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(54) **Antireflective and antistatic coating for, in particular, a cathode ray tube.**

(57) An antireflective and antistatic coating on a substrate 2, in particular a display screen of a cathode ray tube, was manufactured in the form of a double layer consisting of an antistatic layer 4 and an antiglare layer 6. The antistatic layer consisted of silicon dioxide containing at least one conductive metal oxide and was manufactured from an alcoholic solution of a alkoxysilane compound. The antiglare layer consisted of lithium silicate and was manufactured from a lithium oxide-stabilized silicon dioxide sol in water. If desired, the order of both layers may be reversed, in which case the conductive metal oxide may, if required, be incorporated in the lithium silicate.

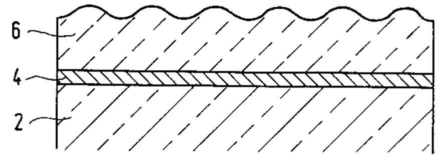

FIG.1

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The invention relates to a antireflective and antistatic coating on a substrate, which coating comprises a double layer consisting of a layer of silicon dioxide and an antiglare layer.

The invention also relates to a cathode ray tube comprising a display screen having a antireflective and antistatic coating comprising a double layer which consists of a layer of silicon dioxide and an antiglare layer.

The invention further relates to a method of manufacturing an antireflective ad antistatic coating on a substrate, which coating comprises a double layer consisting of a antistatic layer and a antiglare layer, said antistatic layer being manufactured by providing a suspension of at least one conductive metal oxide in an alcoholic solution of an alkoxysilane compound, followed by a treatment at an increased temperature to form a layer of a mixture of silicon dioxide and at least one conductive metal oxide.

The invention also relates to a alternative method of manufacturing an antireflective and antistatic coating on a substrate, which coating comprises a double layer consisting of a layer of silicon dioxide and an antiglare layer.

Antireflective coatings are used, for example, on display screens of display devices, on envelopes of light sources and on other optical elements such as windows, to reduce reflection losses of traversing light and to suppress disturbing reflections in images. Coatings as described above are more particularly used to reduce specular reflection (antiglare effect). Antistatic coatings are used, for example, on display screens of display devices. Such layers are sufficiently electroconductive to ensure that a high electrostatic voltage present on the outside surface of the device is removed within a few seconds. Thus, it is precluded that a user upon touching a screen is unpleasantly shocked and, in addition, the attraction of atmospheric dust is reduced.

In United States Patent Specification US 4,945,282, a description is given of a display screen which is provided with an antireflective and antistatic coating which comprises a double layer consisting of a layer of silicon dioxide and a antireflective layer. The silicon dioxide layer is an antistatic layer which contains, for example, a transparent conductive metal oxide, and which is disposed between the substrate ad the antireflective layer and has a thickness of 5 to 50 nm. The antireflective layer also contains silicon dioxide and comprises silicon dioxide particles having diameters of 10 to 1000 nm. If desired, the functions of both layers can be combined in a single layer. Said United States Patent Specification also describes a method of manufacturing an antireflective and antistatic coating. Both layers are manufactured by providing an alcoholic solution of an alkoxysilane compound, followed by a treatment at an increased temperature to form a layer of silicon dioxide. For the manufacture of said antistatic layer, for example, a conductive metal oxide such as tin oxide, indium oxide or antimony oxide, is suspended in the alcoholic solution of the alkoxysilane compound. For the manufacture of the antireflective layer, silicon dioxide particles are suspended in the alcoholic solution of the alkoxysilane compound.

A disadvantage of this known method of manufacturing an antireflective and antistatic coating is that it utilizes a reactive, intrinsically unstable alcoholic solution of an alkoxysilane compound. The solution is sensitive to moisture and has limited keeping qualities. As the structure of the layer thus manufactured is governed, *inter alia*, by the degree of hydrolysis and polymerization of the alkoxysilane compound and by the viscosity of the solution, the reproducibility of the result leaves a lot to be desired. This is important, in particular, for the antireflective layer in which the microstructure substantially influences the optical properties, and it is only of minor importance for the much thinner antistatic layer. A further disadvantage of the known method is formed by the use of an organic solvent which, when used on a large scale, requires a number of safety precautions to be taken. Moreover, the coating manufactured according to the known method is mechanically weak due to the presence of discrete silicon dioxide particles in the surface layer.

