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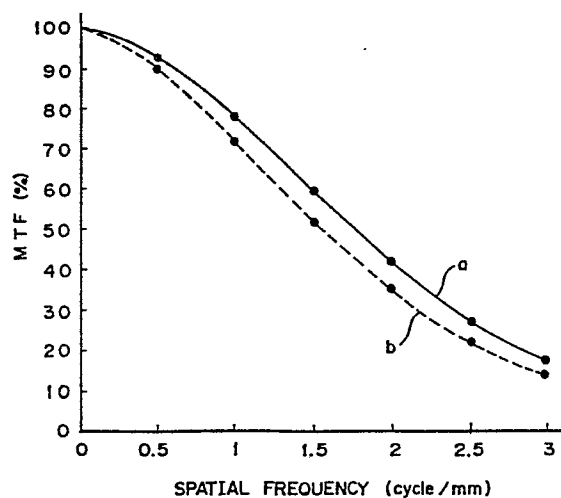
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 (54) **Radiation image storage panel.**

 (57) A radiation image storage panel comprising a support, a phosphor layer which comprises a binder and a stimuable phosphor dispersed therein, an adhesive layer and a protective film, superposed in this order, characterized in that said adhesive layer is colored with a colorant capable of absorbing a portion of stimulating rays for the stimuable phosphor.

*FIG. 1*



RADIATION IMAGE STORAGE PANEL

BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION

This invention relates to a radiation image storage  
5 panel employed in a radiation image recording and repro-  
ducing method utilizing a stimuable phosphor, and more  
particularly, to a radiation image storage panel compris-  
ing a support, a phosphor layer which comprises a stimul-  
able phosphor, an adhesive layer and a protective film,  
10 superposed in this order.

DESCRIPTION OF PRIOR ARTS

For obtaining a radiation image, there has been con-  
ventionally employed a radiography utilizing a combina-  
tion of a radiographic film having an emulsion layer con-  
15 taining a photosensitive silver salt material and a ra-  
diographic intensifying screen.

As a method replacing the above-described radiogra-  
phy, a radiation image recording and reproducing method  
utilizing a stimuable phosphor as described, for in-  
20 stance, in U.S. Patent No. 4,239,968, has been recently  
paid much attention. In the radiation image recording  
and reproducing method, a radiation image storage panel  
comprising a stimuable phosphor (i.e., stimuable phos-  
phor sheet) is used, and the method involves steps of  
25 causing the stimuable phosphor of the panel to absorb  
radiation energy having passed through an object or hav-  
ing radiated from an object; sequentially exciting the  
stimuable phosphor with an electromagnetic wave such as  
visible light or infrared rays (hereinafter referred to  
30 as "stimulating rays") to release the radiation energy

stored in the phosphor as light emission (stimulated emission); photoelectrically detecting the emitted light to obtain electric signals; and reproducing the radiation image of the object as a visible image from the electric  
5 signals.

In the radiation image recording and reproducing method, a radiation image is obtainable with a sufficient amount of information by applying a radiation to the object at considerably smaller dose, as compared with the  
10 conventional radiography. Accordingly, the radiation image recording and reproducing method is of great value especially when the method is used for medical diagnosis.

The radiation image storage panel employed in the radiation image recording and reproducing method has a  
15 basic structure comprising a support and a phosphor layer provided on one surface of the support. Further, a transparent film is generally provided on the free surface (surface not facing the support) of the phosphor layer to keep the phosphor layer from chemical deteriora-  
20 tion or physical shock. The transparent protective film is generally formed on the phosphor layer by combining a thin film which is beforehand prepared, with the phosphor layer through an adhesive agent.

The phosphor layer comprises a binder and stimuable  
25 phosphor particles dispersed therein. The stimuable phosphor emits light (gives stimulated emission) when excited with stimulating rays after having been exposed to a radiation such as X-rays. Accordingly, the radiation having passed through an object or having radiated  
30 from an object is absorbed by the phosphor layer of the radiation image storage panel in proportion to the applied radiation dose, and a radiation image of the object is produced in the panel in the form of a radiation energy-stored image. The radiation energy-stored image  
35 can be released as stimulated emission (light emission) by sequentially irradiating (scanning) the panel with

stimulating rays. The stimulated emission is then photo-electrically detected to obtain electric signals, so as to reproduce a visible image from the electric signals.

The above-described radiation image recording and  
5 reproducing method is very useful for obtaining a radiation image as a visible image as described hereinbefore, and it is desired for the radiation image storage panel employed in the method to provide an image of high quality (high sharpness, high graininess, etc.), as well as a  
10 radiographic intensifying screen employed in the conventional radiography.

The sharpness of the image in the radiation image recording and reproducing method generally depends not on the spread of the light emitted by the stimuable phosphor within the radiation image storage panel, but on the  
15 spread of stimulating rays therewithin. The reason can be described as follows: The radiation image stored and recorded on the panel is sequentially detected, that is, the light emitted by the panel upon excitation with the  
20 stimulating rays for a certain period of time is detected as an output from the area of the panel to be excited for said period. When the stimulating rays are spread through scattering or the like within the panel, an area wider than said area of the panel is excited therewith  
25 and the light emitted by the wider area thereof is detected as the output from said area.

For enhancing the sharpness of an image provided by a radiation image storage panel, it has been proposed to color the panel with a colorant capable of absorbing  
30 stimulating rays for a stimuable phosphor contained therein. A radiation image storage panel colored with such colorant is disclosed, for instance, in Japanese Patent Provisional Publication No. 57(1982)-96300 (corresponding to U.S. Patent Application No. 326,642), and  
35 as an example of such panel, the publication describes a radiation image storage panel comprising a support, a

phosphor layer and a protective film, at least one of which is colored.

A radiation image storage panel employed in the radiation image recording and reproducing method is desirable to have a higher sensitivity and to provide an image more improved in the quality, especially for applying the method to medical diagnosis, from the viewpoint of decreasing the exposure dose for a human body and obtaining much more information. Accordingly, a further improvement in the sensitivity of the panel and the quality of the image provided thereby is desired.

#### SUMMARY OF THE INVENTION

It is an object of the present invention to provide a radiation image storage panel improved in the sharpness of the image provided thereby.

