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Bates, Jr. et al.

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[54] **IMAGE INTENSIFIER PLATE AND METHOD AND COMPOSITIONS FOR MANUFACTURING SAME**

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[52] **U.S. Cl.** ..... **156/306**, 117/33.5 R, 117/46 CA, 117/124 B, 156/67, 156/295, 161/4, 161/165, 161/192, 161/213, 161/410, 161/225, 250/460, 250/483, 250/488

[51] **Int. Cl.** **C09j 5/00**, B32b 31/12

[58] **Field of Search** ..... 161/4, 165, 1, 2, 410, 161/192, 225, 213; 96/82; 156/67, 306, 295; 250/458, 460, 483, 488; 117/33.5 R, 33.5 C, 33.5 CP, 41 CA, 124 B; 252/301.4 R

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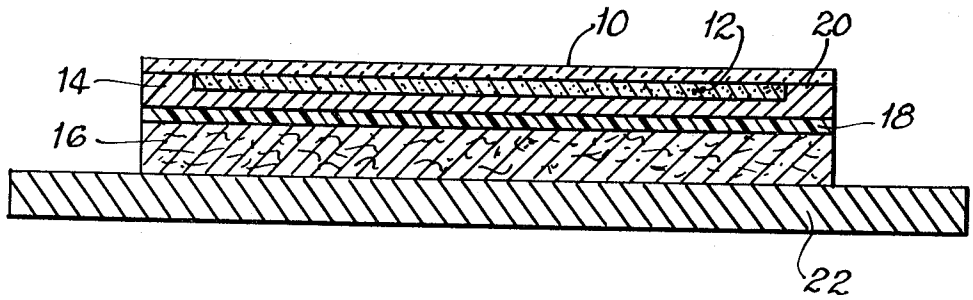
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Assistant Examiner—Ellis P. Robinson

[57] **ABSTRACT**

An image intensifier plate for X-ray radiology formed of a transparent moisture impermeable substrate having a thickness within the range of 2–8 mils, a phosphor layer present as a coating on one surface of the substrate formed of activated particles, such as alkali metal halides and preferably, cesium iodide having an average dimension within the range of 2–10 microns and a protective moisture impermeable coating on the surface of the phosphor layer and in which the cesium iodide or other activated particles are eutectically bonded to a pack density greater than 70 percent.

