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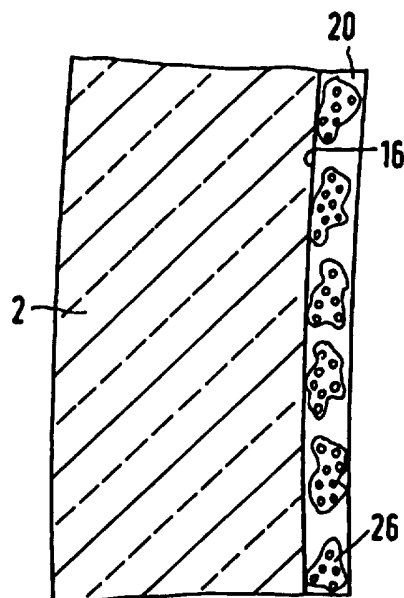
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(54) Title: METHOD OF MANUFACTURING A SUBSTRATE WITH REDUCED GLARE, METHOD FOR MANUFACTURING A DISPLAY WINDOW OF A CATHODE RAY TUBE AND A CATHODE RAY TUBE HAVING A DISPLAY WINDOW

(57) Abstract

Method for manufacturing a glass substrate with reduced glare wherein a suspension comprising sub-micron transparent oxide particles and a binder is coated on the substrate to form a film, whereafter the film is dried in such a manner that *in situ* flocculation of the particles takes place. Said *in situ* flocculation strongly reduces glare on the said surface.



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Method for manufacturing a substrate with reduced glare, method for manufacturing a display window of a cathode ray tube and to a cathode ray tube having a display window.

The invention relates to a method for manufacturing a substrate with reduced reflectivity.

Such methods are for instance used to reduce the glare of a display window of a display device such as a cathode ray tube or an LCD device.

5 The invention also relates to a method for manufacturing a display window of display device and to a display device having a display window.

Reflections on a substrate are often considered bothersome, especially
10 when they occur on a surface of a display window of a display device, since such reflection reduce the contrast, clarity and/or colour reproduction of the displayed image. There are two ways in which the reflection on a surface can be suppressed; by randomly diffusing the reflected image (anti-glare, AG) or by preventing distinct optical interfaces (anti-reflex, AR). To reduce the glare several methods are known such as etching, wet-blasting and spraying of
15 silica-like materials. These methods each have their short-comings. Etching requires the use of a strong etching fluid, which represent an environmental as well as a safety hazard and relatively expensive. Wet-blasting, which is a method in which hard particles suspended in a fluid are blasted against the surface to thereby change the surface structure of said surface, is a relatively expensive and time-consuming method and requires safety measures. Spraying of
20 silica-like materials is a method which is time-consuming and in which relatively easily loose particles are generated and for which it is very difficult to achieve a even distribution of the silica particles over the surface and thus a evenly distributed reduction of the diffuse reflection.

25

The present invention has as its objective to provide an alternative method for reducing glare by which at least some of the above disadvantages are overcome and to provide a display device having a display window with a surface with reduced diffuse

reflection.

To this end, according to the invention, the method for manufacturing a substrate with reduced glare c.q. the method for producing a display window for a display device is characterized in that a suspension comprising sub-micron transparent oxide particles and a binder is coated on the substrate c.q. on a surface of the display window to form a film, whereafter the film is dried in such manner that in situ flocculation of the particles takes place.

A display device according to the invention is characterized in that a coated film is provided on a surface of the display window which film comprises flocculated sub-micron transparent oxide particles.

Flocculation is a process wherein several particles flocculate (agglomerate) to form irregularly shape larger flocs. Said flocs, preferably having an average size of approximately 1-5 μm , affect, namely strongly reduce, the diffuse reflection of visible light on said surface.

Flocculation of a suspension is normally considered a process which is to be prevented. Flocculation usually reduces the life-time of a suspension, the process itself, if it occurs, is very difficult to control, flocculation may notably prevent effective filtering of the suspension (because dust particles have approximately a size of 1-5 μm) and may lead to clogging up of suspension conduit pipes, spraying nozzles etc and reduces the homogeneity of the applied layer leading to striations, patchiness etc of the dried layer.

