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(54) **X-ray intensifying screens**

(57) An x-ray intensifying screen comprises a support having a luminescent composition comprising an isotropic phosphor and a polymer having an index of refraction within 0.02 of that of said phosphor over at least 80 percent of the emission spectrum of said phosphor, said support having an index of refraction up to or equal to 0.05 units higher than that of said phosphor and having a reflection optical density of at least

1.7 to light emitted by said phosphor. A preferred luminescent composition comprises $KI:Tl$, $RbI:Tl$ at $BaSrFCl:Eu$ mixed with two monomers such as 1 naphthylmethacrylate, $S(1\text{-naphthylmethyl})$ thioacrylate, 1-bromo-2-naphthylacrylate, and benzyl methacrylate, coated on black anodised Al and polymerised in situ. The ratio of monomers is adjusted to give the desired refractive index. Other phosphors, polymers and supports are specified together with the preparation of the monomers and polymers.

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SPECIFICATION

X-ray intensifying screens, their preparation and fluorescent compositions

This invention relates to transparent x-ray intensifying screens and their preparation, and to fluorescent compositions comprising an isotropic phosphor transparent to light emitted by said phosphor and a polymeric binder.

Transparent x-ray screens comprising alkali halide, alkaline earth halide, metal sulphide, and metal selenide phosphors have been prepared by various methods. These transparent screens have been shown to be desirable, because they make more efficient use of impinging x-ray radiation than thick conventional scattering screens which "waste" a material amount of the radiation in diffusion of the light emitter near the back of the screen and internal absorption. Thick transparent screens having a decreased number of reflections permit this light to reach the front surface of the screen with minimal deflection and to form a sharper image on the photographic film in contact with the screen. A greater proportion of the x-ray energy absorbed by the phosphor and converted to light is utilized in producing images without loss of sharpness.

Thin transparent screens, prepared by vapour-deposition and containing only a phosphor, have also been made and exhibit lower speeds than scattering screens with equal phosphor coverage. Further, lacking a protective binder, these transparent screens are fragile and highly susceptible to physical damage. Thicker screens have been made by hot pressing but other defects in their manufacture render them expensive to prepare.

U.S. Patent 3,023,313, discloses the use of a polymeric binder with a refractive index as close to that of an alkali metal halide phosphor as possible in order to produce x-ray intensifying screens with improved speed. However, because of substantial differences between the refractive index of selected binders and the refractive index of the phosphor, reflecting pigments must be added to the mixture to prevent "blurring of the image" and improve resolution. Thus, these screens are not truly transparent to light, and some decrease in utilization of absorbed x-rays is observed. The screens comprise a support preferably having a highly reflective base coating.

Swank, *Applied Optics*, 12, 1865—1870 (1973) describes the theoretical calculation of modulation transfer function (MTF), related to resolving power, of x-ray intensifying screens comprising transparent phosphors and a black backing. Swank discloses that although the MTF is enhanced when a black backing is used, 50% of the exposing radiation is absorbed by the backing. Thus, the speed of the x-ray intensifying screen is reduced.

Gasper, *J. Opt. Soc. Am.*, 63, 714—720 (1973) describes the computation of theoretical efficiencies and MTFs of various screen-receiver systems, and reports that if a dark antihalation undercoat is applied to the back surface of a transparent screen, the MTF is only slightly improved. If, on the other hand, the back surface is made perfectly reflecting, there is degradation of MTF, but the efficiency of the screen is advantageously doubled, as is shown in Figure 8 of Gasper.

Experimental verification of the Gasper calculations is provided by measuring the MTF of a transparent hot-pressed zinc sulphide screen coated with a dyed gelatin undercoat. Excellent agreement was found between the measured and computed MTFs. Gasper concludes that attempts to improve the MTF of a transparent screen result in an undesirable loss of efficiency. Given a choice between slight increases in MTF coupled with undesirable losses in efficiency (with an absorbing undercoat), and great increases in efficiency coupled with only slightly lower MTFs (reflective undercoat), the high efficiency screen with a reflective undercoat is clearly preferred by Gasper.

It is seen that transparent x-ray intensifying screens providing high resolution, while maintaining speed and efficiency, and which are resistant to physical damage and are easily and economically manufactured, are extremely desirable.

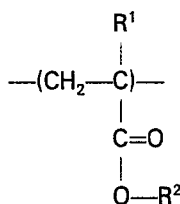
The invention provides an x-ray intensifying screen comprising a support having thereon a fluorescent composition comprising at least one substantially isotropic phosphor which is excited by x-rays and substantially transparent to light emitted by said phosphor in a polymer having an index of refraction within 0.02 of the index of refraction of said phosphor over at least 80 percent of the emission spectrum of said phosphor, and wherein said support has an index of refraction up to or equal to 0.05 units higher than the index of refraction of said phosphor and a reflection optical density of at least 1.7 to light emitted by said phosphor.

