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Multilayered arrangement for electro-optical devices

5 The present invention relates to a multilayered arrangement for electro-optical devices, in particular having a conductive organic layer on a transparent electrode on a substrate, where the substrate is preferably a transparent polymer.

10 Display devices having cathode ray tubes (CRTs) which can be used for televisions or personal computers (PCs), etc., have large-area screens. However, since a screen coated with a luminescent material must be arranged at a pre-determined distance from the electron gun in these display devices, a problem exists in that the total volume of such display devices is too large. Thus, a CRT device of this type cannot be used for electronic equipment having small dimensions and low power consumption, such as for a television set which can be hung on walls, for portable

15 television sets and notebook computers, etc. For devices having small dimensions and low power consumption, flat panel display devices, such as liquid-crystal display devices (LCDs, for example TN, STN and DSTN displays, ferroelectric displays and polymer dispersed LC arrangements (PDLCs)), plasma display panels (PDPs), organic electroluminescent displays (OELDs), electrophosphorescent displays

20 (OELDs with phosphorescent emitters) and vacuum fluorescent displays (VFDs), or electrochromic displays (ECDs) and electronic paper or electronic ink have been developed. Of these flat panel display devices, the LCDs have been the most researched recently, in spite of various disadvantages, since they have high image quality and low power consumption. There are two types of LCD: LCDs having a

25 passive matrix and LCDs having an active matrix (AMLCD, active matrix LCD). Of these LCDs, the AMLCD is the LCD type which has been most used recently, since in these, each pixel can be addressed independently by a switching element, enabling a high contrast ratio and high resolution to be achieved since the interference caused by adjacent pixels is reduced.

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In general, liquid crystals are easily affected by external influences, such as an electric field, a magnetic field, tension, pressure, and the like. Owing to these properties, liquid crystals are used as light diaphragms or even as display devices.

5 In order to utilize these properties of liquid crystals, they can, if necessary, be moved under the influence of the environment. For uniform alignment of liquid crystals, a homogeneous and smooth underlayer (substrate), inter alia, is vital in addition to the actual alignment layer (rubbed polyimide). The multilayered structure of various LCD types is described, for example, in "Displays: Einführung in die Technik aktiver
10 und passiver Anzeigen" [Displays: Introduction to the Technology of Active and Passive Displays], Peter M. Knoll, Hüthig Verlag Heidelberg, 1986.

The interest in flexible displays and display devices has recently been increasing. The transparent substrates used here are polymer films, such as polycarbonate or other
15 transparent polymers. These substrates are provided with a conductive layer, preferably indium-tin oxide (ITO). However, a disadvantage here is the excessive roughness of the conductive layer, which can result in short-circuits during operation and high reject rates during production. For manufacturing reasons, conventional inorganic conductive layers always have greater roughness on plastic substrates than
20 on glass. Furthermore, inorganic conductive layers such as ITO are brittle, with the consequence that cracks occur on flexible substrates owing to the different coefficients of expansion or extensibility and toughness, which may result in interruption of the electrical conductivity. This arises in particular during storage and/or handling of coiled substrates, such as, for example, ITO-PET for roll to roll processes.

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The object of the invention was therefore to develop novel layer arrangements which do not exhibit the said disadvantages.

30 In order to achieve the object, a layer of an organic conductive polymer system is applied directly to the conductive layer, for example ITO, already present on the substrate. Application of the conductive polymer system compensates for surface

roughness of the conductive layer on the substrate, particularly on plastic substrates. Furthermore, the polymer system bridges cracks that are present. Through its extensibility and toughness, it ensures that any cracks present after handling of the layer system according to the invention remain bridged by conductive paths and the surface conductivity is not interrupted.

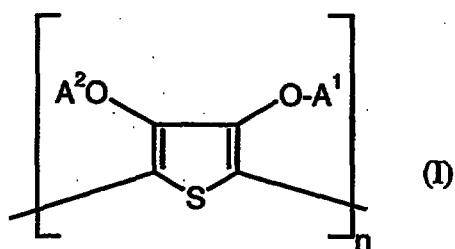
The invention relates to a layer arrangement consisting of at least one transparent substrate having an electrically conductive layer, an electro-optically active layer, and a further substrate having an electrically conductive layer, characterized in that at least one of the two electrically conductive substrates is additionally coated with an organic conductive polymer system.

In a preferred embodiment of the invention, the transparent conductive layer on the substrates in the layer arrangement consists of a metal or metal oxide or mixed oxides, which may also be doped, and the electro-optically active material is a liquid crystal. In a particularly preferred embodiment, the electro-optically active material is a liquid crystal, and at least one of the two substrates is a plastic substrate. For protection against environmental influences, such as mechanical damage, moisture, etc., the layer arrangement may be encapsulated.