The inventors have, however, realized that a film comprising flocculated sub-micron particles suppress diffuse reflection in a broad wavelength range, due to the fact that the size of the flocs is more or less randomly distributed in size. Therefor a very uniform suppression of diffuse reflection occurs. Furthermore it is realized that in situ, i.e. "on the surface of the substrate", flocculation of the sub-micron particles is possible. By applying the suspension on the surface, and thereafter affecting flocculation of the sub-micron particles distribution of the flocs is achieved which is on a centimetre scale evenly distributed, yet is, on a micron scale, truly random.

The layer could be applied by means of for instance flow-coating or spraying or other methods. Preferably, however, the film is applied by means of spin-coating. Spin coating allows in a simple manner to achieve a uniform thickness of the suspension over the surface. This increases the uniformity (on a large scale) of the distribution of the flocs over the display window.

Preferably the size of the sub-micron particles is between approximately

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Flocculation is a process wherein several particles flocculate (agglomerate) to form irregularly shape larger flocs. Said flocs, preferably having an average size of approximately 1-5 μm , affect, namely strongly reduce, the diffuse reflection of visible light on said surface.

Flocculation of a suspension is normally considered a process which is to be prevented. Flocculation usually reduces the life-time of a suspension, the process itself, if it occurs, is very difficult to control, flocculation may notably prevent effective filtering of the suspension (because dust particles have approximately a size of 1-5 μm) and may lead to clogging up of suspension conduit pipes, spraying nozzles etc and reduces the homogeneity of the applied layer leading to striations, patchiness etc of the dried layer.

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colour selection electrode 11 is suspended in front of the display screen by means of suspension means 13.

A surface of the display window, in this example the inner surface 16 is provided with a film to reduce the diffuse reflection on said surface.

5 Fig. 2A and 2B show in cross section a display window as shown in figure 1.

Fig. 2A shows display window 2 being on its inner surface 16 coated with a film 20. On top of the film 20 there is provided a black matrix 21 having apertures 22. In said apertures phosphor elements 23 are provided. Fig. 2B is similar to figure 2A except that
10 only the film 20 is shown. Film 20 comprises a large number of flocs 26.

Fig. 3A to 3C show in top view an aperture 31 in black matrix 21 (figure 3A) and enlargements of the film 20. Clearly is seen that flocs 26 are present. In this example, the size of the flocs is in the range of approximately 1 to 5 μm , which is the preferred range. The size of the sub-micron particles in this example is approximately 125
15 nm. Some single particles are visible in figure 3C. The "average size of the particles" is to be understood the so-called d_{50} .

Preferably the size of the sub-micron particles is between approximately 350 and 30 nm. In this size range the effect of each singular particle on the reflected light is small. Preferably the size of the particle is smaller than 200 nm. The effect of each particle
20 on the light is then negligible.

Fig. 4A to 4C show a film 41 having flocs of particles having an average size of approximately 300 nm. The suppression of the diffuse reflection of such a film is appreciable, but less than the film shown in fig. 3.

The particles are made of transparent oxide particles, in the example
25 shown the sub-micron particles are made of SiO_2 and TiO_2 for figures 3 and 4 respectively.

Fig. 5 shows as a function of wavelength λ (in nm) the suppression of the diffuse reflection. The horizontal axis denotes the wavelength of the light incident of the inner surface of the display window, the vertical axis denotes the amount of diffuse reflection on said surface compared to an untreated surface in %. Line 51 in figure 5 shows that a film
30 as shown in figure 3A to 3C reduces the diffuse reflection to 30-40% of the value for the inner surface without the film. Line 52 shows by comparison the effect of a so-called inside etch. The reductions in the diffuse reflection are comparable.

