

[54] **SYSTEM FORMED BY THE COMBINATION OF A SOLID STATE IMAGE INTENSIFIER AND A COMPATIBLE ADAPTED X-RAY FILM**

[75] Inventors: **Leonard Fass**, Albisola Superiore;  
**Ennio Fatuzzo**, Ferrania, both of Italy

[73] Assignee: **Minnesota Mining and Manufacturing Company**, St. Paul, Minn.

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[58] **Field of Search** ..... 250/483, 484, 370, 320,  
250/487, 460, 217 R, 320, 321, 322, 323,  
460, 475, 480, 482, 485

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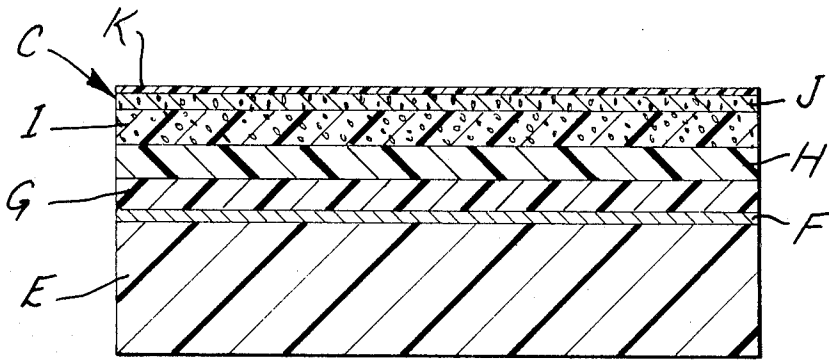
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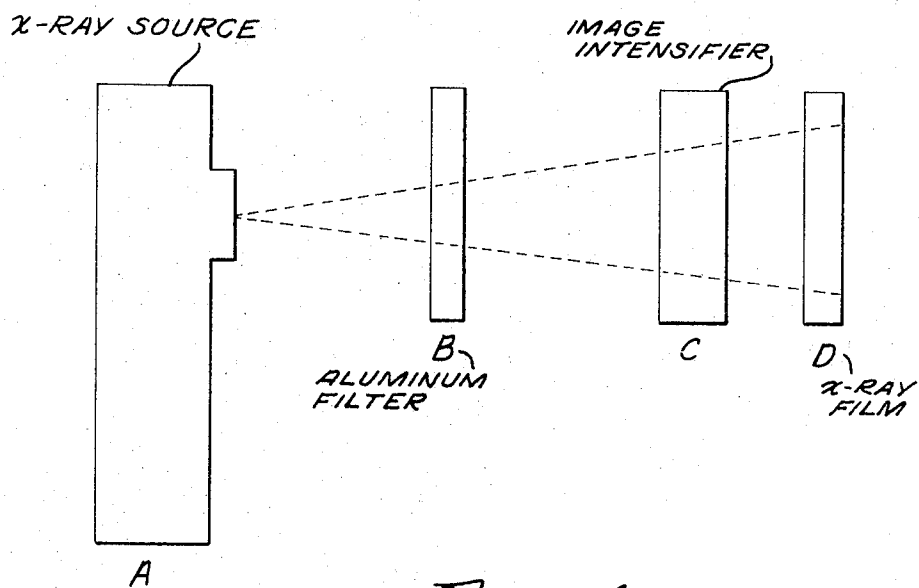
*Primary Examiner*—Harold A. Dixon  
*Attorney, Agent, or Firm*—Alexander, Sell, Steldt & DeLaHunt

[57] **ABSTRACT**

An X-ray image intensifying device comprising  
A. A supporting film base,  
B. A conducting layer which is at least partially transparent to X-rays,  
C. An X-ray sensitive photoconductive layer,  
D. A light opaque layer,  
E. An electroluminescent layer comprising an electroluminescent compound dispersed in a binder,  
F. An at least partially light-transparent electrically conducting layer, and  
G. A protective layer whose thickness is such that the resolving power loss is not greater than 20 percent lower than that of the same element without any protective layer, enables marked sensitivity increases in X-ray photographic systems.

