United States Patent [19]

De Belder et al.

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[45] **Mar. 18, 1975**

[54] **RADIOGRAPHIC INTENSIFYING SCREENS**

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[30] **Foreign Application Priority Data**

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[52] **U.S. Cl.** **250/483,** 250/486

[51] **Int. Cl.** **H01j 1/62**

[58] **Field of Search** .... 250/483, 486, 213 VT

[56] **References Cited**

UNITED STATES PATENTS

3,584,216	6/1971	Tinney	250/486
3,617,285	11/1971	Staudenmayer	250/483 X
3,617,743	11/1971	Rabatin et al.	250/483 X

Primary Examiner—Archie R. Borchelt
Attorney, Agent, or Firm—A. W. Breiner

[57] **ABSTRACT**

A radiographic intensifying screen combination suited for use in radiographic recording of information with a silver halide recording material, which combination comprises (1) at least one metallic layer or sheet composed of or containing at least one metal having an atomic number in the range of 46 to 83, and (2) at least one fluorescent layer or sheet, which in working relationship with said metal(s) consists of or contains at least one fluorescent substance within the scope of the following general formula:

$$M_{(w-n)}\cdot M'_nO_wX$$

wherein:

M is at least one of the metals yttrium, lanthanum, gadolinium or lutetium,

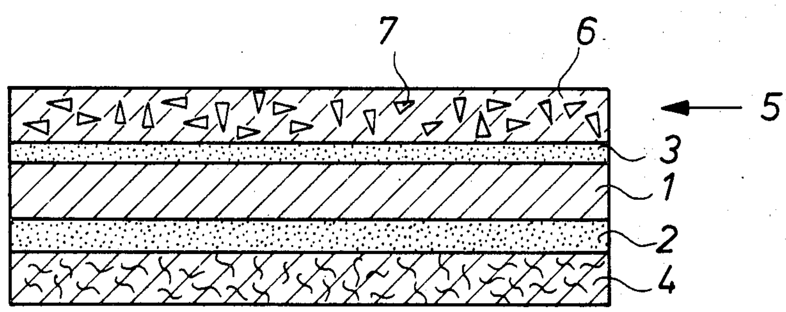
M' is at least one of the rare earth metals dysprosium, erbium, europium, holmium, neodymium, praseodymium, samarium, terbium, thulium or ytterbium,

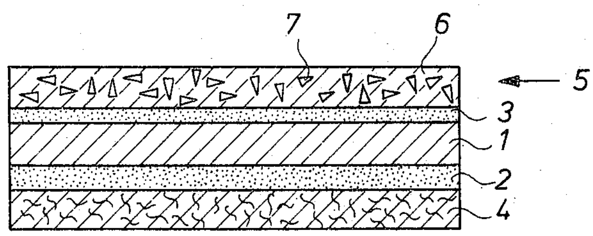
X is sulphur or halogen,

n is 0.0002 to 0.2, and

w is 1 when X is halogen or is 2 when X is sulphur.

26 Claims, 1 Drawing Figure

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RADIOGRAPHIC INTENSIFYING SCREENS

This invention relates to an improved intensifying screen combination for radiography.

The use of metal screens as intensifying screens in radiography is well known.

The intensifying effect of such screens is based on the emission of secondary X-rays and electrons formed by the absorption of primary incident X-rays.

It is also known that said metal screens act as a filter for scattered radiation of lower energy and effectively absorb low energy rays obliquely impinging onto the metal screen.

Fluorescent screens, which contain a layer or sheet comprising solid substances, e.g., calcium tungstate that fluoresce under the influence of X-ray radiation, have been used, e.g., in the field of medical X-ray. However, they are less effective when more energetic X-rays or gamma rays are used, the absorption of the penetrating X-ray and gamma radiation in the fluorescent screens being inversely proportional to their energy. A higher absorption can be obtained by increasing the thickness but such at the expense of a loss in image sharpness. Moreover, secondary scattered radiation originating from the radiographically exposed object by impinging on a fluorescent screen, e.g., a calcium tungstate screen, gives rise to the production of radiographic images of low gradation when silver halide recording materials are used.

It has been established experimentally that the combination of a metallic screen and fluorescent screen in which both screens are arranged in contiguous relationship is particularly useful in radiographic recording.