It is another object of the present invention to provide a radiation image storage panel improved in the sensitivity as well as the sharpness of the image provided thereby.

The objects can be accomplished by a radiation image storage panel comprising a support, a phosphor layer which comprises a binder and a stimuable phosphor dispersed therein, an adhesive layer and a protective film, superposed in this order, characterized in that said adhesive layer is colored with a colorant capable of absorbing a portion of stimulating rays for the stimuable phosphor.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 graphically shows an MTF with respect to the radiation image storage panel of the present invention (Curve a) and an MTF with respect to the conventional radiation image storage panel (Curve b).

Fig. 2 graphically shows relationships between a relative sensitivity and a sharpness with respect to the radiation image storage panels according to the present invention (Lines A and C) and a relationship therebetween with respect to the conventional radiation image storage panels (Line B).

DETAILED DESCRIPTION OF THE INVENTION

According to the radiation image storage panel of the present invention, the improvement of sharpness of the image is achieved by coloring an adhesive layer provided between the phosphor layer and the protective film. The present invention also provides a radiation image storage panel more improved in the sharpness of the image than the known panel in the comparison at the same sensitivity level.

As described hereinbefore, a radiation image storage panel generally has a protective film and the formation thereof is usually carried out by combining a previously prepared thin film with a phosphor layer using an adhesive agent. As a result of the study, the present inventors have found that the sharpness of the image provided by the panel is enhanced by coloring an adhesive layer of a small thickness (several  $\mu\text{m}$  - several tens  $\mu\text{m}$ ) with a colorant capable of selectively absorbing stimulating rays for the stimuable phosphor so as to effectively absorb the stimulating rays which have spread within the protective film.

It has been further confirmed that such coloring of the adhesive layer having the small thickness brings about enhancement in the sharpness of the image without considerably lowering the sensitivity of the panel, as compared with the coloring of another layer having a larger thickness such as a phosphor layer. In other words, by coloring the thin adhesive layer, the absorp-

tion of the emitted light therewithin can be made as small as possible, and the stimulating rays which have spread by scattering or the like in the protective film can be effectively absorbed thereby.

5       Accordingly, the phosphor layer of the radiation image storage panel according to the present invention can be made thinner than that of the conventional panel when both having the same sensitivity, whereby the sharpness of the image provided by the panel of the invention  
10 can be further enhanced in the comparison at the same sensitivity level. This can be said that the sensitivity of the panel can be further enhanced at the same sharpness level basis.

The radiation image storage panel of the present  
15 invention having the above-described advantages can be prepared, for instance, in the following manner.

The support material employed in the present invention can be selected from those employed in the conventional radiographic intensifying screens or those employed  
20 in the known radiation image storage panels. Examples of the support material include plastic films such as films of cellulose acetate, polyester, polyethylene terephthalate, polyamide, polyimide, triacetate and polycarbonate; metal sheets such as aluminum foil and aluminum alloy  
25 foil; ordinary papers; baryta paper; resin-coated papers; pigment papers containing titanium dioxide or the like; and papers sized with polyvinyl alcohol or the like. From the viewpoint of characteristics of a radiation image storage panel as an information recording material,  
30 a plastic film is preferably employed as the support material of the invention. The plastic film may contain a light-absorbing material such as carbon black, or may contain a light-reflecting material such as titanium dioxide. The former is appropriate for preparing a  
35 high-sharpness type radiation image storage panel, while the latter is appropriate for preparing a high-sensitivi-

ty type radiation image storage panel.

In the preparation of a known radiation image storage panel, one or more additional layers are occasionally provided between the support and the phosphor layer, so as to enhance the adhesion between the support and the phosphor layer, or to improve the sensitivity of the panel or the quality of an image (sharpness and graininess) provided thereby. For instance, a subbing layer may be provided by coating a polymer material such as gelatin over the surface of the support on the phosphor layer side. Otherwise, a light-reflecting layer or a light-absorbing layer may be provided by forming a polymer material layer containing a light-reflecting material such as titanium dioxide or a light-absorbing material such as carbon black. In the invention, one or more of these additional layers may be provided on the support.

As described in Japanese Patent Provisional Publication No. 58(1983)-200200 (corresponding to U.S. Patent Application No. 496,278), the phosphor layer-side surface of the support (or the surface of a subbing layer, light-reflecting layer, or light-absorbing layer in the case that such layers are provided on the phosphor layer) may be provided with protruded and depressed portions for enhancement of the sharpness of radiographic image.

On the support, a phosphor layer is formed. The phosphor layer basically comprises a binder and stimuable phosphor particles dispersed therein.

The stimuable phosphor, as described hereinbefore, gives stimulated emission when excited with stimulating rays after exposure to a radiation. From the viewpoint of practical use, the stimuable phosphor is desired to give stimulated emission in the wavelength region of 300 - 500 nm when excited with stimulating rays in the wavelength region of 400 - 900 nm.

Examples of the stimuable phosphor employable in the radiation image storage panel of the present inven-

tion include:

SrS:Ce,Sm, SrS:Eu,Sm, ThO<sub>2</sub>:Er, and La<sub>2</sub>O<sub>2</sub>S:Eu,Sm, as described in U.S. Patent No. 3,859,527;

ZnS:Cu,Pb, BaO·xAl<sub>2</sub>O<sub>3</sub>:Eu, in which x is a number  
5 satisfying the condition of  $0.8 \leq x \leq 10$ , and M<sup>2+</sup>O·xSiO<sub>2</sub>:A, in which M<sup>2+</sup> is at least one divalent metal selected from the group consisting of Mg, Ca, Sr, Zn, Cd and Ba, A is at least one element selected from the group consisting of Ce, Tb, Eu, Tm, Pb, Tl, Bi and Mn, and x is a  
10 number satisfying the condition of  $0.5 \leq x \leq 2.5$ , as described in U.S. Patent No. 4,326,078;

(Ba<sub>1-x-y</sub>,Mg<sub>x</sub>,Ca<sub>y</sub>)FX:aEu<sup>2+</sup>, in which X is at least one element selected from the group consisting of Cl and Br, x and y are numbers satisfying the conditions of  $0 < x+y \leq 0.6$ , and  $xy \neq 0$ , and a is a number satisfying the  
15 condition of  $10^{-6} \leq a \leq 5 \times 10^{-2}$ , as described in Japanese Patent Provisional Publication No. 55(1980)-12143;