Preferably, the screen comprises from 50 to 90 percent by weight of the phosphor and from 10 to 50 percent by weight of the polymer.

Preferably, an x-ray intensifying screen according to this invention comprises a support having thereon a fluorescent composition comprising:

- a) from 50 to 90 percent by weight of a substantially isotropic phosphor which is excited by x-rays and substantially transparent to light emitted by said phosphor; and
- b) from 10 to 50 percent by weight of a polymer, wherein said polymer has an index of refraction within 0.02 of the index of refraction of said phosphor over at least 80 percent of the emission spectrum of said phosphor, said polymer comprising:
 - i) from 5 to 100 mole percent of a polymerized copolymerizable ethylenically unsaturated

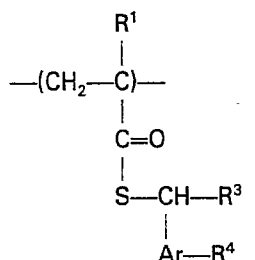
monomer, preferably from 5 to 100 mole percent of recurring units having the formula:



wherein

- 5 R¹ is H or alkyl; and
 R² is alkyl, cycloalkyl, aryl, aralkyl or aryl substituted with alkyl, alkoxy, or heterocyclyl; and 5

ii) from 0 to 95 mole percent of recurring units having the formula:



wherein:

- 10 Ar is arylene;
 R¹ is H or alkyl; 10
 R³ is H, alkyl, aryl, or aralkyl; and

 R⁴ is H, alkyl, alkoxy, amino, halogen, sulphide, sulphoxide, sulphonate or heterocyclyl; said support having an index of refraction equal to or up to 0.05 units higher than the index of refraction of said phosphor and having a reflection optical density of at least 1.7 to light emitted by said phosphor.

- 15 The invention also provides a process for making an x-ray intensifying screen of the invention comprising the steps of: 15

a) coating a mixture comprising:

- i) a substantially isotropic phosphor which is excited by x-rays and substantially transparent to light emitted by said phosphor; and
 ii) at least one copolymerizable monomer or mixture of monomers, said monomer or mixture of monomers, when polymerized, having an index of refraction within 0.02 of the index of refraction of said phosphor over at least 80 percent of the emission spectrum of said phosphor, 20

- on a support having an index of refraction equal to or up to 0.05 units higher than the index of refraction of said phosphor and having a reflection optical density of at least 1.7 to light emitted by said phosphor; and 25

b) polymerizing said mixture coated on said support to produce a polymer comprising recurring units of said monomer or monomer mixture.

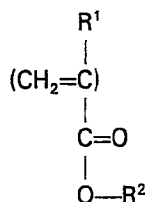
- Preferably, the mixture comprises from 50 to 90 percent by weight of the phosphor and from 10 to 50 percent by weight of the monomer or monomer mixture. 30

 Preferably the process comprises the steps of:

A) coating a mixture comprising:

- i) from 50 to 90 percent by weight of a substantially isotropic phosphor which is excited by x-rays and substantially transparent to light emitted by said phosphor; and
 ii) from 10 to 50 percent by weight of a mixture of copolymerizable monomer comprising 35

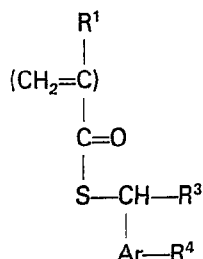
 a) from 5 to 100 mole percent of at least one copolymerizable ethylenically unsaturated monomer, preferably having the formula:



wherein

- 40 R¹ is H or alkyl; and
 R² is alkyl, cycloalkyl, aryl, aralkyl or aryl substituted with alkyl, alkoxy, or heterocyclyl; and 40

b) from 0 to 95 mole percent of at least one copolymerizable monomer having the formula:



wherein

Ar is arylene;
 5 R¹ is H or alkyl; 5
 R³ is H, alkyl, aryl, or aralkyl; and

R⁴ is H, alkyl, alkoxy, amino, halogen, sulphide, sulphoxide, sulphonate or heterocyclyl; said
 mixture, when polymerized, having an index of refraction within 0.02 of the index of refraction of said
 phosphor over at least 80 percent of the emission spectrum of said phosphor,
 10 on a support having an index of refraction equal to or up to 0.05 units higher than the index of
 refraction of said phosphor and having a reflection optical density of at least 1.7 to light emitted by said
 phosphor; and 10

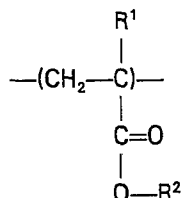
B) polymerizing said mixture coated on said support to produce a polymer.