Such a combination provides a high gain in effective interaction of radiation with photographic materials of the silver halide type without substantial loss of image quality. This high gain in effective interaction may be explained by the fact that the partial transformation of the initial high energy radiation in the metallic screen yields secondary radiation of low energy (X-rays and electrons) that are better absorbed in this lower energy state by the fluorescent substance and give rise to fluorescence radiation mainly in the ultraviolet and visible light range for which silver halide recording materials are inherently particularly sensitive or can be made sensitive by spectral sensitization.

By the fact that in such combination of screens profit is taken of the properties of the metallic screen acting as intensifying and filtering screen, the fluorescent layer is kept rather thin. The light emitted by the fluorescent screen is effectively absorbed by the silver halide grains of a silver halide emulsion layer and radiographic images of improved sharpness and characterized by an increased gradation are obtained. Indeed, ultraviolet radiation and visible light, as is generally known, yield steeper gradation images than X-ray radiation directly interacting with silver halide emulsion layers.

The screen assembly further also offers the advantage of increasing the gradation as a result of the attenuation by the metallic screen of the scattered radiation originating from the object that is radiographed.

In order to obtain optimum recording results on silver halide recording materials the absorption and emission properties of the combined metallic screen and fluorescent substance screen have to be such that as much as possible of the high energy radiation is transformed in the metallic screen in secondary radiation suited for generating in the fluorescent substances of the fluorescent screen a fluorescence radiation in a wave length range to which the silver halide grains are inherently particularly sensitive or are made particularly sensitive by spectral sensitization.

We have now found a radiographic intensifying screen combination that is particularly useful for radiographic recording of information with a silver halide recording material, which combination comprises (1) at least one metallic layer or sheet composed of or containing at least one metal having an atomic number in the range of 46 to 83, and (2) at least one fluorescent layer or sheet which, in working relationship with said metal(s) consists of or contains at least one fluorescent substance within the scope of the following general formula:

$$M_{(w-n)}.M'_nO_wX$$

wherein:

- M is at least one of the metals yttrium, lanthanum, gadolinium or lutetium,
- M' is at least one of the rare earth metals dysprosium, erbium, europium, holmium, neodymium, praseodymium, samarium, terbium, thulium or ytterbium,
- X is sulphur or halogen,
- n is 0.0002 to 0.2, and
- w is 1 when X is halogen or is 2 when X is sulphur.

When using the term "radiographic recording" we designate thereby a recording technique that makes use of penetrating radiation, which includes highly energetic radiation such as X-rays, beta rays, or fast electrons, e.g., as obtained in an electron microscope, gamma rays and neutrons.

The preparation of fluorescent substances falling within the scope of that general formula has been described, e.g., in the French Pat. No. 1,580,544 filed July 25, 1968 by N. V. Phillips Gloeilampenfabrieken, in the U.S. Pat. Nos. 3,418,246 of Martin R. Royce and 3,418,247 of Perry N. yocom both issued Dec. 24, 1968 and in the United Kingdom Pat. specification 1,247,602 filed Oct. 9, 1969 by General Electric and Co.

For use in combination with silver halide emulsion layers that are not spectrally sensitized it is advantageous to use screen combinations in which the fluorescent screen transforms the absorbed X-ray radiation (e.g., 60 kV X-ray radiation) with a high quantum yield in radiation of wavelength bands situated in the 320 to the 450 nm wavelength range. Especially suited for that purpose are the terbium activated yttrium oxysulphide compounds falling within the scope of the above general formula.

In combination with silver halide emulsion layers that are spectrally sensitized in the range of 450–570 nm preferably terbium-activated gadolinium or lanthanum oxysulphides falling within the scope of the above general formula are used.

In combination with silver halide emulsion layers that are spectrally sensitized in the range of 550 to 700 nm preferably an europium(III)-activated mixed oxysulphide of yttrium and lanthanum falling within the scope of the above general formula is used.

A fluorescent screen containing a mixture of

A. yttrium oxysulphide activated with from 0.1 to 10% by weight of terbium or activated with terbium and dysprosium, and

B. gadolinium or lanthanum or lutetium oxysulphide activated with terbium or dysprosium is particularly useful for its high visible light emission capacity. A preferred ratio by weight of (A) and (B) is 25:75.

By using a plurality of fluorescent screen layers of different composition or by using a fluorescent screen containing a mixture of different fluorescent substances of the above general formula a fluorescence over the whole visible spectrum can be obtained. Such combination is particularly useful for the recording on silver halide recording elements that are made spectrally sensitive for light of the whole visible spectrum.