The organic conductive polymer system may be, for example, a system based on polyanilines, polypyrroles or polythiophenes.

The term "conductive polymer systems" is taken to mean a system which may comprise further constituents in addition to the actual organic conductive polymer. These may be, for example, film formers, crosslinking agents, thermosolvents, binders or additives which improve the electrical conductivity. Examples are described in US-A 5,766,515 or EP-A 602 713.

In a preferred embodiment of the invention, the organic conductive polymer is a cationically charged polythiophene comprising structural units of the formula (I)



in which

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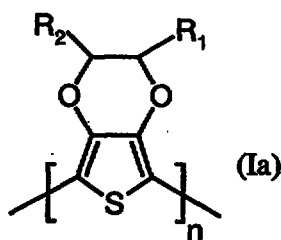
A¹ and A², independently of one another, are optionally substituted (C₁-C₁₈)-alkyl or together form optionally substituted (C₁-C₁₈)-alkylene, and

n is an integer from 2 to 10,000, preferably from 3 to 5000,

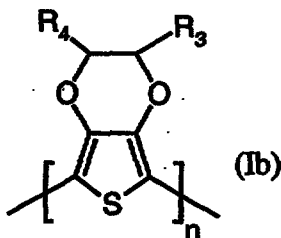
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in the presence of anions or polyanions.

Particularly preferred cationic polythiophenes are built up from structural units of the formula (Ia) or (Ib)



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in which

5 R_1 and R_2 , independently of one another, are hydrogen, optionally substituted (C_1 - C_{18})-alkyl, preferably (C_1 - C_{10})-alkyl, in particular (C_1 - C_6)-alkyl, optionally substituted (C_2 - C_{12})-alkenyl, preferably (C_2 - C_8)-alkenyl, optionally substituted (C_3 - C_7)-cycloalkyl, preferably cyclopentyl or cyclohexyl, optionally substituted (C_7 - C_{15})-aralkyl, preferably phenyl-(C_1 - C_4)-alkyl, optionally substituted (C_6 - C_{10})-aryl, preferably phenyl or naphthyl, optionally substituted (C_1 - C_{18})-alkoxy, preferably (C_1 - C_{10})-alkoxy, for example methoxy, ethoxy, n- or isopropoxy, or optionally substituted (C_2 - C_{18})-alkoxy esters, and

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R_3 and R_4 , independently of one another, are hydrogen, but not both simultaneously, (C_1 - C_{18})-alkyl, preferably (C_1 - C_{10})-alkyl, in particular (C_1 - C_6)-alkyl, which is substituted by at least one sulphonate group, hydroxyl group or carboxyl group, (C_2 - C_{12})-alkenyl, preferably (C_2 - C_8)-alkenyl, which is substituted by at least one sulphonate group, hydroxyl group or carboxyl group, (C_3 - C_7)-cycloalkyl, preferably cyclopentyl or cyclohexyl, which is substituted by at least one sulphonate group, hydroxyl group or carboxyl group, (C_7 - C_{15})-aralkyl, preferably phenyl-(C_1 - C_4)-alkyl, which is substituted by at least one sulphonate group, hydroxyl group or carboxyl group, (C_6 - C_{10})-aryl, preferably phenyl or naphthyl, which is substituted by at least one sulphonate group, hydroxyl group or carboxyl group, (C_1 - C_{18})-alkoxy, preferably (C_1 - C_{10})-alkoxy, for example methoxy, ethoxy, n- or isopropoxy, which is substituted by at least one sulphonate group, hydroxyl group or carboxyl group, or (C_2 - C_{18})-alkoxy ester which is substituted by at least one sulphonate group, hydroxyl group or carboxyl group.

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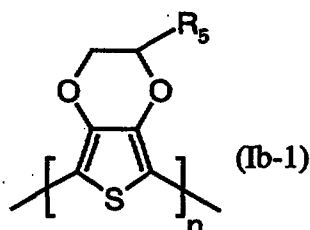
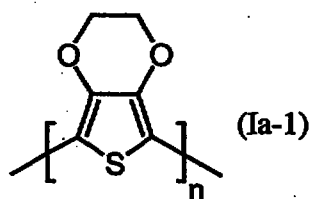
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n is a number from 2 to 10,000, preferably from 3 to 5000.