It is an object of the invention to provide, *inter alia*, an antireflective and antistatic coating on a substrate, which coating can be manufactured in a simple and reproducible manner. In this connection, the invention aims to use stable starting materials having long keeping qualities. A further object of the invention is to provide a mechanically strong layer having stable properties which are not subject to rapid deterioration due to damage, the attack of moisture or contamination. A particular object of the invention is to provide a cathode ray tube comprising a display screen which is provided with such an antireflective and antistatic coating. A still further object of the invention is to provide a simple and reliable method of providing an antireflective and antistatic coating. In this connection, the invention aims at minimizing the use of organic solvents.

The object of providing a substrate, in particular a cathode ray tube comprising a display screen, having an antireflective and antistatic coating is achieved by an antireflective and antistatic coating as described in the opening paragraph, which coating comprises a double layer consisting of a layer of silicon dioxide and an antiglare layer, said coating according to the invention being characterized in that the antiglare layer consists of lithium silicate.

In a suitable embodiment of the coating according to the invention, the layer of silicon dioxide is an antistatic layer which contains at least one conductive metal oxide. Suitable transparent, conductive metal oxides are tin oxide, indium oxide, antimony oxide and mixtures of said oxides. Other materials which are known *per se*, such as hygroscopic materials and metals and metal compounds, in particular palladium compounds, may alternatively be used to provide the antistatic layer with the required electric conductance.

According to a first particular embodiment of the coating according to the invention, the layer of silicon dioxide is located between the substrate and the layer of lithium silicate. If desired, materials may be added to the layers to change the optical, mechanical or other properties. For example, dyes may be used to influence the light transmission properties. Preferably, the silicon dioxide layer contains at least one dye. This is preferred to the addition of a dye to the lithium silicate layer because the incorporation of the dye in such a layer is less durable.

According to a second particular embodiment of the inventive coating, in which the layers are provided in the reverse order as compared with the first embodiment, the layer of lithium silicate is located between the substrate and the layer of silicon dioxide.

According to a third particular embodiment of the inventive coating, in which the antiglare and antistatic functions are combined in a single layer, the layer of lithium silicate is a antistatic layer which contains at least one conductive metal oxide, said layer being located between the substrate ad the layer of silicon dioxide. The conductive metal oxides used, or if desired other materials imparting electric conductance, may be the same as those used in the two above-mentioned embodiments in the layer of silicon dioxide. In this third embodiment, the layer of silicon dioxide serves to ensure that the materials which are added to the layer of lithium silicate are permanently incorporated therein.

If it is desirable to incorporate additional materials such as one or more dyes in the second or third embodiment of the inventive coating, said dyes can be added to each of the layers at will. In particular, at least one of the layers of the double layer contains a dye. In a layer of silicon dioxide, dyes are permanently incorporated, and the layer of lithium silicate according to these embodiments is covered with a layer of silicon dioxide, so that also in this case a definitely stable coating is obtained.

If desired, a substrate comprising a coating according to the invention may additionally be provided with antireflective layers, which are known *per se*, to reduce both the total specular reflection and the total diffuse reflection. For this purpose, for example, a layer of magnesium fluoride having a low refractive index may be provided as the outermost layer, or a stack of layers having alternately high and low refractive indices may be used.

The refractive index may be changed by adding, if desired, dopants to the coating according to the invention, in particular to the silicon dioxide layer. A stack of layers which is suited to reduce total reflection consists, for example, of a first antistatic layer of silicon dioxide which is additionally doped with titanium dioxide (refractive index 1.7), and a second layer of titanium dioxide (refractive index 2.1, to be manufactured according to a method which is analogous to the method of manufacturing the silicon dioxide layer), and with an outermost antiglare layer of lithium silicate (refractive index 1.43). The thickness of each of the layers is 100 to 150 nm.

The object of providing a method of manufacturing an antireflective and antistatic coating is achieved by a method as described in the opening paragraph, in which a double layer is manufactured comprising an antistatic layer and an antiglare layer, the antistatic layer being manufactured by providing a suspension of at least one conductive metal oxide in a alcoholic solution of a alkoxysilane compound, followed by a treatment at an increased temperature to form a layer of a mixture of silicon dioxide and at least one conductive metal oxide, which method according to the invention is characterized in that the antiglare layer is manufactured by providing a lithium oxide-stabilized silicon dioxide sol in water, followed by a treatment at an increased temperature to form a layer of lithium silicate. Corresponding to the above-described first two embodiments of the coating according to the invention, the antistatic layer and the antiglare layer can be provided on a substrate, for example on the display screen of a cathode ray tube, in any desired relative order.