Figure 6 illustrates an embodiment of the method according to the invention. Display window are cleaned using standard procedures (e.g. by means of a

solution of HF followed by a water rinse using demineralized water). Display window 2 is rotated (spun) around rotation axis 61. Via nozzle 62 a colloidal suspension of sub-micron particles is applied to the surface. Due to the spinning of display window the suspension spreads out over the surface to form a film with an evenly distributed thickness. The spun-on film is dried using infra-red drying. After an initial drying period (e.g. approximately 20 seconds) air blowing is additionally applied for complete drying and to floc the sub-micron particles. A forced-drying method step, in this example by means of air blowing, results in the formation of flocs. When a standard drying method is used flocculation does not occur. The start of the air blowing and the air flow regulates the amount of agglomeration (and thus the size of the flocs). The flocs are responsible for the effective suppression of the diffuse reflection. The flocs are randomly formed and therefore the diffuse reflection is suppressed in abroad wavelength range.

The reason for the difference in layer morphology between conventional drying methods and methods in which (air-)forced drying is applied might be the following. In colloidal suspension the particles are charged which prevents agglomeration of the particles into flocs. During conventional drying attractive capillary forces between the sub-micron particles which tend to cause agglomeration of the particles into flocs is balanced by the repelling forces between the charged particles. During forced drying, however, the capillary forces are probably enhanced to be stronger than the repelling forces, leading to agglomeration of the sub-micron particles into flocs. Preferably the forced-drying period is preceded by a conventional drying period in which no flocculation occurs. Such a preceding period allows the coating to form a smooth layer on the surface. Too soon a flocculation of the suspension could interfere with a proper distribution of the flocs over the surface. In this example the suspension is spin-coated over the surface. This is preferred embodiment of the method, especially if the inside surface of a cathode ray tube is supplied with a coating. However, other means of coating could be applied for instance brushing of the suspension over the surface, or using a knife-edge method to apply a layer of suspension. The latter method, in which a layer of a liquid is spread out over a surface by means of a knife-edge, can for instance be used if a flat surface is coated.

Preferably a watery colloidal suspension is used. Watery suspension, i.e. suspension on water basis do not pose a health or environmental hazard. An example of a useful colloidal suspension is a watery colloidal suspension of silica particles of an average radius of 125 nm, for instance the suspension Syton-HT50 from Dupont to which a Lithium polysilicate (LipolySi, Dupont type poly-48) is added as a binder and an adhesive, and PVA

(40-88) as an adhesive, film promoter and binder. The basic suspension composition was 3% (by weight) Syton, PVA: 0.4% and LipolySi 0.4%. Relatively wide variations around these values are possible (1-5% Syton), 0.2-1.5% PVA; 0.05-1.5% LipolySi.

5 The anti-glare layer can be provided on any surface. The above example relate to cathode ray tubes. Other display devices might also be provided with such anti-glare layers on display windows. Example of such other display devices are for instance LCD and plasma display devices.