11 Claims, 2 Drawing Figures



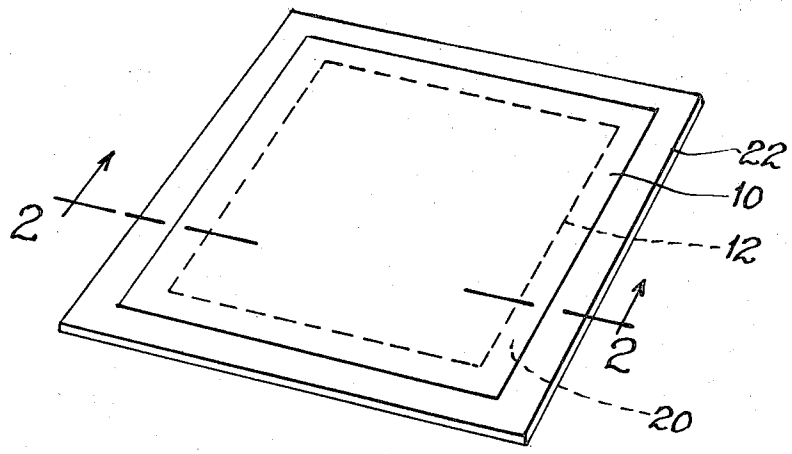


FIG. 1

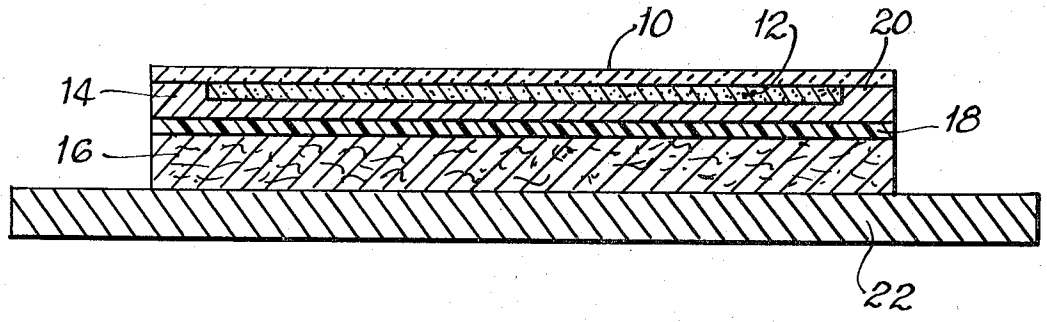


FIG. 2

IMAGE INTENSIFIER PLATE AND METHOD AND COMPOSITIONS FOR MANUFACTURING SAME

This invention relates to a new and improved X-ray intensifier screen of the type which may be used in medical diagnostic and industrial radiology and it relates further to the method for the preparation of same.

X-ray intensifier screens of the type described and their uses are well known in radiology and X-ray technology. For the most part, such intensifier screens have been made of phosphor layers of calcium tungstate in a binder of plastic material. By reason of the high index of refraction of the calcium tungstate and the composition and character of the intensifier layer, the calcium tungstate cannot be packed in the layer beyond a density of about 60 percent.

It is desirable and it is an object of this invention to produce and to provide a method and composition for producing X-ray intensifier screens of the type described which are more efficient as a converter of X-rays in the region of energy of most diagnostic significance, in which the intensifier materials can be packed in the phosphor layer to densities greater than 60 percent and preferably to densities greater than 70 percent whereby use can be made of still thinner layers for greater resolution, strength and flexibility, and which has a lower index of refraction so that the converted rays can get out more easily.

An intensifier screen embodying the improvements of the type described can be produced with cesium iodide as the phosphor material, preferably complexed with sodium or other alkali metal but in which thallium or other rare earths can be used as the dope or complexing component. Other phosphor materials, such as alkali metal halides, can be used instead of or in admixture with cesium iodide, although best results are secured with sodium activated cesium iodide.

Some of the problems in the use of cesium iodide, CsI (Na) or CsI (Tl), arise from the high hydroscopic nature of the material and the ability of moisture to attack the intensifier to the extent that it quickly loses its activity. As a result, it is essential to protect the intensifier material from moisture, as well as to provide means for activation of the intensifier material in position of use in the layer.

These and other objects and advantages of this invention will hereinafter appear and for purposes of illustration, but not of limitation, an embodiment of the invention is shown in the accompanying drawing in which.

FIG. **1** is a perspective view of an intensifier plate embodying the features of this invention, and

FIG. **2** is an elevational cross sectional view taken along the line **2—2** of FIG. **1.**

The invention will be described with reference to the preparation of an X-ray intensifier screen embodying the features of this invention, as represented by FIGS. **1** and **2** of the drawing, but it will be understood that the examples are given herein by way of illustration and not by way of limitation, as will be set forth during the description.

EXAMPLE 1

Preparation of Substrate

A sheet of alkali metal zinc borosilicate glass of minimum commercial thickness (6–10 mils) is etched in a solution of ammonium fluoride (1 part by weight), hydrofluoric acid (2parts by weight), in water (10 parts by weight) uniformly to reduce the thickness of the sheet of glass to about 3 mils. The etched glass sheet is then cleaned with aqueous medium to remove residuals which might remain on the surface and to prepare the glass for surface coating with the phosphor composition.