**10 Claims, 2 Drawing Figures**





**FIG. 1**

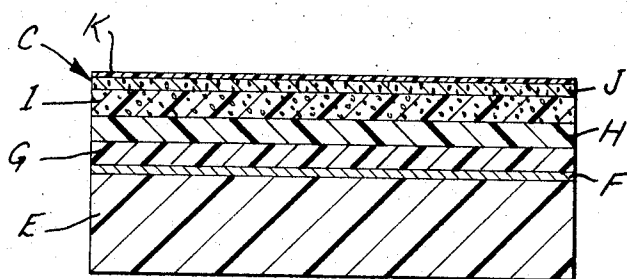


FIG. 2

# SYSTEM FORMED BY THE COMBINATION OF A SOLID STATE IMAGE INTENSIFIER AND A COMPATIBLE ADAPTED X-RAY FILM

The present invention relates to a new improved system for radiography.

Particularly it relates to a device which transforms information contained in an X-ray beam, whose intensity varies from point to point in space, into a light beam, whose intensity variation corresponds to intensity variations of the incident X-rays, such a device being combined with a silver halide X-ray film whose spectral sensitivity is suitably selected to efficiently record the radiations emitted by the above-mentioned device. Moreover, the above-mentioned device can consist of a so-called solid state image intensifier.

Since X-ray films are very insensitive to X-rays, to prevent excessive radiation doses to the patient, so-called intensifying screens consisting of an X-ray fluorescent salt, such as calcium tungstate, dispersed in a suitable binder and coated on an X-ray transparent base, were until now generally used to obtain X-ray images in medical radiography. Such screens are positioned in close contact with an X-ray film in a container known as a cassette.

We have now found that the radiation doses to the patient can be remarkably decreased, that is a higher real sensitivity than that achieved with the fluorescent intensifying screen X-ray film system can be obtained by using a solid state flat X-ray image intensifying element suitable for radiography consisting of various layers arranged in the following way:

- a. a supporting film base
- b. an at least partially transparent to X-rays conducting layer
- c. an X-ray sensitive photoconductive layer
- d. a light opaque layer
- e. an electroluminescent layer formed by an electroluminescent compound dispersed in a binder
- f. an at least partially light-transparent conducting layer
- g. a protective layer whose thickness is such that the resolving power loss is not greater than 20 percent lower than that of the same element without any protective layer.

The above mentioned sensitivity increase can be partially or wholly exploited to obtain a higher resolving power. This can be achieved by using for instance X-ray film having much finer grains than standard X-ray films. This slightly decreases the high sensitivity of the system, but, on the other hand, allows a better resolving power to be obtained.

Such a sensitivity increase can be also exploited by using an X-ray film having a lower silver halide quantity per unit surface area, with a consequent reduction in manufacturing costs and processing times.

The higher sensitivity of the system can be finally exploited by using X-ray films having emulsion coated on only one surface of the base, with a consequent reduction in manufacturing costs, simplification of the processing procedures and of the equipment necessary for the said processing and the possibility of remarkably shortened processing times.

As there is no conventional standard for the measurement of the X-ray intensifying screen sensitivity, as a specimen screen or comparison screen we used a screen or, more precisely, a pair of medium sensitivity

calcium tungstate screens combined with an X-ray film of the so-called rapid processing type.

In practice, 3M Type R X-ray Film made by 3M Italia S.p.A. of Italy was combined with a pair of Par-Speed screens of E. I. DuPont de Nemours and Co., Inc., of Wilmington, Del., and placed in a conventional container or X-ray cassette. Such an X-ray film together with the intensifying screens will be hereinafter called the "conventional system".

A preferred embodiment to obtain such an image intensifier consists of preparing a multi-layer structure formed by the following layers:

1. a supporting base, at least 90 percent transparent to X-rays, formed for example of aluminum foil or polyester of thickness not larger than about 300 microns;
2. an electrically conductive layer which is at least 90 percent transmissive of 20 - 150 kV X-rays. Such layer need not be applied in the case when the supporting base is already conductive. Such a layer can be composed of a metal or other conducting compound deposited by known techniques such as vacuum evaporation, sputtering, spraying, etc.
3. an X-ray sensitive photoconductive layer, the resistance of which varies according to the incident X-ray intensity and which resistance varies by at least a factor of 10 when irradiated by X-rays produced by a tungstate target X-ray tube such as the Machlett OEG/50/T, manufactured by The Machlett Laboratories Incorporated, Springdale, Conn., such tube operated at 40 kV and 1mA at a distance of 20 cm. The radiation from the above tube is emitted through a 0.040 in. thick beryllium window with a 5 mm. focal spot. Suitable X-ray photoconductors are CdS or CdSe or  $CdS_xSe_{1-x}$  doped with copper and in certain cases also with other elements such as Al, B, Cl etc., in the form of powders. The preparation of such photoconductors is described in "The Photoconductivity of Solids" by R. Bube, published by Wiley. The layer is prepared by coating the above mentioned photoconducting powders dispersed in a low dielectric constant binder such as an acrylic or vinyl resin. Such photoconductive layer must be of a thickness (e.g., 100 microns) so as to give acceptable resolution for radiography.
4. A light opaque layer having an impedance lower than and preferably at least a factor of 10 below that of the electroluminescent layer. In a preferred embodiment this layer must be of a highly light-diffusing material, such as particles of  $BaTiO_3$ ,  $TiO_2$  or other such compound dispersed in a high dielectric constant medium such as Cyanocel, a chemically modified cellulose (highly cyanoethylated cellulose), made by the American Cyanamid Company of Connecticut (U.S.A.). This layer must be of such a thickness that its impedance meets the requirements specified above with respect to the impedance of the electroluminescent layer to be described in (5) below:
5. An electroluminescent layer having a dielectric constant of at least 5 and having an impedance normally lower, but not less than 10 percent of that of the non-irradiated photo-conductive layer. This layer is formed by an electroluminescent compound such as commercially available ZnS doped with Cu and/or Ag dispersed in a binder. In a pre-

ferred embodiment the dielectric constant of the layer is at least 5, a result which can be obtained for example by using a high dielectric constant medium, such as Cyanocel, described in (4) above, as the binder.

6. an electrically conducting layer which is at least 50 percent transmissive to light at wavelengths between 500 and 550 nm. This layer is preferably composed of a thin film of metal or other conducting compound deposited by known vacuum techniques such as evaporation, sputtering, etc., as for example described in "Vacuum Deposition of Thin Films" by L. Holland, published by Chapman and Hall Ltd. 1960.

7. A protective layer whose thickness is such that the resolving power loss is not greater than 10 percent lower than that of the same element without any protective layer. Such layer can be composed of a polyurethane resin such as Desmophen 650 - Desmodur N (where Desmophen 650 is 65 percent solution in ethylene glycol of a branched polyester which contains approximately 5 percent of hydroxyl groups, having an acidity value less than 4, a viscosity of approximately  $800 \pm 150$  cP and a fire point greater than  $50^{\circ}\text{C}$  (DIN 51755) and Desmodur N is a 75 percent solution in ethylene glycol acetate/xylene (1:1) of a polyfunctional aliphatic isocyanate having an NCO content of 16-17 percent with a fire point greater than  $33^{\circ}\text{C}$  (DIN 53213), density at  $20^{\circ}\text{C}$  of  $1.06 \text{ gm/c.c.}$  (DIN 51757), viscosity at  $20^{\circ}\text{C}$  of  $250 \pm 100$  cP, of Farbenfabriken Bayer AG, Leverkusen, Germany). Another possible protective layer can be made from a vinyl chloro-acetate copolymer such as Vinylite VAGH (approximately containing 91 percent vinyl chloride, 2.3 percent hydroxyl groups, 3 percent vinyl acetate and having an intrinsic viscosity in cyclohexanone of approximately 0.55 at  $20^{\circ}\text{C}$ ) of the Bakelite Division, Union Carbide and Carbon Corporation, New York, N.Y., USA, hardened with one part of an isocyanate (Desmodur N) for every two parts of Vinylite VAGH. Yet another protective layer can be made from a polyvinylidene chloride copolymer such as that manufactured by the Dow Chemical Corporation of Delaware (USA), under the name of Saran.

In another embodiment the protective layer described in (7) above becomes the supporting base and the other layers are sequentially coated in reverse order to the previous embodiment.

It may be necessary to include a series of intermediate layers to obtain the suitable conditions of electrical contact between the various layers making up the intensifier.

For the purposes of understanding this invention, the photoconductive layer can be considered as being represented by a capacitance and a resistance in parallel, whereby the value of the former is not affected by the X-rays, while the value of the latter is decreased under X-ray irradiation. The electro-luminescent layer on the other hand, can be represented by a capacitance having a very high leakage resistance. The impedance of the unexposed photoconductor at a frequency equal to the frequency of the applied alternating voltage must be higher than that of the electroluminescent layer. The impedance of the X-ray exposed photoconductor (at X-ray exposures such as those described in (3) above)

must be as small as possible and in any case not much larger than twice the impedance of the electroluminescent layer.