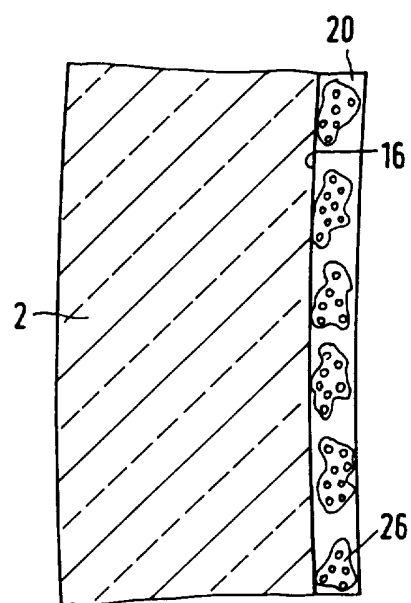
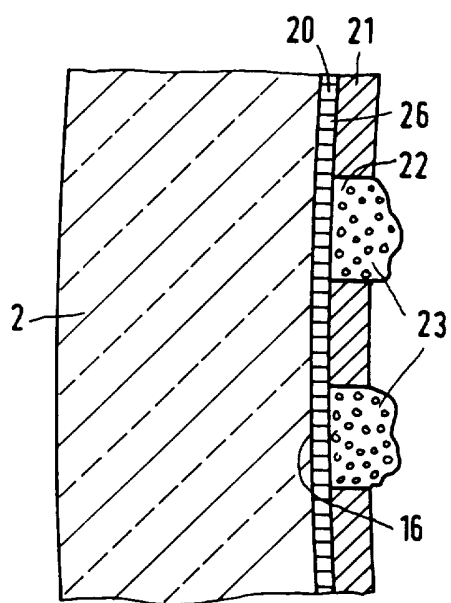
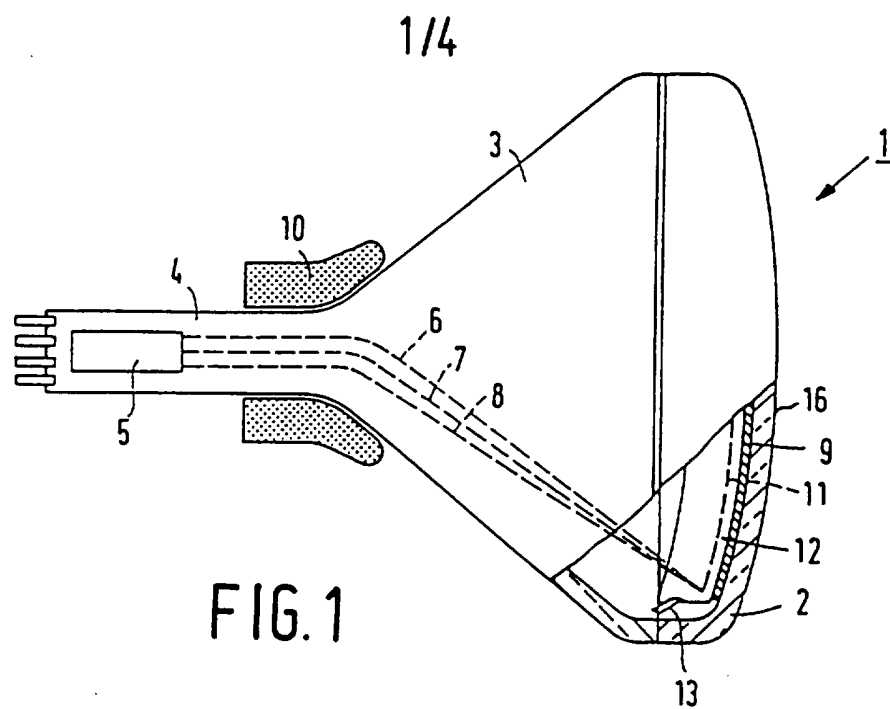
10 The reflection reducing layer in accordance with the invention can advantageously be used in display devices in which a so-called matrix is applied. A matrix is a black layer surrounding the colour elements to increase the sharpness and/or contrast of the image. Devices in which a matrix are applied are for instance CRTs, LCD and plasma display devices. The adherence of the matrix to the layer comprising flocculated micro-particles has been found to be satisfactory. Said matrix is preferably applied over said layer.

15 It will be clear to a person skilled in the art that the invention is not restricted to the above given examples but that within the framework of the invention further embodiments are possible.

For instance other materials can be used for the transparent oxide particles, such as Al_2O_3 (Alumina) or Zirconia.

Claims:

1. Method for manufacturing a glass substrate with reduced reflectivity characterized in that a suspension comprising sub-micron transparent oxide particles and a binder is coated on the substrate to form a film, whereafter the film is dried in such manner that in situ flocculation of the particles takes place.
- 5 2. Method for producing a display window for a display device characterized in that a suspension comprising sub-micron transparent oxide particles, and a binder is coated on a surface of the display window, whereafter the film is dried in such manner that in situ flocculation of the particles takes place.
3. Method as claimed in claim 2 characterized in that the surface is the
10 inside surface of the display window of a cathode ray tube.
4. Method as claimed in claims 1, 2 or 3, characterized in that the average size of the particles is smaller than 350 nm.
5. Method as claimed in claims 1, 2, 3 or 4 characterized in that the flocs have a size of 1-5 μm .
- 15 6. Method as claimed in any of the preceding claims, characterized in that the suspension is a suspension on a water basis.
7. Display device having a display window wherein a surface of the display window is coated with a film, characterized in that the film comprises flocculated sub-micron transparent oxide particles in a binder.
- 20 8. Display device as claimed in claim 7, characterized in that the surface is the inner surface of the display window of a cathode ray tube.
9. Display device as claimed in claims 7 or 8, characterized in that the average size of the sub-micron particles is smaller than 350 nm.
10. Display device as claimed in claims 7, 8, or 9 characterized in that the
25 flocs have a size of 1-5 μm .