In a preferred embodiment the selected fluorescent substance(s) is(are) applied in the form of at least one layer or sheet. A said layer or sheet is preferably constructed to a thickness of 0.05 to 0.5 mm and contains the fluorescent substance(s) dispersed in a binder. Such binder is, e.g., an organic high molecular weight polymer. Preferred binding agents are cellulose nitrate, ethylcellulose, cellulose acetate, polyvinyl acetate, polystyrene, polyvinyl butyral, polymethyl methacrylate and the like.

The proportion of high molecular weight polymer to fluorescent material is generally within the range of 5–15% by weight. A preferred grain size of the fluorescent substances is in the range of 5–50 μ.

The surface of the fluorescent material layer may be protected against moisture and mechanical damage by a coating of an organic high polymer applied at a thickness of 0.001 to 0.05 mm. Such protecting coating is, e.g., a thin film of cellulose nitrate, cellulose acetate, polymethyl methacrylate and the like.

Besides the fluorescence radiation impinging normally to the silver halide layer there is always an amount of scattered radiation that strikes obliquely said layer and gives rise to image unsharpness. The image sharpness can be improved considerably by incorporating a dye absorbing fluorescent light and called here "screening dye" into the fluorescent layer or into a layer adjacent thereto, e.g., covering layer or subjacent anti-halation layer. Hereby the oblique radiation by the fact that it covers a larger path in the fluorescent screen material is attenuated by the screening dye absorbing fluorescent light, to a greater extent than the radiation impinging normally.

An appropriate screening dye for use in combination with fluorescent screens emitting in the green part of the visible spectrum is, e.g., Rouge Feu Neozapon (C.I. Solvent Red 119).

The metallic screen may be composed of a single supported or self-supporting metal layer or of a plurality of superposed metal layers. The metallic screen or a plurality of screen layers may be composed of or incorporates a pure metal having an atomic number as mentioned or may be composed of an alloy containing such metal.

Preferably the intensifying screen combination contains at least one metallic screen layer, which consists of or of which at least 50% by weight is constituted by a metal or metals having an atomic number or having atomic numbers in the range 46 to 83.

Preferred metallic screens mainly (at least 50% by weight) contain or consist of silver, tin, tellurium, thallium, tungsten, platinum, gold, mercury, tantalum, lead or bismuth or mixtures or alloys thereof in layer or sheet form. Among them tungsten and silver offer a particularly useful combination with the cited fluorescent substances.

The thickness of the metal layer or sheet is preferably within the range of 0.005 to 0.1 mm, adapted to the energy spectrum of the radiation used, whereby a particularly good amplification with secondary X-rays and electron rays emitted by the metal foil is obtained and the scattered radiation is eliminated as completely as possible. Suitable supported metal layers can be formed by metallic vapour deposition. Metallic foils of suitable thickness may be obtained by rolling.

The metallic screen may have a grooved or indented surface as described in the U.S. Pat. No. 3,584,216 of Joseph F. Tinney issued June 8, 1971.

In a preferred screen combination of the present invention the metallic screen element (layer(s) or sheet(s)) is supported by the same support as used for the fluorescent screen element. Such support is composed, e.g., of paper, glass, cloth or plastic film, the latter supports being preferably of about 0.2 mm in thickness.

In such a composite screen the metallic screen element is preferably interposed between the support and the fluorescent material layer(s) and adheres thereto e.g. by means of an adhesive layer.

Suitable adhesive layers for bonding the metallic foil or other element to the fluorescent material layer are composed of an organic high polymer such as synthetic rubber, for example, neoprene, nitrile rubber, etc., polyvinyl butyral, alkyd resin and the like. The thickness of the adhesive layer is preferably as thin as possible and below 10 μ, since the amplifying effect of the metallic screen element is lowered by increasing the thickness of said adhesive layer.

An adhesive layer may be used for bonding the supporting layer to the metal foil or other metallic screen element and such adhesive layer may be identical to that used for adhering the fluorescent material to such screen element. The thickness of a said adhesive layer between the support layer and the metallic screen need not necessarily be smaller than 10 μ.

The intensifying effect of the metallic screen-fluorescent screen combination used according to the present invention is particularly high when X-rays of an energy above 100 kV or the commonly known high energetic gamma-rays are used in the radiographic process.

By the elimination of scattered radiation and the high quantum yield of fluorescent light that is effectively used in a suitably spectrally sensitized silver halide material, radiographic images of high contrast are obtained rapidly.

The present invention is illustrated by the following examples and by the drawing which is a cross-section of the screen structure of Example 1.