An alkali metal zinc borosilicate glass is not essential since glass sheets of other composition can be used. While it is preferred to make use of a glass substrate in the form of a glass sheet **10,** which is reduced in thickness to about 3 mils, the thickness of the glass substrate can be within the range of 2–6 mils and preferably within the range of 2.5–4 mils. A sheet of glass having a thickness less than 2 mils is considered to be too flexible and incapable of the desired support, while a glass substrate in excess of 6 mils is too thick and tends to provide a blurred image. The foregoing etch solution for the glass is given by way of illustration as a formulation that produces an etched glass sheet of uniform thickness and clarity, but it will be understood that other etch solutions, well known to the skilled in the art, can be used.

The described etching process of Example 1 is employed for the purpose of reducing the substrate **10** to the desired thickness. Such etching process for reduction of sheet thickness is not necessary where a sheet or film of glass of the desired thickness is made available directly, as by rolling or by stretching, generally referred to as attenuation, of molten strips of glass. By such latter techniques, endless strips of glass in roll form can be made available for subsequent treatment and sheeting of the treated sheets to the dimensions desired for the intensifier plate.

Instead of glass, the substrate of the specified sheet thickness can be made available of other materials which, at the sheet thickness described, are transparent and moisture impervious, such as plastics having the necessary moisture barrier properties and sufficient hardness to resist scratching or crazing, as represented by the polycarbonates.

EXAMPLE 2

Preparation of Cesium Iodide Particles

100 parts by weight of cesium iodide, plus 6 parts by weight of sodium iodide, are dissolved in an amount of water (about 60 ml) to provide a saturated solution at a temperature of about 100°C. To the saturated solution, colloidal silica, such as CAB-O-SIL, marketed by Cabot Corporation of Boston, Massachusetts, or colloidal silica marketed by Harshaw Chemical Company, is added with mixing in an amount within the range of 0.5 to 2 percent by weight of the cesium iodide.

In a separate container, 250 ml isopropyl alcohol is cooled to a temperature within the range of −50°C to −85°C and preferably within the range of −65°C to −75°C.

The CsI (Na) is precipitated during the admixture of the cold alcohol and the cesium iodide — sodium iodide solution, with vigorous agitation. In the preferred practice, the solution of cesium iodide — sodium iodide is poured, with agitation, into the cold isopropyl alcohol. The formed precipitate is separated, as by filtration or centrifugation and washed with one or more increments of isopropyl alcohol and then dried, preferably in an air circulating oven at a temperature within

the range of 35°C to 70°C and preferably at a temperature of approximately 50°C for at least 1 hour.

Instead of isopropyl alcohol, other alcohols in which the cesium iodide is insoluble can be used, as long as the solution remains fluid at temperatures as low as −85°C. The amount of alcohol and the temperature of the alcohol prior to mixing is not critical, as long as an amount is employed at a temperature sufficient to effect reduction of the composite mixture to a temperature not above room temperature and preferably to a temperature below room temperature for precipitation of the CsI (Na) of the desired particle size.

The size of the crystals that are precipitated will depend greatly on the temperature of the solution at the time that the crystals are formed. It is desirable to make use of crystals having an average dimension of less than 10 microns and preferably within the range of 2–8 microns since such small crystals, within the narrow range described, produce phosphor layers of the desired greater density and corresponding improvement in resolution. Use of crystals having an average particle size larger than 10 microns results in loss of resolution by comparison with the preferred range.

Temperature control of the isopropyl alcohol to within the preferred range of −65°C to −75°C is effective to precipitate cesium iodide crystals within the optimum range of 2–8 microns.

To produce thallium activated cesium iodide intensifier, thallium iodide is substituted in equivalent amounts for the sodium iodide in Example 2.

EXAMPLE 3

Annealing the Intensifier Particles

Scintillation depends somewhat on the position of the sodium ion in the formed compound. Such positioning is achieved by heat treatment of the CsI (Na) precipitate. Heat treatment can be achieved while the CsI (Na) is in the crystalline form, produced by Example 2, or, as in the preferred practice of this invention, it can be achieved by heat treatment of the layer of crystals after it has been deposited on the substrate.