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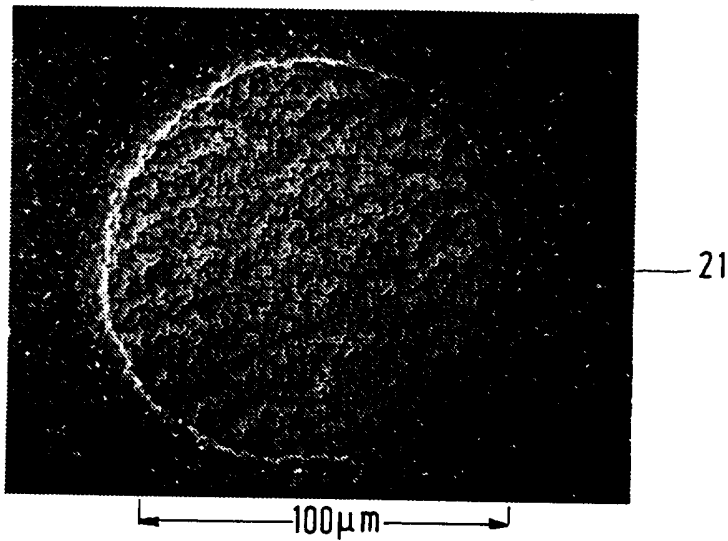