In line with the above-described third embodiment of the coating according to the invention, an alternative method in accordance with the invention is characterized in that an antiglare layer having a antistatic effect is manufactured by providing a suspension of at least one conductive metal oxide in a lithiumoxide-stabilized silicon dioxide sol in water, followed by a treatment at an increased temperature to form a layer of a mixture of lithium silicate and at least one conductive metal oxide, after which a protective layer is manufactured by providing an alcoholic solution of an alkoxysilane compound, followed by a treatment at an increased temperature to form a layer of silicon dioxide.

According to the invention, a layer of silicon dioxide is used which can be manufactured in accordance with a method described in United States Patent Specification US 4,945,282. According to the invention, this layer is used as a antistatic layer or as a protective layer. For both applications a relatively thin layer, having a thickness below 200 nm, preferably between 5 and 50 nm, can be used. By virtue thereof, the required quantities of reactive and, thus, unstable alkoxysilane compound and of the organic solvent are limited as compared with the method according to the state of the art. According to the invention, a layer of lithium silicate is used for the antiglare layer, which lithium silicate layer does not contain discrete particles and, hence, exhibits great mechanical strength. In United States Patent Specification US 3,940,511, an antireflective layer of lithium silicate and a method of manufacturing said layer are described, said layer containing colour-correcting means such as soot and dyes, however, investigations which have led to the invention have shown that, without additional measures, such a layer is unsuitable for the incorporation of permanently conductive metal compounds or dyes. The method according to the invention combines the advantages of both known techniques and minimizes the disadvantages of each of said techniques.

The invention will be explained in greater detail by means of exemplary embodiments and an accompanying drawing, in which

Figs. 1 to 3 are diagrammatic cross-sectional views of different embodiments of a substrate comprising a coating layer according to the invention, and

Fig. 4 is a partly cut-away perspective view of an embodiment of a cathode ray tube according to the invention.

Exemplary embodiment 1.

Fig. 1 shows a substrate 2 having an antireflective and antistatic coating in accordance with a first embodiment of the invention, which coating consists of a double layer comprising an antistatic layer 4 of silicon dioxide with at least one conductive metal oxide, and an antiglare layer 6 of lithium silicate.

Such a coating was manufactured by the following method according to the invention. The display screen of a cathode ray tube was thoroughly cleaned, after which a first, antistatic layer was provided by spin coating. The coating material consisted of a solution of 2% by weight of tetraethyl orthosilicate $Si(OC_2H_5)_4$ in ethanol, wherein 1% by weight of a 1:0.15 mixture of tin oxide SnO_2 and atimony oxide Sb_2O_3 was dispersed as the conductive material. If desired, the coating material contains a dye, for example 0.2% by weight of Rhodamine B, available from Merck. The dimensions of the metal oxide particles and dyes present in the suspension are smaller than 50 nm to preclude light scattering. The layer was dried at 60 °C and had a thickness in the range between 50 and 100 nm.

Subsequently, a second, antiglare layer was provided by spin coating. The coating material consisted of a lithium oxide-stabilized silicon dioxide sol in water having a solid content of 2% by weight and a SiO_2:Li_2O molar ratio of 8:1. The layer thickness was approximately 1000 nm. Next, both layers were cured by a treatment at a temperature of 160 ° C for 30 minutes, in which treatment the first layer was converted to silicon dioxide and the second layer was converted to lithium silicate. Finally, the display screen was washed with running water and dried.

The display screen thus obtained was sufficiently electroconductive and antistatic. The increase in diffuse reflection at the expense of specular reflection assists in the suppression of disturbing images of, for example, external light sources on a display screen.

Instead of the above-mentioned tetraethyl orthosilicate, other alkoxysilane compounds of the type $Si(OR)_4$, which are known *per se*, can alternatively be used, where R is an alkyl group having preferably 1 to 5 carbon atoms. For example, methanol may alternatively be used as the solvent. A quantity of water having, for example, an inorganic acid may be added to the solution to enhance the conversion to silicon dioxide. Suitable compositions are described in, for example, United States Patent Specification US 4,945,282, wherein also suitable conductive metal oxides are mentioned in addition to other compounds which can suitably be used in an antistatic layer. Instead of conductive metal oxides, for example, compounds of palladium, platinum or gold may be used to obtain electric conductance, see United States Patent Specification US 4,563,612. Compositions which are suitable for a lithium oxide-stabilized silicon dioxide sol in water, are described in United States Patent Specifications US 3,940,511 and US 4,563,612.