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Very particular preference is given to cationic or neutral polyalkylenedioxythiophenes of the formulae (Ia-1) and (Ib-1)



5 in which

10 R_5 is (C_1-C_{18}) -alkyl, preferably (C_1-C_{10}) -alkyl, in particular (C_1-C_6) -alkyl, which is substituted by at least one sulphonate group, hydroxyl group or carboxyl group, (C_2-C_{12}) -alkenyl, preferably (C_2-C_8) -alkenyl, which is substituted by at least one sulphonate group, hydroxyl group or carboxyl group, (C_3-C_7) -cycloalkyl, preferably cyclopentyl or cyclohexyl, which is substituted by at least one sulphonate group, hydroxyl group or carboxyl group, (C_7-C_{15}) -aralkyl, preferably phenyl- (C_1-C_4) -alkyl, which is substituted by at least one sulphonate group, hydroxyl group or carboxyl group, (C_6-C_{10}) -aryl, preferably phenyl or naphthyl, which is substituted by at least one sulphonate group, hydroxyl group or carboxyl group, (C_1-C_{18}) -alkoxy, preferably (C_1-C_{10}) -alkoxy, for example methoxy, ethoxy, n- or isopropoxy, which is substituted by at least one sulphonate group, hydroxyl group or carboxyl group, or (C_2-C_{18}) -alkoxy ester which is substituted by at least one sulphonate group, hydroxyl group or carboxyl group, and

20 n is an integer from 2 to 10,000, preferably from 3 to 5000.

In a further preferred embodiment of the invention, n in the said formulae is an integer from 4 to 150, preferably from 4 to 50.

5 The polyanions used are the anions of polymeric carboxylic acids, such as polyacrylic acids, polymethacrylic acids, polymaleic acids and polymeric sulphonic acids, such as polystyrenesulphonic acids and polyvinylsulphonic acids. These polycarboxylic and -sulphonic acids may also be copolymers of vinylcarboxylic and vinylsulphonic acids with other polymerizable monomers, such as acrylates and styrene.

10 The counterion is particularly preferably the anion of polystyrenesulphonic acid (PSA).

The molecular weight of the polyacids supplying the polyanions is preferably from 1000 to 2,000,000, particularly preferably from 2000 to 500,000. The polyacids or
15 their alkali metal salts are commercially available, for example polystyrenesulphonic acids and polyacrylic acids, or alternatively can be prepared by known processes (see, for example, Houben Weyl, Methoden der organischen Chemie [[Methods of Organic Chemistry], Vol. E 20 Makromolekulare Stoffe [Macromolecular Substances], Part 2, (1987), pp. 1141 et seq.).

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Instead of the free polyacids necessary for the dispersions from polyalkylenedioxythiophenes and polyanions, it is also possible to employ mixtures of alkali metal salts of the polyacids and corresponding amounts of monoacids.

25 In the case of the formula (Ib-1), the polyalkylenedioxythiophenes carry positive and negative charges in the structural unit.

The preparation of the polyalkylenedioxythiophenes is described, for example, in EP-A 0 440 957 (= US-A 5,300,575). The polyalkylenedioxythiophenes are prepared
30 by oxidative polymerization. They thus attain positive charges, which are not shown in the formulae since their number and position cannot be determined precisely.

The polythiophene dispersion can be applied to the transparent conductive substrate by established processes, such as pouring, printing, spraying, dipping, flooding or ink-jet printing.

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Suitable transparent substrates which are provided with a conductive layer are glass, ultrathin glass (flexible glass) or plastics.

At least one of the substrates preferably consists of plastic.

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Particularly suitable plastics are: polycarbonates, polyesters, copolycarbonates, polysulphone, polyether sulphone, polyimide, polyethylene, polypropylene or cyclic polyolefins or cyclic olefin copolymers (COCs) or hydrogenated styrene (co)polymers.

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Preferred polymers are polysulphone, polyether sulphone, polyesters, cyclic olefin copolymers, hydrogenated styrene (co)polymers and polycarbonates. From the group consisting of the polyesters, preference is given to PET and PEN (polyethylene terephthalate and polyethylene naphthenate respectively).

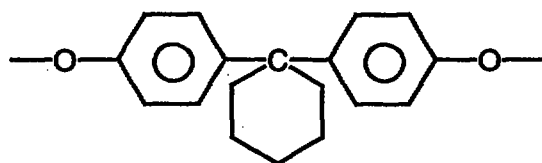
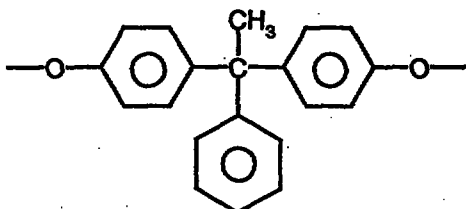
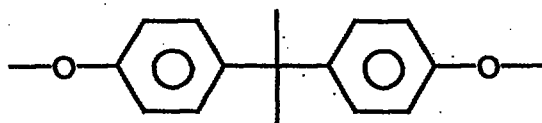
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Suitable polymer substrates are, for example, polyester films, PES films from the Sumitomo company or polycarbonate films from Bayer AG (Makrofol®).

