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[54] Radiation image conversion sheet.

(57) A radiation image conversion sheet comprising a phosphor layer formed on a support and composed of a binder and stimulable phosphor particles dispersed in the binder, and a protective layer formed on the phosphor layer, characterized in that the protective layer is made of an organic film having a percentage haze of from 5 to 40%.

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## RADIATION IMAGE CONVERSION SHEET

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The present invention relates to a radiation image conversion sheet (hereinafter referred to as a "fluorescent sheet") wherein a stimulable phosphor is used. More particularly, the present invention relates to a fluorescent sheet which is provided with a protective layer made of an organic film having a certain specific percentage haze and which scarcely presents undesirable shadows on a radiation image.

When subjected to a radiation such as X-ray, γ-ray, α-ray or β-ray, certain phosphors, i.e. stimulable phosphors, are capable of storing the radiation energy, and subsequently when irradiated by an electromagnetic wave such as visible light or an infrared ray or when stimulated by heat, they emits fluorescent light. A radiation image conversion method is being developed for practical use wherein a radiation passing through an object is irradiated to a fluorescent sheet (which may take a form of a plate or drum, and which will be generally referred to as a "fluorescent sheet" in this specification) which comprises a phosphor layer formed on a support such as a paper sheet, a plastic sheet or a thin metal sheet and composed of such a stimulable phosphor, to store a latent radiation image of the object in the fluorescent sheet,

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and later on the fluorescent sheet is stimulated to emit light by irradiating an electromagnetic wave such as visible light or an infrared ray to the phosphor layer of the fluorescent sheet or by heating the fluorescent layer, whereupon the emitted fluorescence is detected to read out the radiation image of the object stored in and memorized by the fluorescent sheet (e.g. U.S. Patents No. 3,859,527 and No. 4,258,264).

In many cases, a transparent protective layer made of an organic film is provided on the phosphor layer of the fluorescent sheet for the purpose of improving the physical and chemical durability by preventing the wearing or falling off of the phosphor layer or by preventing the reaction with moisture or a chemical substance. However, when a light source having good coherency to the fluorescent sheet having an organic film as a protective layer, such as a laser beam, is used as the stimulating ray, minute lines as fine as from 0.01 to 0.1 µm or local irregularities in thickness will be reproduced as shadows (hereinafter referred to as "radiation image shadows") on the reproduced radiation image, which hinder the interpretation of the image. It is industrially extremely uneconomical to select organic films having a uniform thickness in order to avoid such a disadvantage.

Under the circumstances, it is an object of the present invention to provide a fluorescent sheet having a protective layer and yet scarcely giving rise to radiation image shadows even when a stimulating ray having good coherency such as a laser beam is used. As a result of various researches on the protective layers for the fluorescent sheet, the present inventors have found that there is an interrelation between

the percentage haze of the organic film used as the protective layer of the fluorescent sheet and the appearance of the radiation image shadows, and that when an organic film having a certain specific percentage haze is used as the protective layer, it is possible to obtain a fluorescent sheet which scarcely gives rise to radiation image shadows.

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Thus, the present invention provides a fluorescent sheet comprising a phosphor layer formed on a support and composed of a binder and stimulable phosphor particles dispersed in the binder, and a protective layer formed on the phosphor layer, wherein the protective layer is made of an organic film having a percentage haze of from 5 to 40%.

Now, the present invention will be described in detail with reference to the preferred embodiments.

For the preparation of the fluorescent sheet of the present invention, a stimulable phosphor and a binder are mixed in a proper solvent to prepare a coating dispersion of the phosphor. Then, the coating dispersion may directly be applied onto a support and dried to form a phosphor layer. Alternatively, the coating dispersion of the phosphor may be coated on a flat substrate and dried to form a fluorescent layer, which is then peeled off from the substrate and 20 bonded to a support to form a phosphor layer on the support. Then, a protective layer made of an organic film is bonded to the surface of this phosphor layer. Alternatively, a coating solution of a resin which is capable of forming an organic film when dried, may be applied to the surface of the phosphor layer and dried to form a 25 protective layer of the organic film on the surface of the phosphor layer.

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As the protective layer for the fluorescent sheet of the present invention, there may be used an organic film, for instance, a polyester film of e.g. polyethylene terephthalate, a polymethacrylate film, a nitrocellulose film or a cellulose acetate film, which has a hazy appearance and a percentage haze of from 5 to 40% as measured by the method described in ASTM D-1003. However, it is preferred to use a polyester film, particularly a polyethylene terephthalate film, since it has superior mechanical strength and chemical resistance, and its shrinking property is small. The thickness of the organic film to be used is not critical. However, it is usually preferred to employ a film having a thickness of from 5 to 25 um. The percentage haze of the protective layer varies depending upon the type of the organic film, the degree of polymerization thereof or the impurities contained therein. Further, even when the same type of an organic film is used, the percentage haze varies depending upon the thickness of the film. Furthermore, the percentage haze may be varied by the application of surface treatment such as uniform matting treatment to the surface of the organic film. Accordingly, it is possible to provide a protective layer made of an organic film having a desired percentage haze by properly selecting the type and the thickness of the organic film or by applying a proper surface treatment. However, if the percentage haze of the organic film to be used is less than 5%, the fluorescent sheet thereby obtainable will have little effectiveness for the elimination of shadows from the radiation image. On the other hand, with an increase of the percentage haze of the organic film, the sensitivity of the fluorescent sheet thereby obtinable tends to decrease although the shadows on the radiation image decrease.

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If the percentage haze exceeds 40%, the sensitivity tends to decrease by at least about 10% of the sensitivity of the conventional fluorescent sheet. Therefore, from the practical point of view, the percentage haze should be at most 40%. It is particularly preferred to use an organic film having a percentage haze of from 8 to 25%.