LnOX:xA, in which Ln is at least one element selected from the group consisting of La, Y, Gd and Lu, X is at  
20 least one element selected from the group consisting of Cl and Br, A is at least one element selected from the group consisting of Ce and Tb, and x is a number satisfying the condition of  $0 < x < 0.1$ , as described in the above-mentioned U.S. Patent No. 4,236,078;

(Ba<sub>1-x</sub>,M<sup>II</sup><sub>x</sub>)FX:yA, in which M<sup>II</sup> is at least one  
25 divalent metal selected from the group consisting of Mg, Ca, Sr, Zn and Cd, X is at least one element selected from the group consisting of Cl, Br and I, A is at least one element selected from the group consisting of Eu, Tb,  
30 Ce, Tm, Dy, Pr, Ho, Nd, Yb and Er, and x and y are numbers satisfying the conditions of  $0 \leq x \leq 0.6$  and  $0 \leq y \leq 0.2$ , respectively, as described in U.S. Patent No. 4,239,968;

M<sup>II</sup>FX·xA:yLn, in which M<sup>II</sup> is at least one element  
35 selected from the group consisting of Ba, Ca, Sr, Mg, Zn and Cd; A is at least one compound selected from the

group consisting of BeO, MgO, CaO, SrO, BaO, ZnO, Al<sub>2</sub>O<sub>3</sub>, Y<sub>2</sub>O<sub>3</sub>, La<sub>2</sub>O<sub>3</sub>, In<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub>, GeO<sub>2</sub>, SnO<sub>2</sub>, Nb<sub>2</sub>O<sub>5</sub>, Ta<sub>2</sub>O<sub>5</sub> and ThO<sub>2</sub>; Ln is at least one element selected from the group consisting of Eu, Tb, Ce, Tm, Dy, Pr, Ho, Nd, Yb, Er, Sm and Gd; X is at least one element selected from the group consisting of Cl, Br and I; and  $\underline{x}$  and  $\underline{y}$  are numbers satisfying the conditions of  $5 \times 10^{-5} \leq x \leq 0.5$  and  $0 < y \leq 0.2$ , respectively, as described in Japanese Patent Provisional Publication No. 55(1980)-160078;

10  $(Ba_{1-x}, M^{II}_x)F_2 \cdot aBaX_2 : yEu, zA$ , in which M<sup>II</sup> is at least one element selected from the group consisting of Be, Mg, Ca, Sr, Zn and Cd; X is at least one element selected from the group consisting of Cl, Br and I; A is at least one element selected from the group consisting of Zr and Sc; and  $\underline{a}$ ,  $\underline{x}$ ,  $\underline{y}$  and  $\underline{z}$  are numbers satisfying the conditions of  $0.5 \leq a \leq 1.25$ ,  $0 \leq x \leq 1$ ,  $10^{-6} \leq y \leq 2 \times 10^{-1}$ , and  $0 < z \leq 10^{-2}$ , respectively, as described in Japanese Patent Provisional Publication No. 56(1981)-116777;

20  $(Ba_{1-x}, M^{II}_x)F_2 \cdot aBaX_2 : yEu, zB$ , in which M<sup>II</sup> is at least one element selected from the group consisting of Be, Mg, Ca, Sr, Zn and Cd; X is at least one element selected from the group consisting of Cl, Br and I; and  $\underline{a}$ ,  $\underline{x}$ ,  $\underline{y}$  and  $\underline{z}$  are numbers satisfying the conditions of  $0.5 \leq a \leq 1.25$ ,  $0 \leq x \leq 1$ ,  $10^{-6} \leq y \leq 2 \times 10^{-1}$ , and  $0 < z \leq 2 \times 10^{-1}$ , respectively, as described in Japanese Patent Provisional Publication No. 57(1982)-23673;

30  $(Ba_{1-x}, M^{II}_x)F_2 \cdot aBaX_2 : yEu, zA$ , in which M<sup>II</sup> is at least one element selected from the group consisting of Be, Mg, Ca, Sr, Zn and Cd; X is at least one element selected from the group consisting of Cl, Br and I; A is at least one element selected from the group consisting of As and Si; and  $\underline{a}$ ,  $\underline{x}$ ,  $\underline{y}$  and  $\underline{z}$  are numbers satisfying the conditions of  $0.5 \leq a \leq 1.25$ ,  $0 \leq x \leq 1$ ,  $10^{-6} \leq y \leq 2 \times 10^{-1}$ , and  $0 < z \leq 5 \times 10^{-1}$ , respectively, as described in Japanese Patent Provisional Publication No. 57(1982)-

23675;

$M^{III}OX:xCe$ , in which  $M^{III}$  is at least one trivalent metal selected from the group consisting of Pr, Nd, Pm, Sm, Eu, Tb, Dy, Ho, Er, Tm, Yb, and Bi; X is at least one  
5 element selected from the group consisting of Cl and Br; and  $x$  is a number satisfying the condition of  $0 < x < 0.1$ , as described in Japanese Patent Provisional Publication No. 58(1983)-69281;

$Ba_{1-x}M_{x/2}L_{x/2}FX:yEu^{2+}$ , in which M is at least one  
10 alkali metal selected from the group consisting of Li, Na, K, Rb and Cs; L is at least one trivalent metal selected from the group consisting of Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Al, Ga, In and Tl; X is at least one halogen selected from the group  
15 consisting of Cl, Br and I; and  $x$  and  $y$  are numbers satisfying the conditions of  $10^{-2} \leq x \leq 0.5$  and  $0 < y \leq 0.1$ , respectively, as described in U.S. Patent Application No. 497,805;

$BaFX \cdot xA:yEu^{2+}$ , in which X is at least one halogen  
20 selected from the group consisting of Cl, Br and I; A is at least one fired product of a tetrafluoroboric acid compound; and  $x$  and  $y$  are numbers satisfying the conditions of  $10^{-6} \leq x \leq 0.1$  and  $0 < y \leq 0.1$ , respectively, as described in U.S. Patent Application No. 520,215;