EXAMPLE 1

A solution of neoprene in toluene is spray-coated on a surface of a 0.03 mm tungsten foil to form an adhesive layer **2** of 0.015 mm in thickness when dried. By a laminating press the thus obtained material is pressed with its adhesive layer in contact with a paper sheet **4** of 0.2 mm in thickness.

Thereupon, the free surface of the tungsten foil is coated with the same solution of neoprene in toluene forming again an adhesive layer **3**, but having now a thickness of only 0.005 mm after drying. To that adhesive layer a solution comprising:

Gd_2O_2S activated with traces of Tb	300 g
cellulose nitrate	36 g
dibutyl phthalate	11 g
butyl acetate	450 g

was applied. After drying the fluorescent coating **5** containing fluorescent substance **7** dispersed in binder **6** had a thickness of 0.12 mm.

Gd_2O_2S activated with traces of Tb has been prepared as follows:

1 mole of Gd_2O_3 and 0.01 mole of Tb_2O_3 were blended together with Na_2S_4 and kept in an inert atmosphere (N_2) at 1,100°C for 3 hours. The reaction mixture was then washed in hot water to remove the soluble sodium sulphide reaction product.

The so prepared fluorescent material emits green light under the effect of X-rays proceeding from a 100 kV generator.

Said intensifying screen material is particularly suitable for forming radiographs in light-sensitive silver halide materials spectrally sensitized to green light.

EXAMPLE 2

A solution of neoprene in toluene is spray-coated on a surface of a 0.03 mm silver foil to form an adhesive layer of 0.015 mm in thickness when dried. By a laminating press the thus obtained material is pressed with its adhesive layer in contact with a paper sheet of 0.2 mm in thickness.

Thereupon, the free surface of the silver foil is coated with the same solution of neoprene in toluene forming again an adhesive layer, but having after drying now a thickness of only 0.005 mm. To that adhesive layer a solution comprising:

Y_2O_2S activated with traces of Tb	300 g
cellulose nitrate	36 g
dibutyl phthalate	11 g
butyl acetate	450 g

was applied. After drying, the fluorescent coating had a thickness of 0.12 mm.

Y_2O_2S activated with traces of Tb has been prepared as follows:

1 mole of Y_2O_3 and 0.001 mole of Tb_2O_3 were blended together with Na_2S_4 and kept in an inert atmosphere (N_2) at 1,100°C for 3 hours. The reaction mixture was then washed in hot water to remove the soluble sodium sulphide reaction product.

The so prepared fluorescent material emits ultraviolet radiation and blue light. The composite intensifying screen has been exposed in combination with a spectrally non-sensitized radiographic silver halide film, the X-rays being produced under 60 kV. Sharp contrasty radiographic images have been obtained.

We claim:

1. A radiographic intensifying screen combination suited for use in radiographic recording of information with a silver halide recording material, said combination comprising (1) a metallic substrate including at least one metal having an atomic number in the range of 46 to 83, and (2) at least one fluorescent substrate in working relationship with said metal and including at least one fluorescent substance having the formula:

$$M_{(w-n)} \cdot M'_nO_wX$$

wherein:

M is at least one of the metals selected from the group consisting of yttrium, lanthanum, gadolinium and lutetium,

M' is at least one of the rare earth metals selected from the group consisting of hysprosium, erbium, europium, holmium, neodymium, praseodymium, samarium, terbium, thulium and ytterbium,

X is selected from the group consisting of sulphur and halogen,

n is 0.0002 to 0.2, and

w is 1 when X is halogen and 2 when X is sulphur.

2. An intensifying screen combination according to claim **1**, in which said metallic substrate mainly contains a member of the group consisting of silver, tin, tellurium, thallium, tungsten, platinum, gold, mercury, tantalum, lead and bismuth and mixtures thereof.

3. An intensifying screen combination according to claim **1**, wherein the fluorescent substrate includes a substance in which absorbed X-ray radiation effects therein the emission of fluorescent light of wavelength bands situated in the 320 to 450 nm range.

4. An intensifying screen combination according to claim **1**, wherein the fluorescent substrate includes a substance in which absorbed X-ray radiation effects therein the emission of fluorescent light of wavelength bands situated in the 450–570 nm range.

5. An intensifying screen combination according to claim **1**, wherein the fluorescent substrate includes a substance in which absorbed X-ray radiation effects therein the emission of fluorescent light of wavelength bands situated in the 550–700 nm range.