Heat treatment to provide the desired activation of the cesium iodide is a time-temperature relationship. For example, the desired heat treatment of the separated crystals can be achieved by heating at a temperature of 350°C for at least 3 hours and preferably for a time within the range of three to twelve hours but it is preferred to accelerate heat treatment by heating to a temperature above 500°C but below the melting point for the cesium iodide crystals for a time within the range of 1½ to 2 hours, and preferably at a temperature of about 525°C to 550°C for about 1½ hours.

In the event that the heat treatment is carried out on the crystals, prepared in accordance with Example 2, it is desirable to protect the heat treated crystals by packaging in a hermetcially sealed container which is free of moisture and preferably provided with a dry inert atmosphere such as nitrogen gas.

EXAMPLE 4

Coating Composition

Vehicle **1**

5 parts by volume butyl carbitol
1 part by volume isopropyl alcohol
1 percent by weight polyvinyl acetate
0.1 to 0.2 percent by weight surface active agent

Vehicle **2**

5 parts by volume butyl carbitol
1 part by volume isopropyl alcohol
10 percent by volume, based upon the total volume of butyl carbitol and isopropyl alcohol, of "Silbond" — marketed by Stauffer Chemical Company

0.1 to 0.2 percent by weight surface active agent

100 grams of the sodium activated cesium iodide of Example 2 is suspended in 65 to 100 ml. (preferably about 70 ml) of vehicle 1 or vehicle 2. The cesium iodide is preferably worked into the vehicle, as by means of a higher speed mixer or by milling with a ball mill, roll mill or the like to produce a stable suspension.

The suspension is applied as a thin coating onto the glass substrate **10,** as by means of brush coating, but it has been found that packing densities of the cesium iodide in the phosphor layer to 70 percent and greater can be achieved if the suspension is applied to form the thin coating on the substrate by spray coating, such as in an aerosol type coating, using Freon as the carrier. A spray coating system of the type described, using Freon as the carrier, is marketed by Zicon Corporation under the name of Zicon Vapor-Carrier Precision-Coating Application System. With the spray coating technique, a phosphor layer **12,** having the preferred thickness within the range of 3–5 mils, can be produced with a pack density of 70–80 percent.

Instead of butyl carbitol, other carbitols and esters can be used. Similarly, other alcohols such as butyl alcohol, isobutyl alcohol and the like lower and intermediate alcohols can be substituted in whole or in part for the isopropyl alcohol in the coating composition.

As the surface active agent, use can be made of an anionic or non-ionic interface modifier, such as described by Harris et al. in "Oil and Soap," Vol. XVIII, No. 9, September 1941, p. 179, and represented by Triton X-100, marketed by Rohm & Haas. The surface active agent is not essential but its presence in the vehicle enables the use of a coating composition containing higher concentrations of the sodium activated cesium iodide crystals whereby higher pack densities can be obtained in the phosphor coating. For this purpose, the vehicle can be formulated to contain 0.01 to 1.0 percent by weight surface active agent with an amount within the range of 0.05 to 0.2 percent by weight being preferred.

"Silbond" is a 40 percent solution of ethyl silicate. Other hydrophobic silicate binders, such as ethyl silicate, can be used in an amount within the range of 3 to 10 percent by weight of the cesium iodide in the coating suspension.

Since the pack density of the sodium activated cesium iodide, CsI (Na) or CsI (Tl) will depend somewhat on the amount of vehicle in the coating composition, it is desirable to make use of as little vehicle as practical, consistent with the ability to effect the desired coating of uniform thickness on the substrate. The ratio of cesium iodide to vehicle can be varied, depending somewhat upon the particle size of the cesium iodide crystals, with the large particles enabling the formulation of suspension with higher solids content. Thus the ratio of cesium iodide to vehicle can be varied within the range of 100 grams of CsI (Na) or CsI (Tl) to 50–500 ml of vehicle and preferably 100 grams of the cesium iodide per 65–100 ml of vehicle.