$BaFX \cdot xA:yEu^{2+}$ , in which X is at least one halogen  
25 selected from the group consisting of Cl, Br and I; A is at least one fired product of a hexafluoro compound selected from the group consisting of monovalent and divalent metal salts of hexafluoro silicic acid, hexa-  
30 fluoro titanic acid and hexafluoro zirconic acid; and  $x$  and  $y$  are numbers satisfying the conditions of  $10^{-6} \leq x \leq 0.1$  and  $0 < y \leq 0.1$ , respectively, as described in U.S. Patent Application No. 502,648;

$BaFX \cdot xNaX':aEu^{2+}$ , in which each of X and X' is at  
35 least one halogen selected from the group consisting of Cl, Br and I; and  $x$  and  $a$  are numbers satisfying the

conditions of  $0 < x \leq 2$  and  $0 < a \leq 0.2$ , respectively, as described in Japanese Patent Provisional Publication No. 59(1984)-56479;

$M^{II}FX \cdot xNaX' : yEu^{2+} : zA$ , in which  $M^{II}$  is at least one  
5 alkaline earth metal selected from the group consisting of Ba, Sr and Ca; each of X and X' is at least one halogen selected from the group consisting of Cl, Br and I; A is at least one transition metal selected from the group consisting of V, Cr, Mn, Fe, Co and Ni; and  $x$ ,  $y$  and  $z$   
10 are numbers satisfying the conditions of  $0 < x \leq 2$ ,  $0 < y \leq 0.2$  and  $0 < z \leq 10^{-2}$ , respectively, as described in U.S. Patent Application No. 535,928; and

$M^{II}FX \cdot aM^IX' \cdot bM'^{II}X''_2 \cdot cM^{III}X'''_3 \cdot xA : yEu^{2+}$ , in which  
15  $M^{II}$  is at least one alkaline earth metal selected from the group consisting of Ba, Sr and Ca;  $M^I$  is at least one alkali metal selected from the group consisting of Li, Na, K, Rb and Cs;  $M'^{II}$  is at least one divalent metal selected from the group consisting of Be and Mg;  $M^{III}$  is at least one trivalent metal selected from the group  
20 consisting of Al, Ga, In and Tl; A is at least one metal oxide; X is at least one halogen selected from the group consisting of Cl, Br and I; each of X', X'' and X''' is at least one halogen selected from the group consisting of F, Cl, Br and I;  $a$ ,  $b$  and  $c$  are numbers satisfying the  
25 conditions of  $0 \leq a \leq 2$ ,  $0 \leq b \leq 10^{-2}$ ,  $0 \leq c \leq 10^{-2}$  and  $a+b+c \geq 10^{-6}$ ; and  $x$  and  $y$  are numbers satisfying the conditions of  $0 < x \leq 0.5$  and  $0 < y \leq 0.2$ , respectively, as described in U.S. Patent Application No. 543,326.

Among the above-described stimuable phosphors, the  
30 divalent europium activated alkaline earth metal fluoro-halide phosphor and rare earth element activated rare earth oxyhalide phosphor are particularly preferred, because these show stimulated emission of high luminance. The above-described stimuable phosphors are given by no  
35 means to restrict the stimuable phosphor employable in the present invention. Any other phosphors can be also

employed, provided that the phosphor gives stimulated emission when excited with stimulating rays after exposure to a radiation.

Examples of the binder to be contained in the phosphor layer include: natural polymers such as proteins (e.g. gelatin), polysaccharides (e.g. dextran) and gum arabic; and synthetic polymers such as polyvinyl butyral, polyvinyl acetate, nitrocellulose, ethylcellulose, vinylidene chloride-vinyl chloride copolymer, polyalkyl (meth)acrylate, vinyl chloride-vinyl acetate copolymer, polyurethane, cellulose acetate butyrate, polyvinyl alcohol, and linear polyester. Particularly preferred are nitrocellulose, linear polyester, polyalkyl (meth)acrylate, a mixture of nitrocellulose and linear polyester, and a mixture of nitrocellulose and polyalkyl (meth)acrylate. These binders may be crosslinked with a crosslinking agent.

The phosphor layer can be formed on the support, for instance, by the following procedure.

In the first place, stimuable phosphor particles and a binder are added to an appropriate solvent, and then they are mixed to prepare a coating dispersion comprising the phosphor particles homogeneously dispersed in the binder solution.

Examples of the solvent employable in the preparation of the coating dispersion include lower alcohols such as methanol, ethanol, n-propanol and n-butanol; chlorinated hydrocarbons such as methylene chloride and ethylene chloride; ketones such as acetone, methyl ethyl ketone and methyl isobutyl ketone; esters of lower alcohols with lower aliphatic acids such as methyl acetate, ethyl acetate and butyl acetate; ethers such as dioxane, ethylene glycol monoethylether and ethylene glycol monoethyl ether; and mixtures of the above-mentioned compounds.

The ratio between the binder and the stimuable

phosphor in the coating dispersion may be determined according to the characteristics of the aimed radiation image storage panel and the nature of the phosphor employed. Generally, the ratio therebetween is within the 5 range of from 1 : 1 to 1 : 100 (binder : phosphor, by weight), preferably from 1 : 8 to 1 : 40.

The coating dispersion may contain a dispersing agent to improve the dispersibility of the phosphor particles therein, and may contain a variety of additives 10 such as a plasticizer for increasing the bonding between the binder and the phosphor particles in the phosphor layer. Examples of the dispersing agent include phthalic acid, stearic acid, caproic acid and a hydrophobic surface active agent. Examples of the plasticizer include 15 phosphates such as triphenyl phosphate, tricresyl phosphate and diphenyl phosphate; phthalates such as diethyl phthalate and dimethoxyethyl phthalate; glycolates such as ethylphthalyl ethyl glycolate and butylphthalyl butyl glycolate; and polyesters of polyethylene glycols with 20 aliphatic dicarboxylic acids such as polyester of triethylene glycol with adipic acid and polyester of diethylene glycol with succinic acid.

The coating dispersion containing the phosphor particles and the binder prepared as described above is applied evenly onto the surface of the support to form a 25 layer of the coating dispersion. The coating procedure can be carried out by a conventional method such as a method using a doctor blade, a roll coater or a knife coater.