FIG. 3a

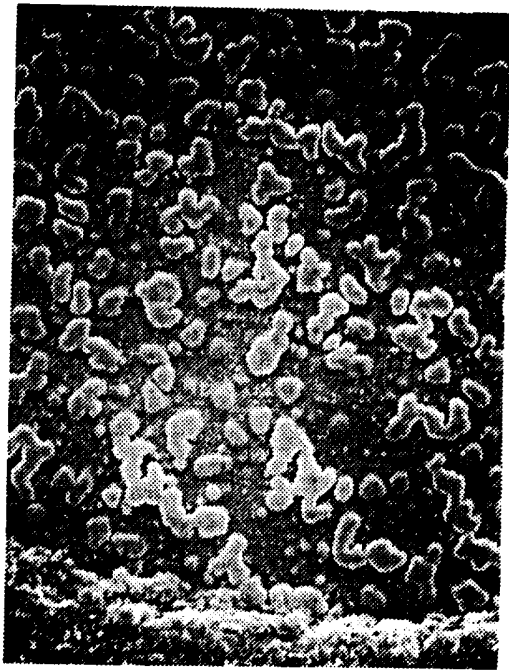


FIG. 3b

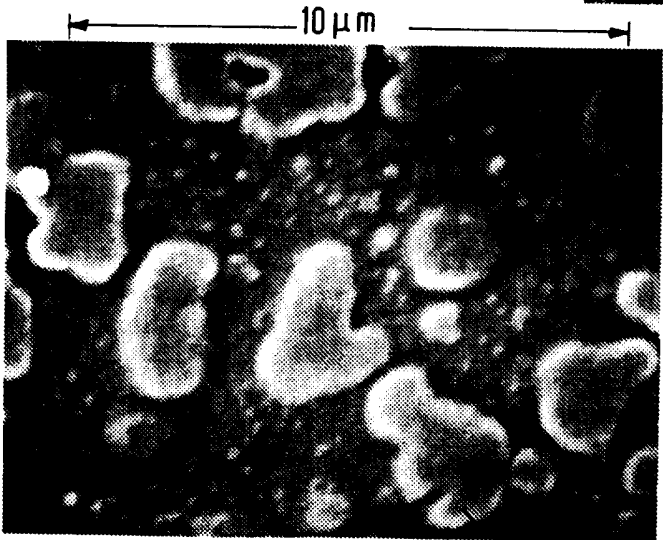


FIG. 3c

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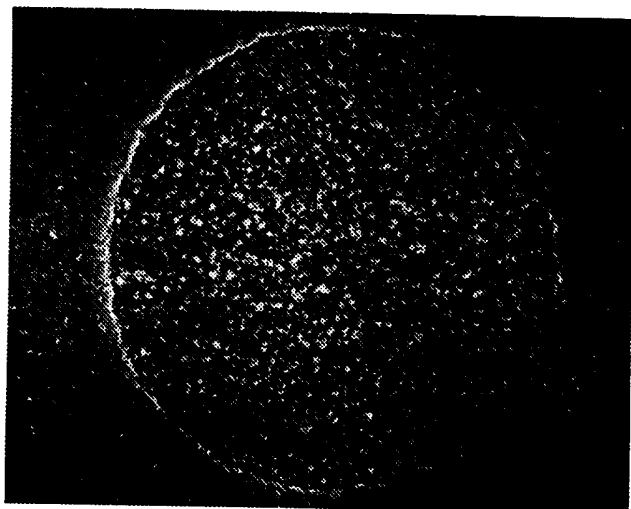