Exemplary embodiment 2.

Fig. 4 diagrammatically shows a cathode ray tube, which is known *per se*, comprising a glass envelope 31 having a display window 32, a cone 33 and a neck 34. In the neck there is provided an electron gun 35 for generating an electron beam 36. Said electron beam 36 is focused on a display screen 37 to form a target spot 38. The electron beam 36 is deflected across the display screen 37 in two mutually perpendicular directions x-y by means of the deflection coil system 39. A layer of a luminescent material (phosphor) is present on the display screen 37. The outside of the display window 32 is provided with an antireflective and antistatic coating 40 which was manufactured as described in exemplary embodiment 1.

Exemplary embodiment 3.

Fig. 2 shows a substrate 12 having an antireflective and antistatic coating in accordance with a second embodiment of the invention, which coating consists of a double layer comprising an antiglare layer 16 of lithium silicate and an antistatic layer 14 of silicon dioxide containing at least one conductive metal oxide.

Such a coating was manufactured by using the materials and the method in accordance with exemplary embodiment 1, except that the sequence in which the layers were provided was reversed. After providing a first layer of a lithium oxide-stabilized silicon dioxide sol, said layer was dried at 60 ° C. After providing the second layer containing the alkoxysilane compound, both layers were annealed at a temperature of 160 ° C for 30 minutes, after which the display screen was washed with running water and dried. The result obtained was the same as described in exemplary embodiment 1.

Exemplary embodiment 4.

Fig. 3 shows a substrate 22 having an antireflective and antistatic coating in accordance with a third embodiment of the invention, which coating consists of a double layer comprising an antiglare and antistatic layer 26 of lithium silicate containing at least one conductive metal oxide, and a protective layer 28 of silicon dioxide.

Such a coating was manufactured by using the materials and the method in accordance with exemplary embodiment 3, except that the conductive metal oxides were suspended in the lithium oxide-stabilized silicon dioxide sol in water instead of in the alcoholic solution of the alkoxysilane compound. The quantities used, the process steps and the results were the same as in exemplary embodiment 3.

By means of the invention, effective coatings were manufactured in a simple and reproducible manner, which coatings were suitable for display screens of cathode ray tubes and exhibited satisfactory antiglare and antistatic properties as well as a satisfactory resistance against various ambient influences such as moisture and mechanical damage.

Claims

1. An antireflective and antistatic coating on a substrate, which coating comprises a double layer consisting of a layer of silicon dioxide and an antiglare layer, characterized in that the antiglare layer consists of lithium silicate.

2. A coating as claimed in Claim 1, in which the layer of silicon dioxide is a antistatic layer which contains at least one conductive metal oxide.

3. A coating as claimed in Claim 2, in which the layer of silicon dioxide is located between the substrate and the layer of lithium silicate.

4. A coating as claimed in Claim 3, in which the layer of silicon dioxide contains at least one dye.

5. A coating as claimed in Claim 2, in which the layer of lithium silicate is located between the substrate and the layer of silicon dioxide.

6. A coating as claimed in Claim 1, in which the layer of lithium silicate is an antistatic layer which contains at least one conductive metal oxide, said layer being located between the substrate and the layer of silicon dioxide.

7. A coating as claimed in Claim 5 or 6, in which at least one of the layers of the double layer contains a dye.

8. A cathode ray tube comprising a display screen having a antireflective and antistatic coating which comprises a double layer consisting of a layer of silicon dioxide and an antiglare layer, characterized in that the antiglare layer is made from lithium silicate.

9. A method of manufacturing an antireflective and antistatic coating on a substrate, which coating comprises a double layer consisting of an antistatic layer and an antiglare layer, the antistatic layer being manufactured by providing a suspension of at least one conductive metal oxide in an alcoholic solution of a alkoxysilane compound, followed by a treatment at an increased temperature to form a layer of a mixture of silicon dioxide and at least one conductive metal oxide, characterized in that the antiglare layer is manufactured by providing a lithium oxide-stabilized silicon dioxide sol in water, followed by a treatment at an in-

creased temperature to form a layer of lithium silicate.