- The above implies that the capacitive part of the impedance of the photoconductor must be as large as possible as compared to the resistance of the photoconductor and in any case not significantly smaller than said resistance. This condition can be fulfilled by using a low dielectric constant binder for the photoconductive powder. Such binders can consist for example of acrylic or vinylic resins.

Another type of image intensifier useful for the scope of the present invention can be based on the principle described in U.S. Pat. No. 3,215,847 with proper modifications to make it suitable for use in radiography together with a silver halide X-ray film, whose spectral sensitivity has been suitably selected to efficiently record the radiation generated by the above mentioned device.

- A series of patents, such as U.S. Pats. Nos. 3,264,479; 3,300,645; 3,215,847 and 3,394,261, relate to image intensifiers which transform a signal consisting of a suitably modulated X-ray beam into a light beam, whose modulation corresponds to the X-ray modulation. Such image intensifiers however are not suitable for radiography but only for radio-scopic. In these intensifiers, generally, light is emitted through a very thick front protection panel (such as for instance through a relatively thick glass plate, 1 mm or greater). Therefore, such panels are not suitable for contact recording with an X-ray film due to the loss of resolution. Furthermore, it is not always possible to use the most suitable photoconductors in the prior art type image intensifiers, because often they have a too long a time constant.

According to the present invention, on the contrary, the electrode and the protective layer are sufficiently thin to allow the recording of the image formed on the electroluminescent compound, substantially without any loss of resolving power. Furthermore, in the present invention the most suitable photoconducting compounds can be used even if they have a time constant too long to be used in radioscopes.

- FIG. 2 illustrates an X-ray intensifying device of the present invention. E represents the film base, F a conductive layer, G a photoconductive layer, H a light opaque layer, I an electroluminescent layer, J a conducting layer, and K represents the thin surface protective layer whose thickness is such that the resolving power loss is not greater than 20 percent lower than that of the same element without any protective layer.

As mentioned above, the higher sensitivity of the system, which can be obtained by using the intensifier of the present invention, can be partially or wholly used to obtain a better resolving power and therefore a clearer image, or can be used with an X-ray film having a lower silver coating weight, thus allowing lower production costs and shorter processing times.

- By using an X-ray film with a silver bromo-iodide emulsion having a grain size of 0.75 microns, a part of the remarkable sensitivity increase of the system according to the present invention is sacrificed. On the other hand, the resolving power of the system turns out to be increased by at least 30 percent more than that of the conventional system.

Following the methods known to those skilled in the art, viz. using emulsions having a grain size ranging

from 0.7 to 0.8 microns and suitable gelatin substitutes capable of increasing the covering power of the developed silver, it has been possible to prepare X-ray films having an approximately 40 percent lower silver coating weight than the X-ray material used in the compared conventional system. Although the sensitivity of such X-ray films turns out to be reduced by more than one half, the sensitivity increase obtained by means of the image intensifier of the present invention still allows exposure times or dosages lower than those required by the above mentioned conventional system.

The following examples are illustrative of the methods and compositions of the present invention but should not be construed as limiting the scope of the present invention.

#### EXAMPLE 1

According to known techniques a less than 1 micron thick tin oxide layer was deposited on a 1.5 mm glass base (see for example R. Gomer, *The Review of Scientific Instruments*, p. 993 V.24 (1953)). An approximately 100 micron thick photoconducting layer formed by photoconductive grade copper doped cadmium selenide grains obtained from E.S.P.I. (Electronic Space Products, Inc.) of California, U.S.A., and subsequently doped with 5 p.p.m. of aluminum dispersed in a nitrocellulose binder, was coated on the above mentioned conducting layer. An opaque layer of thickness about 15 microns made from particles of titanium dioxide dispersed in Cyanocel was coated on top of the photoconducting layer. An approximately 30 micron thick electroluminescent layer consisting of copper doped zinc sulphide powder type EL - CB3 of Levy-West Laboratories, Bush Fair, Harlow, Essex, England, dispersed in Cyanocel was coated on the opaque layer. An approximately 100 Å thick semi-transparent electrode consisting of chromium was deposited by vacuum evaporation on the electroluminescent layer. A protective layer of thickness approximately 10 microns thick consisting of a polyurethane enamel made of Desmophen 650-Desmodur as described in point (7) above, was coated on the semi-transparent electrode. Two conductors connected the two electrodes to an alternating current source, which was in this case a normal 220 volt 50 Hz power point.