30 After applying the coating dispersion onto the support, the coating dispersion is then heated slowly to dryness so as to complete the formation of a phosphor layer. The thickness of the phosphor layer varies depending upon the characteristics of the aimed radiation 35 image storage panel, the nature of the phosphor, the ratio between the binder and the phosphor, etc. Gener-

ally, the thickness of the phosphor layer is within a range of from 20  $\mu\text{m}$  to 1 mm, and preferably from 50 to 500  $\mu\text{m}$ .

The phosphor layer can be provided onto the support 5 by the methods other than that given in the above. For instance, the phosphor layer is initially prepared on a sheet (false support) such as a glass plate, metal plate or plastic sheet using the aforementioned coating dispersion and then thus prepared phosphor layer is superposed 10 on the genuine support by pressing or using an adhesive agent.

On the phosphor layer, a protective film is formed through a colored adhesive layer, which is a characteristic requisite of the present invention.

15 Examples of adhesive agents employable for the preparation of the adhesive layer in the invention include a polyacrylic resin, a polyester resin, a polyurethane resin, a polyvinyl acetate resin and ethylene-vinyl acetate copolymers. However, the adhesive agent employable 20 in the invention is by no means restricted to the above-listed resins, and for instance, other known resins which are conventionally used as an adhesive agent can be employed.

The colorant employed for coloring the adhesive 25 layer is one capable of absorbing at least a portion of the stimulating rays for the stimuable phosphor constituting the phosphor layer of the radiation image storage panel. The colorant preferably has such reflection characteristics that the mean reflectance in the wave- 30 length region of the stimulating rays for the stimuable phosphor is lower than the mean reflectance in the wavelength region of the light emitted by said stimuable phosphor upon stimulation thereof.

From the viewpoint of improving the sharpness of the 35 image provided by the panel, it is desired that the mean reflectance of the colorant in the wavelength region of

the stimulating rays is as low as possible. On the other hand, from the viewpoint of improving the sensitivity of the panel, it is desired that the mean reflectance of the colorant in the wavelength region of the light emitted by the stimuable phosphor is as high as possible.

Accordingly, the preferred colorant depends on the nature of the stimuable phosphor employed in the radiation image storage panel. From the viewpoint of practical use, the stimuable phosphor is preferred to give stimulated emission in the wavelength region of 300 - 500 nm when excited with stimulating rays in the wavelength region of 400 - 900 nm as described above. Employable for such a stimuable phosphor is a colorant having a body color ranging from blue to green so that the mean reflectance thereof in the wavelength region of the stimulating rays is lower than the mean reflectance thereof in the wavelength region of the emitted light and that the difference therebetween is as large as possible.

Examples of the colorant employable in the invention include the colorants disclosed in Japanese Patent Provisional Publication No. 55(1980)-163500 (corresponding to U.S. Patent No. 4,394,581), that is: organic colorants such as Zapon Fast Blue 3G (available from Hoechst AG), Estrol Brill Blue N-3RL (available from Sumitomo Chemical Co., Ltd.), Sumiacryl Blue F-GSL (available from Sumitomo Chemical Co., Ltd.), D & C Blue No.1 (available from National Aniline), Spirit Blue (available from Hodogaya Chemical Co., Ltd.), Oil Blue No.603 (available from Orient Co., Ltd.), Kiton Blue A (available from Ciba-Geigy), Aizen Cathilon Blue GLH (available from Hodogaya Chemical Co., Ltd.), Lake Blue A.F.H (available from Kyowa Sangyo Co., Ltd.), Rodalin Blue 6GX (available from Kyowa Sangyo Co., Ltd.), Primocyanine 6GX (available from Inahata Sangyo Co., Ltd.), Brillacid Green 6BH (available from Hodogaya Chemical Co., Ltd.), Cyanine Blue BNRS (available from Toyo Ink Mfg. Co., Ltd.), Lionol Blue SL

(available from Toyo Ink Mfg. Co., Ltd.), and the like; and inorganic colorants such as ultramarine blue, cobalt blue, ceruleanblue, chromium oxide,  $TiO_2$ -ZnO-CoO-NiO pigment, and the like.

5       Examples of the colorant employable in the invention also include the colorants described in the aforementioned U.S. Patent Application No. 326,642, that is: organic metal complex salt colorants having Color Index  
No. 24411, No. 23160, No. 74180, No. 74200, No. 22800,  
10 No. 23150, No. 23155, No. 24401, No. 14880, No. 15050,  
No. 15706, No. 15707, No. 17941, No. 74220, No. 13425,  
No. 13361, No. 13420, No. 11836, No. 74140, No. 74380,  
No. 74350, No. 74460, and the like.

      Among the above-mentioned colorants having a body  
15 color from blue to green, particularly preferred are the organic metal complex salt colorants which show no emission in the wavelength region longer than that of the stimulating rays as described in the latter U.S. Patent Application No. 326,642, from the viewpoint of the grain-  
20 iness and the contrast of the resulting image.

      A colored adhesive layer can be arranged in combination with protective film on the phosphor layer, for instance, by the following procedure: The above-described resin and a colorant are added to an appropriate solvent  
25 and they are sufficiently mixed to prepare a homogeneous coating dispersion for an adhesive layer. The solvent can be selected from the solvents employable in the preparation of a phosphor layer as mentioned hereinbefore.

30       The coating dispersion is applied evenly onto the transparent thin film to form a layer thereof. The coating procedure can be carried out by a conventional method such as a method using a doctore blade, a roll coater or a knife coater. Subsequently, the transparent thin film  
35 having the layer of the coating dispersion is placed on the phosphor layer in such a manner that the layer of the

coated dispersion faces the phosphor layer and then fixed (laminated) thereto, so as to complete the simultaneous formation of the colored adhesive layer and the protective film on the phosphor layer.

5       The thickness of the colored adhesive layer varies depending upon the characteristics of the aimed radiation image storage panel, the nature of the phosphor layer or the protective film, the natures of the resin and the colorant. In general, the thickness of the colored adhesive layer is within the range of from 0.1 to 10  $\mu\text{m}$ .

10       The ratio between the resin and the colorant in the coating dispersion is within the range of from 10 : 1 to  $10^6$  : 1 (resin : colorant, by weight) in the case of a dye colorant. The ratio therebetween is within the range of from 1 : 10 to  $10^5$  : 1, (resin : colorant, by weight) in the case of a pigment colorant.