FIG. 4a

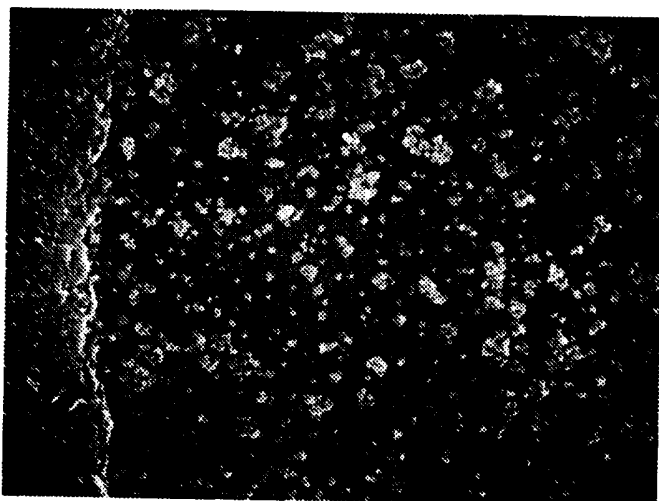


FIG. 4b

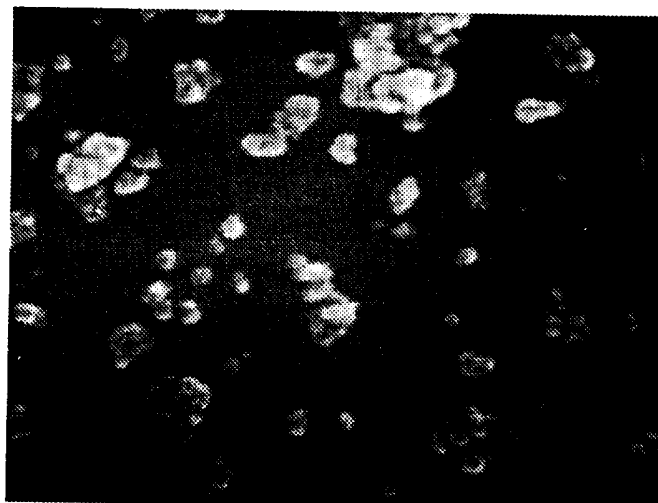


FIG. 4c

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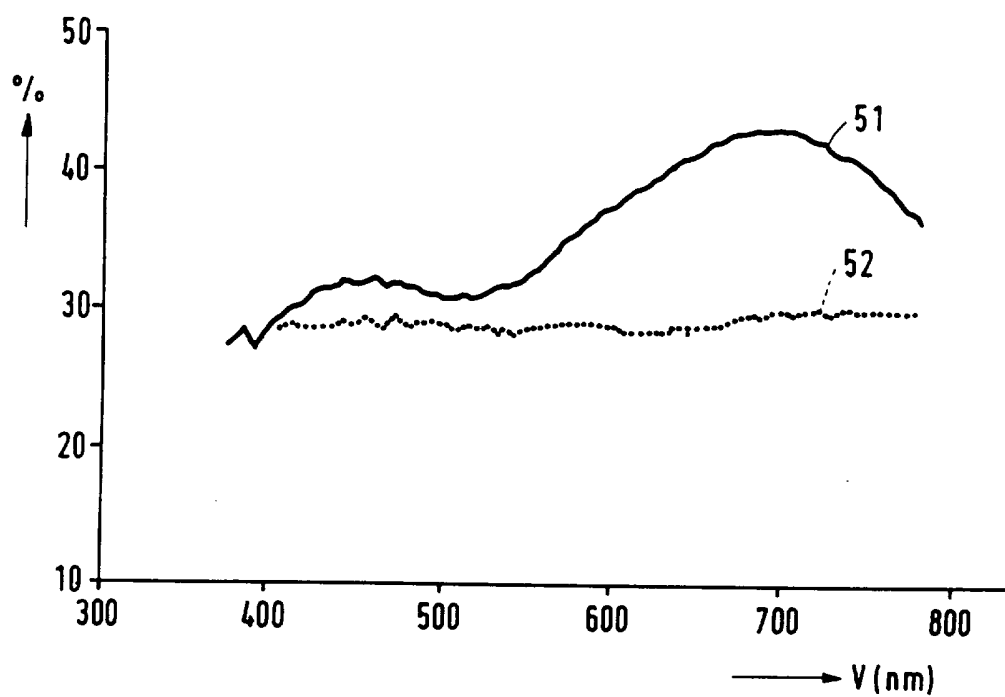


FIG.5

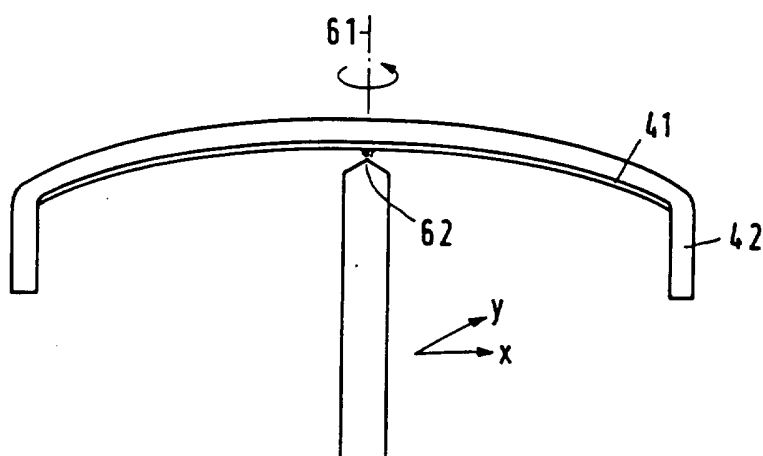


FIG.6

INTERNATIONAL SEARCH REPORT

International application No.

PCT/IB 95/01037

A. CLASSIFICATION OF SUBJECT MATTER

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According to International Patent Classification (IPC) or to both national classification and IPC

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Minimum documentation searched (classification system followed by classification symbols)

IPC6: C03C, G02B, H01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

DIALOG, WPI, CLAIMS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	Dialog Information Services, File 351, DERWENT WPI, Dialog accession no. 009953548, WPI accession no. 94-221261/27, HITACHI LTD; NITTO DENKO CORP: "Low reflection member for CRT or LCD of television - consists of silica layer consisting of single particle layer of silica particles fixed on substrate board surface with binder contg cation polymerisation monomer"; & JP,A,6155652, 940603, 9427 (Basic) -- -----	1-10

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Date of the actual completion of the international search

18 April 1996

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