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(54) IMPROVEMENTS IN X-RAY IMAGE CONVERTERS AND PHOSPHORS

(71) We, GENERAL ELECTRIC COMPANY, a corporation organised and existing under the laws of the laws of the State of New York, United States of America, of 1 River Road, Schenectady 12305, State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

The present invention pertains to rare earth phosphor admixtures utilizing thulium-activated lanthanum and/or gadolinium oxyhalide phosphor material particularly to increase the relative speed and resolution of an x-ray image compared with conventional rare earth phosphors.

In recently issued U.S. Patent 3,795,814, there is described and claimed lanthanum and gadolinium oxyhalide phosphors activated with thulium as efficient materials to convert x-radiation to visible light. Various image converter devices utilizing said luminescent materials are also described for conversion of the x-rays to blue emission. A particular x-ray intensifying screen is disclosed for use with photographic film which is sensitive to the "blue-near ultraviolet" radiation being emitted by said phosphors.

On the other hand, green-sensitive photographic film is customarily employed with known La_2O_2S:Tb and Gd_2O_2S:Tb phosphor admixtures. This combination has been found to exhibit poorer resolution along with a blurred photographic image if the radiographic screen is employed with a double emulsion film. Specifically, a crossover problem is encountered which is attributable to light emission from said phosphor admixture being in a spectral wavelength region greater than 400 nm. While the known phosphor admixture is selected for light emission in a spectral region where the green-sensitive photographic film is most responsive, such selection results in a serious problem.

The present invention provides an x-ray image converter comprising well-formed (as herein defined) crystals of a phosphor admixture utilizing a green emitting rare earth phosphor in combination with a phosphor having the general formula:

$$LnOx : Tm^{3+}$$

wherein

Ln is one or more of La and Gd,

x is one or more of Cl and Br, and

Tm is present as an activator from 0.05 to 1 mole percent of the LnOx host.

In another aspect this invention provides a rare earth phosphor admixture comprising 20 - 80 parts by weight of a green-emitting rare earth phosphor in combination with 80 - 20 parts by weight of a phosphor having the general formula:

$$LnOx : Tm^{3+}$$

wherein

Ln is one or more of La and Gd,

x is one or more of Cl and Br, and

Tm is present as an activator from 0.05 to 1 mole percent of the LnOx host.

In certain of its embodiments, the green-emitting rare earth phosphor is:

Gd_2O_2S : Tb

but it is contemplated to substitute:

LnOx : Tb

wherein

Ln is one or more of La and Gd,

x is one or more of Cl, Br and I with comparable results.

A rare earth phosphor admixture of the present invention utilizes 20-80 parts by weight of said green-emitting rare earth phosphor with 80 - 20 parts by weight of the thulium-activated lanthanum or gadolinium oxyhalide phosphor above defined. That such latter blue-emitting phosphor can provide improved resolution capability when used in combination with green-sensitive photographic film is a surprising result especially upon further considering that the present phosphor admixtures exhibit more linear speed response over the medical diagnostic range of 50 to 130 KVp than is obtained with a La_2O_2S:Tb and Gd_2O_2S:Tb phosphor admixture now in commercial use.

An important factor in the improvement found as applied to image converters resides in the relatively fine particle size of the LaOBr:Tm phosphor constituent. Said phosphor constituent comprises well-formed crystals which means crystals having a size and uniformity to avoid optical scattering which produces a blurred image when the phosphor particles are irregular in shape. The preferred phosphor size range for a 8 mil thick radiographic screen is not less than about 2 microns in particle size and not more than about 12 microns particle size.

The present invention will be further described with reference to the accompanying Examples 1 to 10. Examples 1 to 3, 5, 9 and 10 are comparative examples.