15       From the viewpoint of the sensitivity of the resulting radiation image storage panel, the mean reflectance of thus formed colored adhesive layer in the wavelength region of the light emitted by the stimuable phosphor upon stimulation thereof is as high as possible. Generally, the mean reflectance of the colored adhesive layer is preferably not lower than 20 % of the mean reflectance of an adhesive layer equivalent to said adhesive layer except for being uncolored with the colorant in the same wavelength region.

20       On the other hand, from the viewpoint of the sharpness of an image provided by the panel, the mean reflectance of the colored adhesive layer in the wavelength region of the stimulating rays for the stimuable phosphor is as low as possible. Generally, the mean reflectance of the colored adhesive layer is not higher than 95 % of the mean reflectance of the uncolored adhesive layer equivalent to said adhesive layer in the same wavelength region. The term "reflectance" used herein means a reflectance measured by use of an intergrating-sphere

photometer.

Examples of the material for the transparent protective film which can be formed as above include previously prepared transparent thin films which are made of poly-  
5 ethylene terephthalate, polyethylene, vinylidene chloride, polyamide, etc. The transparent protective film preferably has a thickness within the range of approx. 3 to 20  $\mu\text{m}$ .

The following examples further illustrate the pre-  
10 sent invention, but these examples are by no means understood to restrict the invention.

#### Example 1

To a mixture of a divalent europium activated barium fluorobromide ( $\text{BaFBr:Eu}^{2+}$ ) phosphor particles and a  
15 acrylic resin was added methyl ethyl ketone to prepare a dispersion containing the phosphor particles and the binder in the ratio of 30 : 1 (phosphor : binder, by weight). Tricresyl phosphate, n-butanol and methyl ethyl ketone were added to the dispersion and the mixture  
20 was sufficiently stirred by means of a propeller agitater to obtain a homogeneous coating dispersion having a viscosity of 25 - 35 PS (at 25°C).

Subsequently, the coating dispersion was applied evenly onto a polyethylene terephthalate sheet (support,  
25 thickness: 250  $\mu\text{m}$ ) placed horizontally on a glass plate. The application of the coating dispersion was carried out using a doctor blade. After the coating was complete, the support having the coating dispersion was placed in an oven and heated at a temperature gradually rising from  
30 25 to 100°C. Thus, a phosphor layer having the thickness of approx. 300  $\mu\text{m}$  was formed on the support.

Independently, a polyester resin (adhesive agent; Byron #300, manufactured by Toyobo Co., Ltd.) was dissolved in methyl ethyl ketone to prepare a solution of

the adhesive agent. To the solution was added a dye colorant (copper phthalocyanine) in the amount of 0.5 % (by solid content) of the adhesive agent to prepare a coating dispersion. Then, the coating dispersion was  
5 applied onto a transparent polyethylene terephthalate film (protective film, thickness: 12  $\mu\text{m}$ ) in the amount of 2  $\text{g./m}^2$  in the same manner as described above to form a layer of a colored adhesive agent.

The transparent film provided with the layer of the  
10 colored adhesive agent was placed on the phosphor layer in such a manner that said layer faced the phosphor layer and then combined therewith through the colored adhesive layer. Thus, a radiation image storage panel consisting of a support, a phosphor layer, a colored adhesive layer  
15 and a transparent protective film was prepared (Panel a).

Further, the amount of the dye colorant employed for coloring the adhesive layer was varied within the range of 0.1 - 1.0 % (by solid content) of the adhesive agent, to prepare a variety of radiation image storage panels  
20 consisting of a support, a phosphor layer, a colored adhesive layer and a transparent protective film, in which the adhesive layers were colored in the different degrees (Panels A).

#### Comparison Example 1

25 A colored phosphor layer was formed on the support in the same manner as described in Example 1 except that a dye colorant (copper phthalocyanine) was added to the coating dispersion for a phosphor layer in the amount of 0.1 % (by solid content) of the binder.

30 Subsequently, the procedure of Example 1 was repeated except for adding no dye colorant to the coating dispersion for an adhesive layer, to prepare a radiation image storage panel consisting of a support, a colored phosphor layer, an adhesive layer and a transparent

protective film (Panel b).

Further, the amount of the dye colorant employed for coloring the phosphor layer was varied within the range of 0.1 - 1.0 % (by solid content) of the binder, to prepare a variety of radiation image storage panels consisting of a support, a colored phosphor layer, an adhesive layer and a transparent protective film, in which the phosphor layers were colored in the different degrees (Panels B).

10 The radiation image storage panels (Panels a, A, b and B) prepared as above were evaluated on the sharpness of the image provided thereby and the sensitivity thereof according to the following test.

(1) Sharpness of image

15 The radiation image storage panel was exposed to X-rays at voltage of 80 KVp through an MTF chart and subsequently scanned with an He-Ne laser beam (wavelength: 632.8 nm) to excite the phosphor particles contained in the panel. The light emitted by the phosphor layer of  
20 the panel was detected and converted to electric signals by means of a photosensor (photomultiplier having spectral sensitivity of type S-5). From the electric signals a radiation image of the MTF chart was reproduced as a visible image by an image reproducing apparatus, and the  
25 modulation transfer function (MTF) value of the visible image was determined.

(2) Sensitivity

The radiation image storage panel was exposed to X-rays at voltage of 80 KVp and subsequently scanned with  
30 an He-Ne laser beam (wavelength: 632.8 nm) to excite the phosphor. The light emitted by the phosphor layer of the panel was detected by means of the above-mentioned photosensor to measure the sensitivity thereof.

The results of the evaluation on the sharpness of the image provided by the radiation image storage panels are graphically shown in Fig. 1.

Fig. 1 illustrates;

5 Curve a: a relationship between a spatial frequency and an MTF value with respect to Panel a (Example 1); and

10 Curve b: a relationship between a spatial frequency and an MTF value with respect to Panel b (Com. Example 1).

The results of the evaluation on the sharpness of the image provided by the panels and the sensitivity thereof are graphically shown in Fig. 2.

15 In Fig. 2, as abscissa a difference (decrement) of the relative sensitivity is plotted and as ordinate a difference (increment) of the sharpness of the image is plotted, both being calculated by employing Panel b as a criterion (relative sensitivity: 100, MTF value at the spatial frequency of 2 cycle/mm: 35 %).