The image amplifying element, thus prepared, was exposed to X-ray radiations generated in a Machlett OEG-50-T type X-ray tube working at a voltage of 40kV and a current of 10mA. The distance between the source and the sample was 20 cm. A 7 mm. thick aluminum filter had been placed between the X-ray source and the intensifier.

In such conditions, we obtained a photon emission increase 10 times higher than the one obtained with a DuPont Par-Speed Screen.

The photographic test was carried out as follows: An XV 5 X-ray film of 3M Italia S.p.A. was exposed as shown in FIG. 1, wherein: A is the X-ray source; B is the aluminum filter; C is the image intensifier according to the present invention; and D is the X-ray film.

Layers C and D are in intimate contact but are shown separately for clarity. The sensitivity of the system of the present example can be measured with one of the methods known to those skilled in the art, such as for instance an aluminum step wedge having 2 mm. steps.

The sensitivity, thus measured, has been compared with that obtained by exposing the above defined con-

ventional system to the same X-ray source. The results, thus obtained, show a sensitivity increase of the system by a factor of at least 6.

#### EXAMPLE 2

Example 1 was performed again, with the exception that a Gevaert Scopic 1 S Film of Gevaert-Agfa N.V. was used instead of the XV 5 Film of 3M Italia S.p.A. The electroluminescent compound used for the preparation of the image intensifier was the EL-CB4 type of Levy West. Also in this case, the sensitivity resulted to be 6 times higher than the sensitivity obtained with the conventional system described in Example 1.

We claim:

1. An X-ray image intensifying device for radiography comprising the following sequential layers:
  - A. A supporting film base,
  - B. A conducting layer which is at least partially transparent to X-rays,
  - C. An X-ray sensitive photoconductive layer,
  - D. A light opaque layer,
  - E. An electroluminescent layer comprising an electroluminescent compound dispersed in a binder,
  - F. An at least partially light-transparent electrically conducting layer, and
  - G. A protective layer whose thickness is such that the resolving power loss is not greater than 20 percent lower than that of the same element without any protective layer.
2. The X-ray image intensifying device of claim 1 wherein the thickness of said protective layer is not more than 50 microns.
3. A device for radiography comprising a light-sensitive recording element positioned in close contact with the intensifying device of claim 1.
4. The image intensifier of claim 1 having a wavelength emission maximum longer than 500 nm, combined with an X-ray film containing a sensitizer imparting a sensitization maximum substantially in the same emission range of the image intensifier.
5. The image intensifier in claim 1 combined with an X-ray film particularly sensitive to those wavelengths emitted by the said intensifier.
6. The X-ray image intensifying device of claim 1 wherein the supporting base is also a conducting layer at least partially transparent to X-rays.
7. An X-ray image intensifying device for radiography comprising the following sequential layers:
  - A. A supporting base, at least 90 percent transparent to X-rays, having a thickness no greater than about 300 microns,
  - B. An electrically conductive layer which is at least 90 percent transmissive of 20 - 150 kV X-rays,
  - C. An X-ray sensitive photoconductive layer the resistance of which varies according to the incident X-ray intensity and which resistance varies by at least a factor of 10 when irradiated by X-rays produced by a tungsten target X-ray tube operated at 40 kV and 1 mA at a distance of 20 cm, the radiation from the said tube being emitted through a 0.040 inch thick beryllium window with a 5 mm. focal spot, the said electron conductive layer being not greater than 200 microns in thickness,
  - D. A light opaque layer having an impedance lower than that of the electroluminescent layer,
  - E. An electroluminescent layer having a dielectric constant of at least 5 and having an impedance

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lower than that of the non-irradiated photoconductive layer, but not less than 10 percent of the impedance of said non-irradiated photoconductive layer,

F. An electrically conducting layer which is at least 50 percent transmissive to light at wavelengths between 500 and 550 mm, and

G. A protective layer whose thickness is such that the resolving power loss is not more than 20 percent lower than that of the same element without any protective layer.

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8. The X-ray image intensifying device of claim 2 wherein the thickness of said protective layer is not more than 50 microns.

9. The X-ray intensifying devices of claim 8 wherein the light opaque layer has an impedance lower than that of the electroluminescent layer by at least a factor of 10.

10. The X-ray image intensifying device of claim 7 wherein the supporting base (A) is also the electrically conductive layer (B).

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