While it is preferred to coat the substrate with the suspension to provide a coating thickness within the range of 0.003 to 0.005 inch, use can be made of phospher layers having a thickness within the range of 0.002 to 0.008 inch (2–8 mils.). Layers having a thickness much less than 0.002 inch lose luminescence while resolution decreases when the thickness extends beyond 0.008 inch.

EXAMPLE 5

Heat Treatment of Phosphor Layer

The coated substrate is heated in an air circulating oven to a temperature sufficient to effect removal, as by evaporation or preferably by "burning out" of the organic components and to set the binder. To effect removal of the isopropyl alcohol and the butyl carbitol, it is sufficient if the coated substrate is heated to a temperature above 350°C for a matter of from 1 to 3 hours, but it is desirable to subject the substrate to heat treatment at higher temperatures, such as up to 500°–550°C for from ½ to 1 hour or more to effect more rapid removal of the organic materials and to set the binder.

In the event that the cesium iodide (Na) or (Tl) has not been heat treated in accordance with Example 3, or in the event that reactivation of the cesium iodide is desirable, heat treatment to effect the desired orientation of the elements can be combined with the step of heat treatment for removal of the organic materials and to set the binder. For this purpose, the coated substrate is heated for gradual increase in temperature to within the range of 500°–550°C for a period of time which will range from ½ to 1 hour at 550°C to 2 hours at 500°C and preferably for 1½ to 2 hours at a temperature of about 520°C.

At such temperature, the particles become interbonded, to form a cohesive phosphor layer **12** which becomes strongly bonded to the glass substrate. There is reason to believe that, at such temperature, a eutectic is formed, as between the silica components introduced by the colloidal silica and/or the ethyl silicate, by which the interbonded relationship is established. In any event, it appears that sintering takes place during heat treatment at temperatures in excess of 350°C whereby a strong and permanent bonded relationship is established between the particles in the phosphor layer and between the phosphor layer and the glass substrate.

EXAMPLE 6

Plate Assembly

The coated substrate is assembled onto a reflective backing or support which is adapted also hermetically to seal the phosphor layer. In the illustrated modification of this invention, use is made of a composite laminate formed of an inner layer **14** of reflective aluminum, an outer layer **16** of paper, and an intermediate layer **18** of polyethylene, with the composite sheet laminate being dimensioned to extend beyond the portion of the glass substrate **10** covered with the phosphor coating **12** to overlap the border **20** of uncoated glass substrate which extends all around the phosphor layer **12.** In the preferred practice of the invention, the sealing sheet will be dimensioned to correspond with the glass substrate to which it is bonded throughout the entire area with the reflective aluminum surface adjacent the phosphor layer. Thus the laminate will be bonded to the phosphor coating throughout the area of the coating while the portions beyond the coating will be bonded directly to the glass border of the substrate hermetically to seal the edges of the phosphor layer as well as the entire area thereof.

In order to protect the phospor layer, it is desirable to make use of an aluminum layer which is free of pinholes and, for this purpose, it is desirable to make use of an aluminum layer having a thickness of at least 0.0007 inch. Instead of aluminum, use can be made of other sheet material, such as glass, plastics or other metal or foil which is moisture impervious and which is preferably provided with a reflective surface, such as a white pigmented background or the like.

While the thickness of polyethylene layer and paper backing is not critical, it is desirable to avoid excessive thickness of materials making up the assembly. Thus a paper backing of 0.015 inch and a polyethylene film of 0.0008 inch to 0.01 inch can be used in forming the laminate.

It will be apparent that such sealing and backing member need not be a laminate of the type described but use can instead be made of a metal layer alone, a plastic layer alone or a glass layer alone, preferably with reflective surfaces, or use can be made of such moisture impervious films laminated onto a metal, plastic, glass or paper backing or various combinations thereof as described.

As the bonding adhesive, use can be made of conventional adhesives which are capable of providing a strong and permanent bonded relationship between the sealing layer and the exposed portions of the substrate, such for example as a GPC-35 adhesive, marketed by the Guardian Packaging Corporation.