10. A method of manufacturing an antireflective and antistatic coating on a substrate, which coating comprises a double layer consisting of a layer of silicon dioxide and an antiglare layer, characterized in that an antiglare layer having a antistatic effect is manufactured by providing a suspension of at least one conductive metal oxide in a lithium oxide-stabilized silicon dioxide sol in water, followed by a treatment at an increased temperature to form a layer of a mixture of lithium silicate and at least one conductive metal oxide, after which a protective layer is manufactured by providing a alcoholic solution of an alkoxysilane compound, followed by a treatment at an increased temperature to form a layer of silicon dioxide.

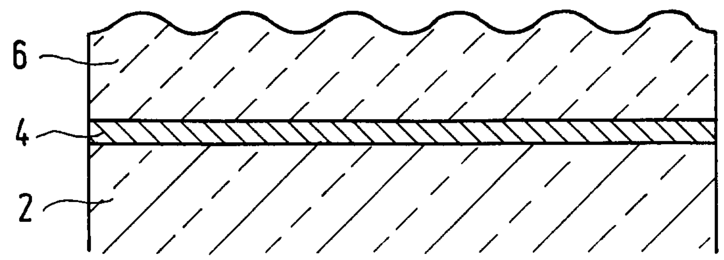

FIG.1

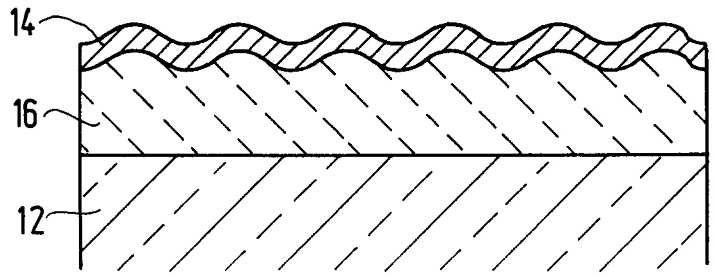

FIG.2

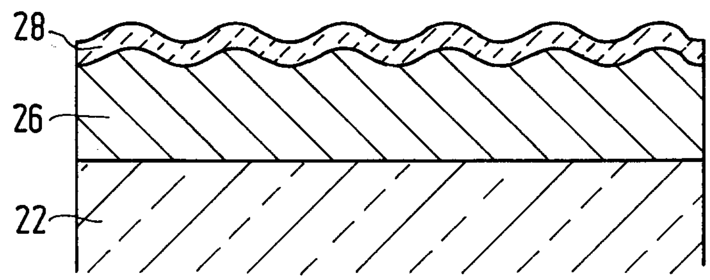

FIG.3

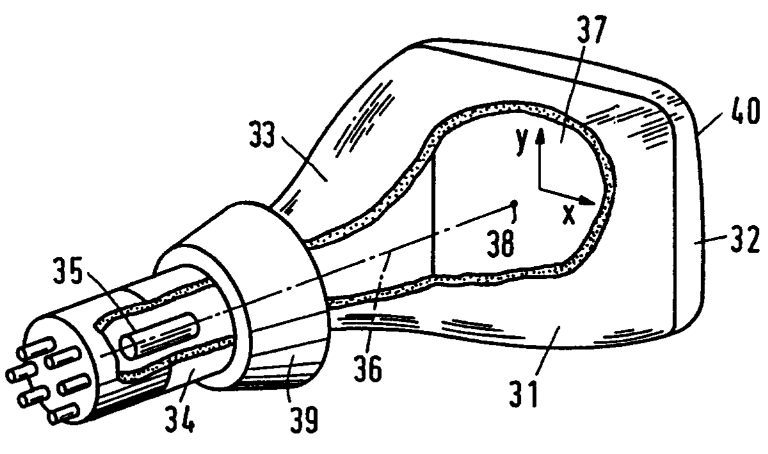

FIG.4

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EUROPEAN SEARCH REPORT

Application Number
EP 92 20 3161

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
D,A	FR-A-2 629 268 (HITACHI) * Abstract * * Claims 1-3 * * Figs. 2-4 * ---	1,8-10	H01J29/86 H01J29/89 H01J29/18
D,A	US-A-3 940 511 (S.B.DEAL ET AL.) * Abstract * * Claims 1-6 * ---	1,8-10	
A	DATABASE WPIL Week 8145, Derwent Publications Ltd., London, GB; AN 81-82406 & JP-A-56 121 661 (PENTEL) 24 September 1981 * abstract * ---	1	
D,A	GB-A-2 161 320 (RCA) * the whole document * -----	1,8-10	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

H01J

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	12 JANUARY 1993	DAMAN M.A.

CATEGORY OF CITED DOCUMENTS

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