 4 hours at that temperature. Afterwards, the polymerization was stopped by solvent extraction. For that purpose the reaction mixture was added into n-heptanol (12 mol) and the solvent extraction was conducted in a separating funnel using distilled water, acidified with 1 molar hydrochloric acid (pH 2-3, 5 times the volume of the organic phase) as aqueous phase. For entirely removing the oxidizing agent from the organic phase the solvent extraction process was repeated three times with the same amount of the acidified aqueous phase. The obtained deep blue dispersion (organic phase) was filtered via a syringe filter (5 µm). Finally, the solid content of the dispersion was adjusted to 7.5 wt. % by addition of n-butanol (36 mol). FIG. 5 shows the results of the (in situ) spectro-electrochemical measurements of the colloidal coating dispersion according to Example 3. These measurements represent the most important properties of an electrochromic ink.

#### Deposition of Electrochromic Layers

[0128] Electrochromic layers were deposited from the dispersion obtained from Examples 1 and 2 within the scope of pilot plant trials on a fully automatic roll-to-roll coating plant. The substrate—a polyethylene terephthalate coated with tin-doped indium oxide—was subjected to corona pretreatment (1.00 kW). By using a slot-die with a 50 µm shim, wet films of various thicknesses were applied to the substrate. For this purpose, the slot-die is filled with an Oerlikon Barmag gear pump (type: 1-012-8055). The wet film thickness can be controlled via the pump frequency and the web speed. The pump frequency is in the range of 5 to 60 Hz and the web speed in the range between 0.1 and 1.0 m/min. After application of the coating dispersion the wet film is dried in four oven modules (2×100° C., 2×120° C.), wherein the drying temperature can be varied between 80 and 140° C. A wet film thickness of 18 µm has been obtained by applying a web speed of 0.5 m/min and a pump frequency of 18 Hz.

[0129] As can be gathered from the table below, the optical properties and the layer adhesion for a substrate coated from a colloidal dispersion according to the present invention and coated by in-situ polymerization are almost the same. However, the colloidal coating dispersion according to the present invention allows not only to deposit layers by well-scalable and straightforward standard processes, but additionally allows to obtain smooth and homogenous layers that will not produce substantial haze (diffuse light scattering). Further the present invention is to avoid the in-situ-polymerization processes for depositing layers of pure electrochromic polymers on a substrate leading to a technically less demanding, less solvent consuming and more economic coating process.

	Comparative Example 1 <sup>a</sup>	Example 2
Transmission hub (625 nm) [%]	61	66
Layer adhesion	GT0	GT0

<sup>a</sup>Comparative Example 1 corresponds to sample TCM431 in table 6 of EP 2 570 846 A1

1-18. (canceled)

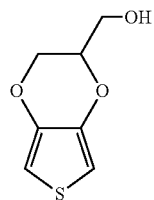
19. A colloidal coating dispersion comprising electrochromic polymer particles having an average particle size  $d_{50}$  in the range from 1 to 200 nm as solid phase and at least one organic solvent as liquid phase; wherein

the solids content of the colloidal coating dispersion is from 0.1 to 20 wt.-% based on the total mass of the colloidal coating dispersion; the electrochromic polymer particles are derived from a water-insoluble monomer; and the colloidal coating solution contains a maximum of 5 wt.-% of stabilizers and dispersing agents.

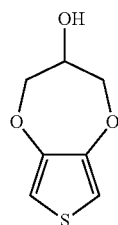
20. The colloidal coating dispersion according to claim 19, wherein the average particle size  $d_{50}$  of the electrochromic polymer particles is in the range from 10 to 200 nm; and/or the solids content of the colloidal dispersion is from 0.5 to 10 wt.-%, based on the total mass of the colloidal coating dispersion.

21. The colloidal coating dispersion according to claim 19, wherein the water-insoluble monomer is selected from the group consisting of pyrrole and pyrrole derivatives, thiophene and thiophene derivatives, sidechain-modified alkylene-3,4-dioxythiophenes, obtained by subsequently performing the following steps:

- a) reacting a solution comprising a mixture of a compound having the general formula (I) and a compound having the general formula (II) in a molar ratio of (I):(II) which is equal to  $m:(100-m)$  wherein  $m$  has a value from 60 to 99

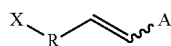


(I)



(II)

with a compound of the general formula (III)



(III)

wherein X is selected from the group consisting of Y—, Y—C(O)—, OCN— or Y—CH<sub>2</sub>C(O)O— in which Y is selected from halides, mesylates, and triflates, R is a linear and/or branched alkylene chain with 1 to 16 carbon atoms, and

A is a linear and/or branched alkyl chain with 1 to 16 carbon atoms or hydrogen;

b) optionally further reacting the mixture of compounds derived from step a) by either

b1) a vinyl copolymerisation or

b2) a hydrosilylation of the vinyl moiety with a silane of the general formula HSiR'<sub>u</sub>(R'')<sub>3-u</sub>, wherein:

R' is selected from the group consisting of linear or branched alkyl or alkenyl chains with 1 to 12 carbon atoms in the main chain, wherein the chains can be substituted with acryloxy-, methacryloxy-, succinyl-, amino-, hydroxyl-, mercapto-, and/or glycidyl groups and/or interrupted by O- and/or S-atoms and/or a NR group,

R'' is selected from the group consisting of halogens, hydroxyl groups, alkoxy groups and/or acyl groups with 1 to 4 carbon atoms, and

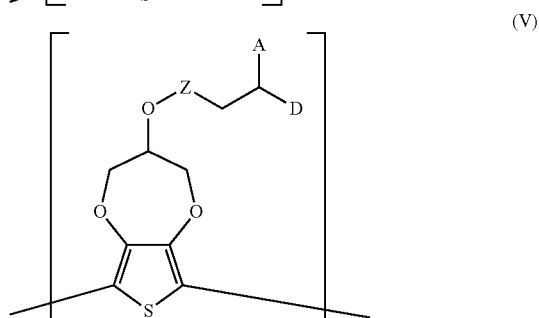
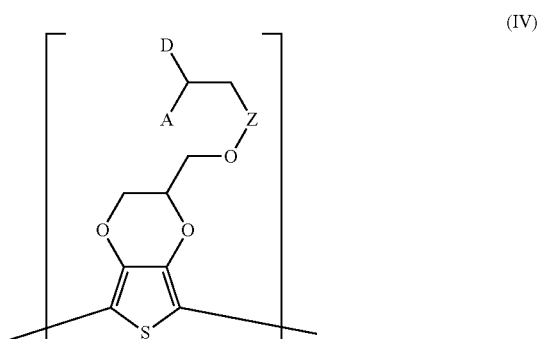
u=0, 1, 2, 3; and further

b3) a thiol-ene addition to the vinyl moiety with a compound of the general formula HS—R—SiR'<sub>u</sub>(R'')<sub>3-u</sub>,

wherein R, R', R'' and u have the same meaning as indicated above; and

c) chemical oxidative polymerisation of a solution of the compound and/or the compounds derived from step b); and/or the organic solvent is an alcohol.

**22.** The colloidal coating dispersion according to claim **21**, wherein the sidechain-modified alkylene-3,4-dioxythiophene comprises the units according to the following general formulae (IV) and (V)



wherein

Z is selected from the group consisting of the structural elements —R—, —C(O)—R—,

—C(O)—NH—R—, and —CH<sub>2</sub>—C(O)O—R—, wherein R is a linear and/or branched alkylene chain with 1 to 16 carbon atoms,

D is selected from the group consisting of:

H, —SiR'<sub>u</sub>(R'')<sub>3-u</sub>, and —S—R—SiR'<sub>u</sub>(R'')<sub>3-u</sub>, wherein R has the same meaning as indicated above,

R' is selected from the group consisting of linear or branched alkyl chains and linear or branched alkenyl chains, each with 1 to 12 carbon atoms in the main chain, wherein the chains are optionally substituted with acryloxy-, methacryloxy-, succinyl-, amino-, hydroxyl-, mercapto-, and/or glycidyl groups and/or interrupted by O- and/or S-atoms and/or a NR' group, wherein R' has the same meaning as indicated above,

R'' is selected from the group consisting of halogens, hydroxyl groups, and alkoxy groups and acyl groups each with 1 to 4 carbon atoms, and u=0, 1, 2, 3; or alternatively represents a chemical bonding to corresponding positions D of neighbored monomers of the formulae (IV) and/or (V), and

A is a linear and/or branched alkyl chain with 1 to 16 carbon atoms or hydrogen, and the compounds of the general formulae (IV) and (V) are comprised in a molar ratio of (IV):(V)=m/(100-m), wherein m has a value in the range from 1 to 99.

**23.** The colloidal coating dispersion according to claim **19**, wherein the colloidal coating dispersion comprises additives selected from the group consisting of non-polymeric binder materials, surfactants, and polymeric binders.

**24.** The colloidal coating dispersion according to claim **19**, wherein, after 12 months of storage, no agglomeration, precipitation, or phase separation occurs.

**25.** A method for manufacturing the colloidal coating dispersion according to claim **19**, comprising the following steps:

- (i) providing at least one water-insoluble monomer;
- (ii) providing at least one organic solvent;
- (iii) dissolving the water-insoluble monomer from step (i) in the organic solvent from step (ii);
- (iv) adding at least one oxidizing agent before, during or after step (iii) to initiate polymerization of the water-insoluble monomer;
- (v) polymerizing the water-insoluble monomer; and
- (vi) removing the oxidizing agent added in step (iv) to stop the polymerization and obtain the colloidal coating dispersion.

**26.** The method according to claim **25**, wherein the molar ratio between the at least one water-insoluble monomer provided in step (i) and the at least one organic solvent provided in step (ii) is from 1:25 to 1:510; and/or

the molar ratio between the at least one oxidizing agent provided in step (iv) and the at least one water-insoluble monomer provided in step (i) is from 1:1.50 to 1:3.00; and/or

step (v) is carried out for a period of time from 1 to 72 h.