20 Fig. 2 illustrates;

Line A: a relationship between a relative sensitivity and a sharpness with respect to Panels A (Example 1), and

25 Line B: a relationship between a relative sensitivity and a sharpness with respect to Panels B (Com. Example 1).

30 As is evident from the results shown in Fig. 1, the radiation image storage panel of the present invention (Panel a) is remarkably improved in the sharpness of the image as compared with the conventional radiation image storage panel (Panel b).

35 As is evident from the results indicated by Lines A and B of Fig. 2, the radiation image storage panels according to the present invention (Panels A) provided images of higher sharpness than those provided by the conventional radiation image storage panels (Panels B,

described in U.S. Patent Application No. 326,642), when the comparison was made on the same sensitivity level basis.

Example 2

5       The procedure of Example 1 was repeated except that the phosphor layer was formed in the thickness of 150  $\mu$ m, to prepare a radiation image storage panel consisting of a support, a phosphor layer, a colored adhesive layer and a transparent protective film.

10       Further, the amount of the dye colorant employed for coloring an adhesive layer was varied within the range of 0.1 - 1.0 % (by solid content) of the adhesive agent, to prepare a variety of radiation image storage panels consisting of a support, a phosphor layer, a colored adhesive layer and a transparent protective film, in which  
15       the adhesive layers were colored in different degrees (Panels C).

Comparison Example 2

20       The procedure of Comparison Example 1 was repeated except that the colored phosphor layer was formed in the thickness of 150  $\mu$ m, to prepare a radiation image storage panel consisting of a support, a colored phosphor layer, an adhesive layer and a transparent protective film (Panel d).

25       The radiation image storage panels (Panels C and d) prepared as above were evaluated on the sharpness of the image provided thereby and the sensitivity thereof according to the above-described tests.

30       The results of the evaluation are graphically shown in Fig. 2.

In Fig. 2, Line C indicates a relationship between a

relative sensitivity and a sharpness with respect to Panels C (Example 2). As a criterion, Panel d (relative sensitivity: 100, MTF value at the spatial frequency of 2 cycle/mm: 55 %) was employed.

5       As is evident from the results indicated by Line C of Fig. 2, the radiation image storage panels according to the present invention (Panels C) had the same tendencies on the sharpness and the sensitivity as Panels A even when the phosphor layers were made thinner, and  
10 improved in the sharpness of the image as compared with the conventional radiation image storage panel on the same sensitivity level basis.

CLAIMS:

1. A radiation image storage panel comprising a support, a phosphor layer which comprises a binder and a stimuable phosphor dispersed therein, an adhesive layer  
5 and a protective film, superposed in this order, characterized in that said adhesive layer is colored with a colorant capable of absorbing a portion of stimulating rays for the stimuable phosphor.

2. The radiation image storage panel as claimed in  
10 claim 1, in which said adhesive layer is colored with such a colorant that the mean reflectance thereof in the wavelength region of the stimulating rays for the stimuable phosphor is lower than the mean reflectance thereof in the wavelength region of the light emitted by the  
15 stimuable phosphor upon stimulation thereof.

3. The radiation image storage panel as claimed in claim 2, in which the mean reflectance of said colored adhesive layer in the wavelength region of the stimulating rays for the stimuable phosphor is not higher  
20 than 95 % of the mean reflectance of an adhesive layer equivalent to said adhesive layer except for being uncolored with the colorant in the wavelength region of said stimulating rays.

4. The radiation image storage panel as claimed in  
25 claim 2, in which the mean reflectance of said colored adhesive layer in the wavelength region of the light emitted by the stimuable phosphor upon stimulation thereof is not lower than 20 % of the mean reflectance of an adhesive layer equivalent to said adhesive layer  
30 except for being uncolored with the colorant in the wavelength region of said emitted light.

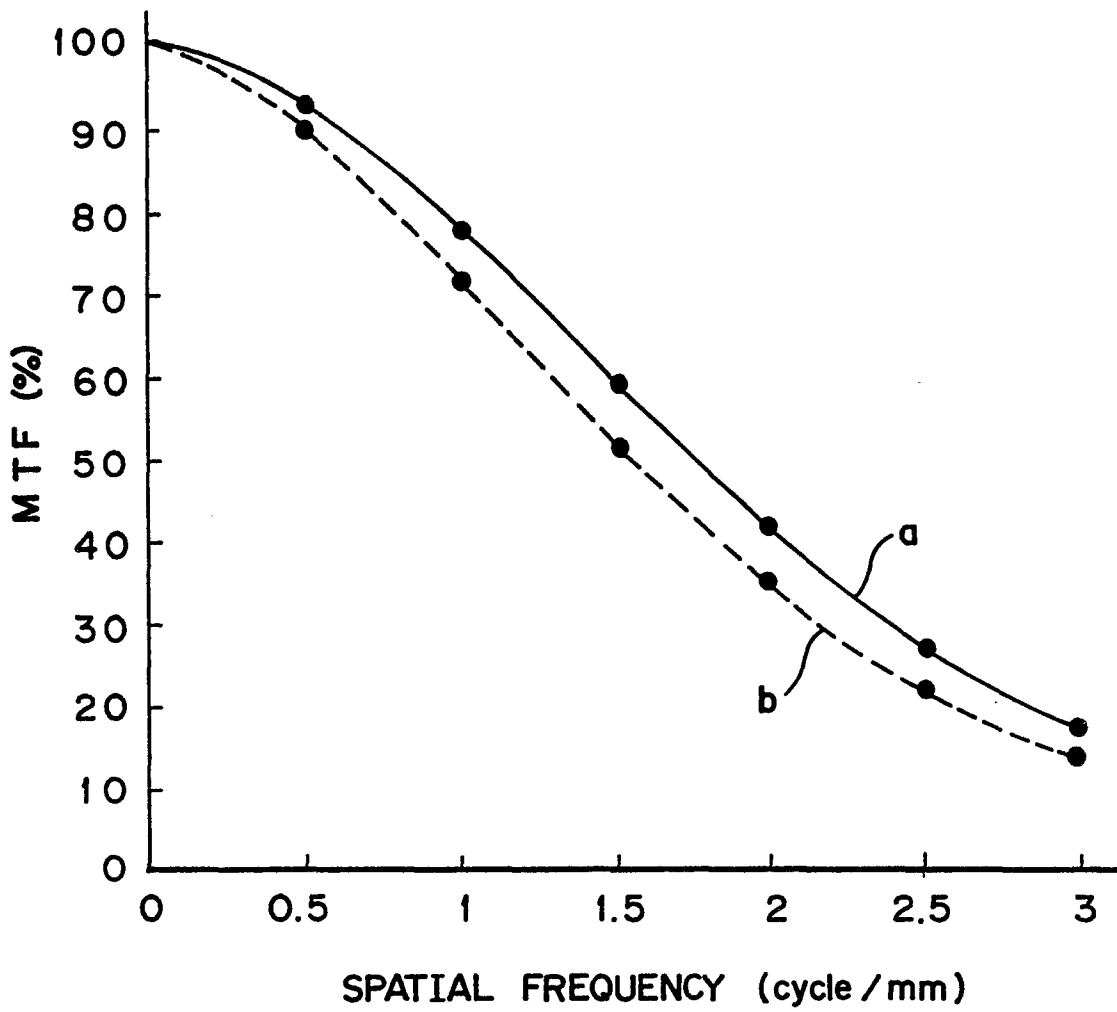
5. The radiation image storage panel as claimed in any one of claims 1 through 4, in which said stimuable phosphor is a phosphor capable of showing stimulated emission in the wavelength region of 300 - 500 nm upon stimulation with stimulating rays in the wavelength region of 400 - 900 nm.