Except for the protective layer, various materials to be used for the fluorescent sheet of the present invention may be the same as the materials commonly used for the conventional fluorescent sheets. Namely, as the stimulable phosphor, there may be used a phosphor such as SrS:Ce, Eu; SrS:Eu, Sm; ZnS:Cu, Pb; (Zn, Cd)S:Mn, X (where X is halogen); LnOX:A (where Ln is at least one of La, Y, Gd and Lu, X is at least one of Cl and Br, and A is at least one of Ce and Tb); or  $(Ba_{1-x}, M_x^{II})FX:Ln$  (where  $M^{II}$  is at least one of Mg, Ca, Sr, Zn and Cd, X is at least one of Cl, Br and I, Ln is at least one of Eu, Tb, Ce, Tm, Dy, Pr, Ho, Nd, Yb and Er, and x is  $0 \le x \le 0.6$ ), which is capable of emitting a fluorescent light when, after subjected to a radiation, stimulated by an electromagnetic wave such as visible light or an infrared ray, or heated. As the binder resin, there may be used nitrocellulose, a vinyl chloride-vinyl acetate copolymer or polyvinyl butyral. As the support, a plastic film such as a cellulose acetate film, a polyester film, a polyimide film or a polycarbonate film, a paper sheet, a glass plate or a thin metal sheet such as an aluminum sheet, may be used. If required, a light absorptive layer or a light reflective layer may be provided on the surface of the support.

When a radiation image of an object stored in and memorized by the fluorescent sheet of the present invention prepared in the abovementioned manner, is reproduced by stimulating the fluorescent sheet by a stimulating ray having good coherency such as a laser beam, the shadows on the radiation image can be substantially minimized although the sensitivity tends to be somewhat lower than the case where the conventional fluorescent sheet is used.

Now, the present invention will be described in further detail with reference to Examples.

## EXAMPLE 1:

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With use of a solvent, 8 parts by weight of a BaFBr:Eu<sup>2+</sup> phosphor (i.e. a stimulable phosphor) and 1 part by weight of nitrocellulose (i.e. a binder) were mixed to obtain a coating dispersion of the phosphor. Then, this coating dispersion was uniformly coated on a horizontally placed black polyethylene terephthalate film (i.e. a support) having a thickness of 250 µm by means of a knife coater and dried to form a phosphor layer having a thickness of about 300 µm. Then, a protective layer made of a polyethylene terephthalate film having a thickness of 12 µm and a percentage haze of 14.3% (LUMIRROR Type P-30, manufactured by Toray Industries Inc.) was bonded to the surface of this phosphor layer, whereby Fluorescent Sheet A was obtained.

Separately, Fluorescent Sheet R was prepared as a Comparative Example in the same manner as the preparation of Fluorescent Sheet A except that a polyethylene terephthalate film having a thickness of 12  $\mu$ m and a percentage haze of 2.5% (LUMIRROR Type S-10, manufactured by Toray Industries Inc.) was used as the protective layer.

With respect to Fluorescent Sheets A and R, the radiation images of the same object obtained by using a He-Ne laser beam as the stimulating ray (i.e. the images of the respective radiation image information reproduced on photographic films when the respective

fluorescent sheets were stimulated by the He-Ne laser beam) were compared. The sensitivity of Fluorescent Sheet A was about 95% of the sensitivity of Fluorescent Sheet R. However, when the reproduction of the images onto the photographic films were adjusted to compensate the sensitivity difference between the fluorescent sheets so that the reproduced images had the same level of the black densities for the corresponding images, the radiation image obtained by Fluorescent Sheet R contained a number of distinct undesirable shadow lines observable by naked eyes, whereas the corresponding image obtained by Fluorescent Sheet A had no substantial shadow lines as observed on the image obtained by Fluorescent Sheet R.

EXAMPLE 2:

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Fluorescent Sheet B was prepared in the same manner as the preparation of Fluorescent Sheet A of Example 1 except that a polyethylene terephthalate film having a thickness of 12  $\mu$ m and a percentage haze of 22% (polyester film type E1512, manufactured by Toyobo Co., Ltd.) was used as the protective layer.

With respect to Fluorescent Sheet B and the above-mentioned Fluorescent Sheet R prepared for the purpose of comparison, the radiation images of the same object obtained by using a He-Ne laser beam as the stimulating ray (i.e. the images of the radiation image information reproduced on photographic films when the respective fluorescent sheets were stimulated by the He-Ne laser beam) were compared. The sensitivity of Fluorescent Sheet B was about 90% of that of Fluorescent Sheet R. However, when the reproduction of the images onto the photographic films were adjusted to compensate the sensitivity difference between the fluorescent sheets so that the reproduced images had the same level of the black densities for the corresponding images.

the radiation image obtained by Fluorescent Sheet R contained a number of distinct shadow lines observable by naked eyes, whereas the corresponding image obtained by Fluorescent Sheet B had no shadow lines as observed on the image obtained by Fluorescent Sheet R.

## CLAIMS:

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- 1. A radiation image conversion sheet comprising a phosphor layer formed on a support and composed of a binder and stimulable phosphor particles dispersed in the binder, and a protective layer formed on the phosphor layer, characterized in that the protective layer is made of an organic film having a percentage haze of from 5 to 40%.
- 2. The radiation image conversion sheet according to Claim 1, wherein the percentage haze of the organic film is from 8 to 25%.
- 3. The radiation image conversion sheet according to Claim 1, wherein the protective layer has a thickness of from 5 to 25  $\mu m$ .
- 4. The radiation image conversion sheet according to Claim 1, wherein the protective layer is made of a polyethylene terphthalate film.
- 5. The radiation image conversion sheet according to Claim 3,15 wherein the protective layer is made of a polyethylene terephthalate film.