EXAMPLE 7

Though not essential, an intensifier plate of greater utility can be produced when the assembly of Example 6 is mounted on a rigid support preferably characterized by low X-ray absorption, such as a rigid metal plate **22,** as represented by an aluminum plate having a thickness within the range of 0.01 to 0.05 inch, or a plastic sheet, as represented by a molded sheet of phenol formaldehyde (Bakelite) thereon having a thickness of 1/64 to ⅛ inch.

For protection of the plate from destruction by impact, it is desirable to make use of a backing plate on which the assembly is mounted in which the backing plate is dimensioned to be greater than that of the assembly so as to extend beyond the edges thereof.

By way of modification, the surface of the glass substrate can be converted from a hydrophilic surface to one that is hydrophobic before depositing the phosphor layer, by treatment of the surface with an organo silicon compound in the form of asilane or polysiloxane. This will prevent the formation of a water film which otherwise forms and tenaciously adheres to the glass surface and it will provide a more receptive base for adherence of the phosphor layer whereby a more stable intensifier plate will be formed with greater utility.

The intensifier plate is capable of mounting in a frame separate and apart from the X-ray film so that the plate with the mounting is capable of repeated use with only the replacement of film for exposure. The separate mounting of the plate in the frame provides protection which enables the frame and plate to be employed in high speed automated systems for X-ray analysis of rapidly changing processes.

Aside from the improved X-ray utilization and conversion efficiency that is obtained by the intensifier plates of this invention, the plate is capable of increased utilization from the standpoint of the number of exposures that can be made therewith and the expanded usage that can be made thereof in X-ray radiology.

It will be understood that changes may be made in the details of formulation and construction without departing from the spirit of the invention, especially as defined in the following claims.

We claim:

1. In the method of producing an image intensifier plate comprising the steps of coating a transparent, moisture impermeable substrate formed of glass or plastic having a thickness within the range of 2–8 mils with activated cesium iodide particles having an average particle size within the range of 2–10 microns to a pack density greater than 70 percent, heating the coated substrate to a temperature above 350°C but below the fusion temperature for the particles to burn out organic components from the coating and set the binder, and sealing the coating with a moisture impermeable layer on the side opposite the substrate in which the moisture impermeable layer is selected from the group consisting of a metal, glass and plastic.

2. The method as claimed in claim **1** in which the activated particles of cesium iodide are activated with sodium iodide CsI(Na) or thallium iodide CsI(Tl).

3. The method as claimed in claim **2** in which the CsI(Na) and CsI(Tl) of the desired particle size are prepared by dissolving cesium iodide in water to form a substantially saturated solution plus a small amount of sodium or thallium halide, admixing the solution with agitation with an alcohol in which the cesium iodide is insoluble and which has been precooled to a temperature within the range of −50°C to −85°C to precipitate the CsI(Na) or CsI(Tl).

4. The method as claimed in claim **3** in which the alcohol is isopropyl alcohol.

5. The method as claimed in claim **3** in which the precipitated particles are annealed by heating to a temperature above 350°C but below the fusion temperature for the particles.

6. The method as claimed in claim **5** in which the particles are heated to a temperature within the range of 525°–550°C.

7. The method as claimed in claim **3** in which the cesium iodide solution includes colloidal silica in an amount within the range of 0.5 to 2 percent by weight of the cesium iodide.

8. The method as claimed in claim **1** in which the heating step includes heating the coating to a temperature above 500°C but below the fusion temperature of the activated particles, if the activated particles have not previously been subjected to an annealing step.

9. The method as claimed in claim **1** in which the sealing layer is a sheet of aluminum which is pin-hole free.

10. The method as claimed in claim **1** in which the sealing layer includes a reflective surface on the side adjacent the coating.

11. The method as claimed in claim **1** in which the coating of activated cesium iodide is applied to the substrate by spraying.

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