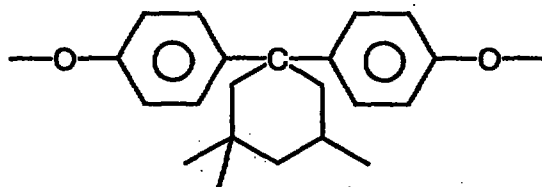
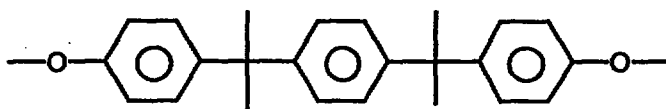
These substrates may be provided with a scratch-resistant and/or chemical-resistant finish by means of an additional layer, for example Marnot® films (Bayer AG).

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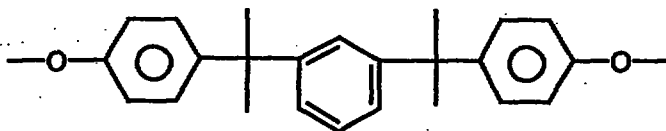
From the group consisting of the polycarbonates, the polycarbonates or copolycarbonates which contain one of the following segments are particularly suitable:



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Further bisphenols for the synthesis of polycarbonates are described, for example, in EP-A 359 953.

Examples**1. Application of a conductive polythiophene layer (Baytron®P)****5 Application of the Baytron® P layer to the ITO:**

About 10 ml of the approximately 1.2% strength poly(ethylenedioxythiophene)/poly-styrenesulphonic acid solution (BAYER AG, Leverkusen, Baytron® P) are filtered (Millipore HV, 0.45 µm). The substrate is subsequently placed on a spin coater, and the filtered solution is distributed on the ITO-coated side of the substrate. The excess solution is subsequently spun off by rotating the plate at 500 rpm for a period of 3 minutes. The substrate coated in this way is subsequently dried for 5 minutes at 110°C on a hot plate. The layer thickness is 60 nm (Tencor, Alphastep 200).

15 Table 1 shows the effect of the Baytron®P solution on the surface roughness of the substrate.

Table 1

	<u>Substrate</u>	<u>Roughness r_s (nm)</u>
	a) Glass/ITO	2.5
20	b) Glass/ITO/Baytron®P	1.6
	c) Polyester (PET)/ITO	3.9
	d) Polyester (PET)/ITO/Baytron®P	2.5

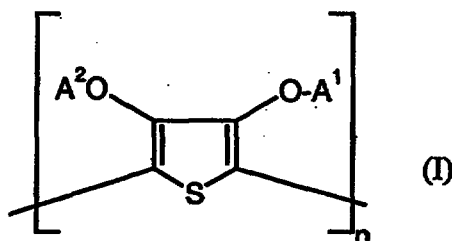
25 The roughness values were determined with the aid of an atomic force microscope (AFM).

The smoothing action exerted by the conductive layer on the substrate surface is clearly evident. Sample d) shows no visible surface cracks even after repeated mechanical treatment – flexing, rolling, etc. The Baytron®P-coated substrates can be employed for the construction of conventional electro-optically active arrangements, such as, for example, liquid-crystal displays, electrochromic displays, etc.



Patent Claims

1. Layer arrangement consisting of at least one transparent substrate having an electrically conductive layer, an electro-optically active layer, and a further substrate having an electrically conductive layer, characterized in that at least one of the two electrically conductive substrates is additionally coated with an organic conductive polymer system.
2. Layer arrangement according to Claim 1, characterized in that the transparent conductive layer on the substrates consists of a metal or metal oxide or mixed oxides, which may also be doped.
3. Layer arrangement according to Claim 1, characterized in that the organic conductive polymer system is a polyaniline, polypyrrole or polythiophene system.
4. Layer arrangement according to Claim 3, characterized in that the organic conductive polymer system is a cationically charged polythiophene comprising structural units of the formula (I)



in which

A¹ and A², independently of one another, are optionally substituted (C₁-C₁₈)-alkyl or together form optionally substituted (C₁-C₁₈)-alkylene, and



n is an integer from 2 to 10,000, preferably from 3 to 5000,

in the presence of anions or polyanions.

- 5 5. Layer arrangement according to Claim 1, characterized in that the transparent substrate consists of glass or a plastic.
6. Layer arrangement according to Claim 1, characterized in that at least one of the two substrates is a plastic substrate.
- 10 7. Layer arrangement according to Claim 5 or 6, characterized in that the plastic is polycarbonate or copolycarbonate, polyester, polysulphone, polyether sulphone, polyimide, polypropylene, polyethylene or a cyclic olefin copolymer or hydrogenated styrene (co)polymer.
- 15 8. Layer arrangement according to Claim 7, characterized in that the plastic substrate is provided with a scratch-resistant and/or chemical-resistant finish.
9. Layer arrangement according to Claim 1, characterized in that the electro-
- 20 optically active layer is a liquid-crystal layer.
10. Layer arrangement according to Claim 1, characterized in that the arrangement is encapsulated.