Various radiographic screens were prepared by dispersing one or more of the phosphor materials reported in Table 1 on the following page in a suitable resin binder and then casting the screens on a supporting member according to conventional techniques well-known in the art. The speed of said screens was measured at 80 KVp with 1 inch aluminum filtration while resolution measurements were carried out at 50 KVp with 1/8 inch aluminum filtration. The reported measurements provide comparison between the present phosphor admixtures and a commercial admixture having 40% by weight La_2O_2S:Tb with 60% by weight Gd_2O_2S : Tb. Performance of the individual constituents in the commercial admixture are also reported.

TABLE I

Example No.	Screen Composition	Screen (mils) Thickness	Relative Speed	Res., LP/mm.	Quantum Mottle
1.	40% La_2O_2S:Tb, 60% Gd_2O_2S:Tb	14 mil	8.0	5.6	most
2.	LaOBr .003 Tm	10 mil	8.1	7.0	least
3.	La_2O_2S:Tb	8 mil	4.3	5.8	least
4.	50% La_2O_2S:Tb, 50% LaOBr .003 Tm	8 mil	6.1	7.0	least
5.	40% La_2O_2S:Tb, 60% Gd_2O_2S:Tb	14 mil	8.0	5.6	most
6.	50% LaOBr .003 Tm, 50% Gd_2O_2S:Tb	8 mil	7.0	7.0	medium
7.	50% LaOBr .003 Tm, 50% Gd_2O_2S:Tb	12 mil	8.4	---	medium
8.	50% LaOBr .003 Tm, 50% Gd_2O_2S:Tb	16 mil	8.9	---	medium
9.	Gd_2O_2S:Tb	8 mil	6.8	5.6	most
10.	Gd_2O_2S:Tb	12 mil	7.8	---	most

The preferred admixtures of the present invention utilize LaOBr:Tm with Gd_2O_2S:Tb for a more linear speed response over the entire medical diagnostic KVp range.

It will be apparent from the foregoing description that novel phosphor admixtures have been disclosed for x-ray image converter devices which exhibit particular advantages when employed in radiographic screens using green-sensitive photographic film.

WHAT WE CLAIM IS:-

1. An x-ray image converter comprising well-formed (as hereinbefore defined) crystals of a phosphor admixture utilizing a green emitting rare earth phosphor in combination with a phosphor having the general formula:

$$LnOx:Tm^{3+}$$

wherein

Ln is one or more of La and Gd,

x is one or more of Cl and Br, and

Tm is present as an activator from 0.05 to 1 mole percent of the LnOx host.

2. An x-ray image converter as claimed in claim 1 wherein the green-emitting rare earth phosphor is Gd_2O_2S:Tb.

3. An x-ray image converter as claimed in claim 1 wherein the green-emitting rare earth phosphor has the general formula:

$$LnOx:Tb$$

wherein

Ln is one or more of La and Gd, and

x is one or more of Cl, Br, and I.

4. An x-ray image converter as claimed in claim 1 wherein the phosphor admixture comprises Gd_2O_2S:Tb and $LaOBr:Tm^{3+}$ thulium being present in an amount from 0.05 to 1 mole percent of the LnOx host.

5. An x-ray image converter as claimed in any one of the preceding claims comprising a radiographic screen having the phosphor admixture supported on a base member.

6. A rare earth phosphor admixture comprising 20 - 80 parts by weight of a green-emitting rare earth phosphor in combination with 80 - 20 parts by weight of a phosphor having the general formula:

$$LnOx:Tm^{3+}$$

wherein

Ln is one or more of La and Gd

x is one or more of Cl and Br, and

Tm is present as an activator from 0.05 to 1 mole percent of the LnOx host.

7. A rare earth phosphor admixture as claimed in claim 6 wherein the green-emitting rare earth phosphor is Gd_2O_2S:Tb and the other phosphor is LaOBr:Tm, thulium being present in an amount from 0.05 to 1 mole percent of the LnOx host.

8. An x-ray image converter as claimed in claim 1 substantially as hereinbefore described in any one of Examples 4 and 6 to 8.

9. A rare earth phosphor admixture as claimed in claim 6 substantially as hereinbefore described in any one of Examples 4 and 6 to 8.

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