6. An intensifying screen combination according to claim **1**, wherein the fluorescent substrate includes yttrium oxysulphide activated with terbium.

7. An intensifying screen combination according to claim **1**, wherein the fluorescent substrate includes a member of the group consisting of gadolinium and lanthanum oxysulphide activated with terbium.

8. An intensifying screen combination according to claim **1**, wherein the fluorescent substrate includes a oxysulphide of yttrium and lanthanum activated with europium(III).

9. An intensifying screen combination according to claim **1**, which includes a plurality of metallic substrates having the same or different composition.

10. An intensifying screen combination according to claim **1**, which includes a plurality of fluorescent substrates having the same or different composition.

11. An intensifying screen combination according to claim **1**, wherein the metallic substrate is supported by a member of the group consisting of paper, glass, cloth and plastic film.

12. An intensifying screen combination according to claim **1**, wherein the fluorescent substrate contains a mixture of different fluorescent substances included within the formula of claim **1**.

13. An intensifying screen combination according to claim **1**, wherein the thickness of the fluorescent substrate is from 0.05 to 0.5 mm and the fluorescent substance is dispersed in a binder.

14. An intensifying screen combination according to claim **13**, wherein said binder is an organic high molecular weight polymer.

15. An intensifying screen combination according to claim 13, wherein the fluorescent substance dispersed in said binder has a grain size ranging from 5 to 50 μ.

16. An intensifying screen combination according to claim 1, wherein the fluorescent substrate includes a screening dye.

17. An intensifying screen combination according to claim 1, wherein the fluorescent substrate is coated with a protective polymer having a thickness ranging from 0.001 to 0.05 mm.

18. An intensifying screen combination according to claim 1, wherein the metallic substrate and the fluorescent or sheet substrate are incorporated in a composite screen material in which the said substrates are in adhering relationship.

19. An intensifying screen combination according to claim 18, wherein the metallic substrate is supported by the same support used to support the fluorescent substrate.

20. An intensifying screen combination according to claim 19, wherein the metallic substrate is interposed between the support and the fluoresecent substrate.

21. An intensifying screen combination according to claim 20, wherein the metallic substrate is fixed to the support and to the fluorescent substrate by means of an adhesive layer.

22. An intensifying screen combination according to claim 21, wherein the thickness of said adhesive layer is below 10 μ.

23. An intensifying screen combination according to claim 22, wherein the adhesive layer is composed of a member of the group consisting of synthetic rubber, polyvinyl butyral, and an alkyd resin.

24. A method of recording information comprising the steps of information-wise irradiating an intensifying screen to X-rays or gamma-rays and of receiving the fluorescent light emitted by the intensifying screen onto a photographic material which is sensitive to said fluorescent light, wherein in said method the intensifying screen comprises:

1. at least one metallic substrate containing at least one metal having an atomic number in the range of 46 to 83, and
2. at least one fluorescent substrate which is arranged in conjunction with said metallic substrate in such a way that electrons emitted by said metal can penetrate into the fluorescent substrate, said fluorescent substrate containing at least one fluorescent substance having the formula:

$$M_{(w-n)} \cdot M'_nO_wX$$

wherein:

M is at least one of the metals selected from the group consisting of yttrium, lanthanum, gadolinium and lutetium,

M' is at least one of the rare earth metals selected from the group consisting of dysprosium, erbium, europium, holmium, neodymium, praseodymium, samarium, terbium, thulium and ytterbium,

O is oxygen,

X is a member of the group selected from sulphur and halogen,

n is 0.0002 to 0.2, and

w is 1 when X is halogen and 2 when X is sulphur.

25. A method according to claim 24, wherein the photographic material contains silver halide.

26. A method according to claim 24, wherein the fluorescent substrate includes a member of the group consisting of gadolinium and lanthanum oxysulphide activated with terbium.

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UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 3,872,309

DATED : March 18, 1975

INVENTOR(S) : Maurice H. DE BELDER ET AL

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, line 38, "Phillips" should read --Philips--;

Column 2, line 40, "yocom" should read --Yocom--;

Column 4, line 60, after "foil" insert --1--;

Column 6, line 8, claim 1, "hysprosium" should read --dysprosium--;

Column 6, line 44, claim 8, "a" should read --an--; and

Column 7, line 13, claim 18, "or sheet" should be deleted.

Signed and Sealed this

Twenty-sixth **Day of** *August 1980*

[SEAL]

Attest:

SIDNEY A. DIAMOND

Attesting Officer *Commissioner of Patents and Trademarks*