6. The radiation image storage panel as claimed in claim 5, in which the stimuable phosphor is a divalent europium activated alkaline earth metal fluorohalide phosphor.

7. The radiation image storage panel as claimed in claim 5, in which the stimuable phosphor is a rare earth element activated rare earth oxyhalide phosphor.

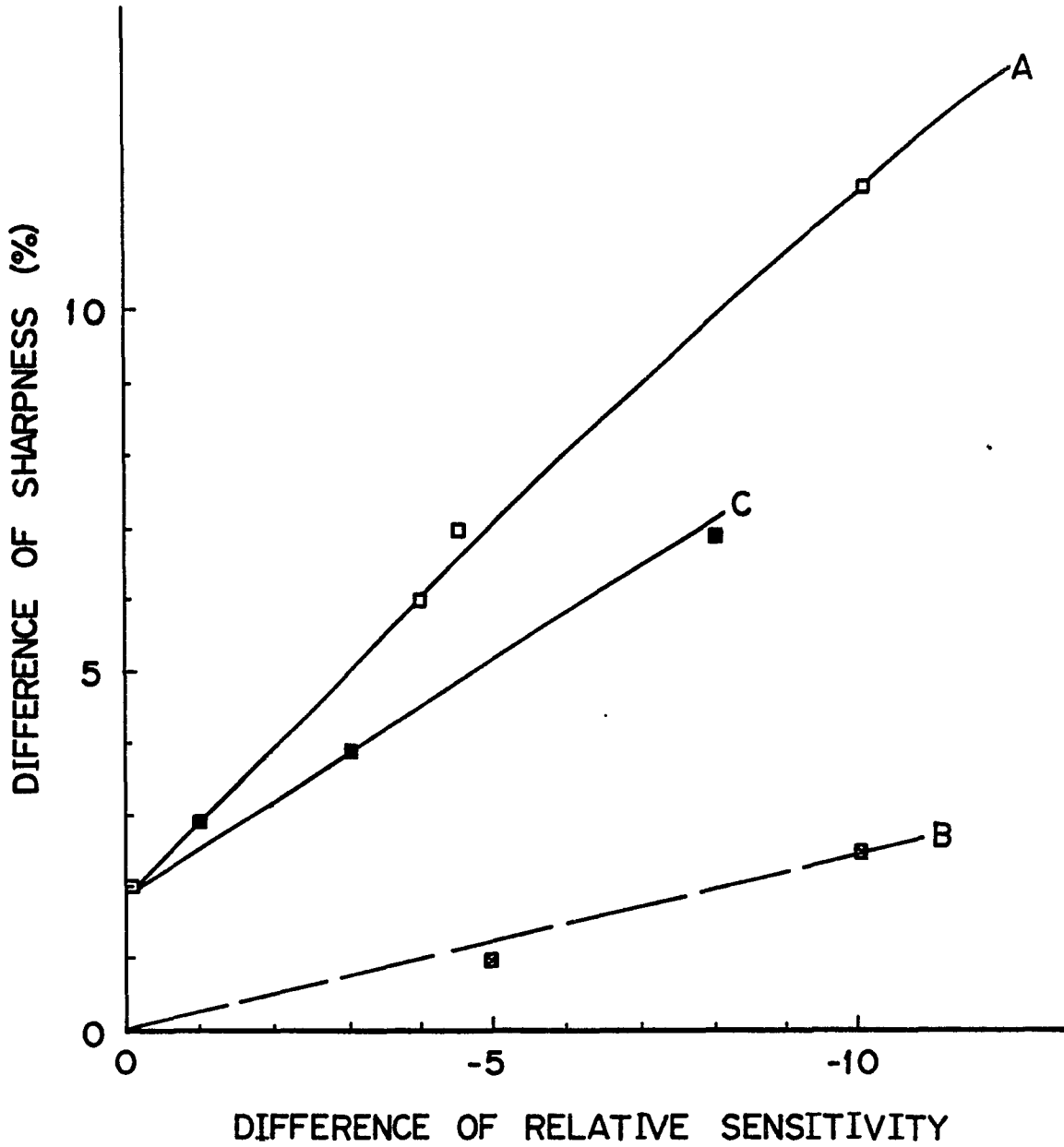
712

FIG. 1



212

FIG. 2



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.4)
A	FR-A-2 305 758 (AGFA-GEVAERT) * Claims 1-13 *  -----	1	G 21 K 4/00
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			G 21 K 4/00
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 28-06-1985	Examiner DROUOT M.C.
<p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>X : particularly relevant if taken alone  Y : particularly relevant if combined with another document of the same category  A : technological background  O : non-written disclosure  P : intermediate document</p> <p>T : theory or principle underlying the invention  E : earlier patent document, but published on, or after the filing date  D : document cited in the application  L : document cited for other reasons  &amp; : member of the same patent family, corresponding document</p>			