**27.** The method according to claim **26**, wherein, the water-insoluble monomer is selected from the group consisting of pyrrole and pyrrole derivatives, thiophene

and thiophene derivatives, sidechain-modified alkylene-3,4-dioxythiophenes, and mixtures thereof; and/or the organic solvent is an alcohol, optionally in combination with one or more additional organic solvent(s); and/or the oxidizing agent is selected from the group consisting of iron(III)-salts.

**28.** The method according to claim **26**, wherein the oxidizing agent iron(III)-salt is selected from the group consisting of iron(III)-chloride, iron-(III)-sulphate, iron-(III)-perchlorate, iron(III) butylnaphthaenesulphonate, iron-(III)-alkylsulphonates, iron-(III)-carboxylate, iron(III) camphorsulphonate, iron-(III)-dodecylsulphonate, iron-(III)-salts of aromatic sulphonic acids, hydrogen peroxide, dichromates, peroxydisulphates, perchlorates, persulphates, perborates, permanganates, and mixtures thereof.

**29.** The method according to claim **25**, wherein step (vi) is carried out by diluting the mixture with an organic solvent, and stirring the resulting mixture,

adding water to obtain an aqueous phase and an organic phase, and separating the aqueous phase containing the oxidizing agent.

**30.** The method according to claim **29**, wherein after step (vi), at least one organic solvent is added to adjust the solids content in the range from 0.1 to 20 wt.-% based on the total weight of the colloidal coating dispersion.

**31.** The method according to claim **25**, wherein:

water is added before or during step (iii); the organic solvent provided in step (ii) is acetonitrile, and/or steps (ii) to (v) are conducted in a temperature range from  $-5$  to  $-15^{\circ}$  C., and/or step (v) is conducted over a period of time from 1.5 to 4.5 hours; or

the organic solvent provided in step (ii) is n-butanol, and/or steps (ii) to (v) are conducted in a temperature range from  $15$  to  $25^{\circ}$  C., and/or step (v) is conducted over a period of time from 60 to 80 hours.

**32.** The method according to claim **25**, wherein additives are added before, after or during step (v), and the additives are selected from the group consisting of non-polymeric binder materials, surfactants, polymeric binders, inorganic-organic hybrid polymers and mixtures thereof.

**33.** A coated substrate deposited with a coating produced from the colloidal coating solution according to claim **19**.

**34.** The coated substrate according to claim **33**, wherein the deposition is conducted by spin coating, slot-die coating or a printing process.

**35.** The coated substrate according to claim **33**, wherein the coated substrate is selected from the group consisting of transparent conducting plastic films coated with a transparent conducting oxide selected from the group consisting of tin-doped indium oxide, fluorine-doped tin oxide, aluminium-doped zinc oxide, aluminium-doped zirconium

oxide, antimony-doped tin oxide, antimony/tin-doped zinc oxide, indium/tin-doped zinc oxide, and/or mixtures thereof,

glass coated with a transparent conducting oxide selected from the group consisting of tin-doped indium oxide, fluorine-doped tin oxide, aluminium-doped zinc oxide, aluminium-doped zirconium oxide, antimony-doped tin oxide, antimony/tin-doped zinc oxide, indium/tin-doped zinc oxide, and/or mixtures thereof,

metal coated with a transparent conducting oxide selected from the group consisting of tin-doped indium oxide, fluorine-doped tin oxide, aluminium-doped zinc oxide, aluminium-doped zirconium oxide, antimony-doped tin oxide, antimony/tin-doped zinc oxide, indium/tin-doped zinc oxide, and/or mixtures thereof,

textiles and fabrics comprising metal wires, or a conducting oxide selected from the group consisting of tin-doped indium oxide, fluorine-doped tin oxide, aluminium-doped zinc oxide, aluminium-doped zirconium oxide, antimony-doped tin oxide, antimony/tin-doped zinc oxide, indium/tin-doped zinc oxide, and/or mixtures thereof,

plastic film, glass, metal, and fabrics coated with an intrinsically conducting polymer, preferably PEDOT:PSS and combinations thereof;

plastic film, glass, metal, and fabrics coated with a transparent conducting oxide selected from the group consisting of tin-doped indium oxide, fluorine-doped tin oxide, aluminium-doped zinc oxide, aluminium-doped zirconium oxide, antimony-doped tin oxide, antimony/tin-doped zinc oxide, indium/tin-doped zinc oxide, and/or mixtures thereof and an intrinsically conducting polymer, preferably PEDOT:PSS and combinations thereof;

plastic film, glass, metal, and fabrics coated with a transparent layer stack comprising insulator/metal/insulator, semi-conductor/metal/insulator or semi-conductor/metal/semi-conductor layers or multiples thereof, an optionally over- or under-coated metal mesh or grid, an optionally over- or undercoated metal or carbon nanowire deposit, carbon nanotubes, graphene and mixtures thereof.

**36.** An article comprising at least one layer deposited from the colloidal coating solution according to claim **19**.

**37.** The article according to claim **36**, wherein the deposited layer consists of at least one electrochromic polymer; and/or

the layer adhesion determined according to DIN EN ISO 2409 is rated with GT0;

and/or the visual transmission hub determined according to DIN EN 410 is in the range from 55 to 60%.

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