15 In another aspect, the invention provides a fluorescent composition comprising: 15

a) from 50 to 90 percent by weight of a substantially isotropic phosphor which is excited by x-
 rays and substantially transparent to light emitted by said phosphor; and

b) from 10 to 50 percent by weight of a polymer having an index of refraction within 0.02 of the
 index of refraction of said phosphor over at least 80 percent of the emission spectrum of said
 phosphor, said polymer comprising:

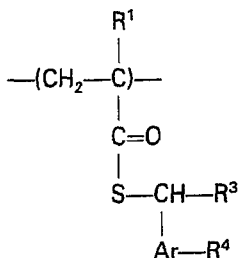
20 i) from 5 to 99 mole percent of recurring units having the formula: 20



wherein:

R¹ is H or alkyl; and
 25 R² is alkyl, cycloalkyl, aryl, aralkyl or aryl substituted with alkyl, alkoxy, or heterocyclyl; and 25

ii) from 1 to 95 mole percent of recurring units having the formula:



wherein:

Ar is arylene;
 30 R¹ is H or alkyl; 30
 R³ is H, alkyl, aryl, or aralkyl; and
 R⁴ is H, alkyl, alkoxy, amino, halogen, sulphide, sulphoxide, sulphonate or heterocyclyl.

Any substantially isotropic phosphor which is excited by x-rays and substantially transparent to
 the light emitted by the excited phosphor may be used in preparing the fluorescent composition. The
 35 term "substantially isotropic phosphor" is used herein to mean a crystalline phosphor having 35
 substantially the same optical properties in all directions of the crystal, and that the crystalline
 phosphor is substantially free from defects, such as cracks and inclusions, which cause scattering of

light. Useful phosphors include activated alkali metal halides, such as KCl:Sb, CsBr:Tl, KI:Tl, KBr:Tl, KCl:Tl, RbCl:Tl, RbBr:Tl and RbI:Tl; alkaline earth halides such as BaF₂ and BaFCl; activated alkaline earth halides such as CaF₂:Eu, SrCl₂:Sm, SrF₂:Eu, BaFCl:Eu, SrF₂:Sm; activated metal silicates such as BaSiO₃:Eu, CaSiO₃:Mn and Zn₂SiO₄:Mn; mixed metal fluorides such as KCdF₃:Mn and CsCdF₃:Mn; metal sulphates such as lanthanide-activated metal sulphates such as BaSO₄:Sr, Eu, SrSO₄:Eu, BaSO₄:Eu, ZnSO₄:Mn and Cs₃SO₄:Ce; metal gallates such as ZnGa₂O₄:Mn; and phosphates such as lanthanide-activated phosphates such as Ba₂P₄O₇:Eu and Ca₃(PO₄)₂:Ce. Further examples of phosphors are described in U.S. Patent Nos. 4,100,101; 2,303,963; 3,163,610; 3,163,603 and 3,506,584 and in R. C. Pastor et al, Mat. Res. Bull., 15 469—475 (1980). Typical transparent phosphors include RbI:Tl; KI:Tl; BaFCl:Eu, Sr, Eu; BaSO₄:Sr, Eu; CsCdF₃:Mn; BaF₂; KCdF₃:Mn; and SrF₂. Preferred phosphors are RbI:Tl; KI:Tl; BaFCl:Eu, Sr, Eu; CsCdF₃:Mn; BaSO₄:Sr, Eu; and BaSO₄:Pb.

The above-described phosphors are prepared by any conventional method for preparing isotropic phosphors, such as by introducing the anions and cations which form the phosphor into a reaction solution, maintaining an excess of up to 1 molar of an anion or cation throughout the reaction mixture, preventing local excesses of cations or anions, and thus slowly growing crystals of the phosphor to at least 0.5 micron, as described in U.S. Patent No. 3,668,142. Other methods for preparing isotropic phosphors which are excited by x-rays and substantially transparent to the emitted light, include precipitation at elevated temperatures and super-atmospheric pressures as described in U.S. Patent No. 2,285,464; precipitation followed by firing, fusion, and grinding to the desired particle size; and ignition in the presence of a flux. The method of U.S. Patent 3,668,142 is the preferred method for preparing the isotropic phosphors.

The screens can be modified so that they are useful in the apparatus and methods for producing images that are described in U.S. Patent No. 3,859,527; German Patent No. 2,951,501; and German Patent No. 2,928,246. In this modification an essentially isotropic storage phosphor is coated in a binder on a support that has the characteristics described below. The phosphor is excited by a pattern of radiation of a first wavelength. The phosphor is then exposed to radiation of a second wavelength which causes the said storage medium to emit a third wavelength of radiation having an intensity pattern representative of the stored image. The binder used in making this screen matches the index of refraction of the phosphor at the second wavelength and the support for the screen is selected so that it does not reflect the radiation at the second wavelength. The index of refraction of the third wavelength is preferably selected so that it does not match that of the phosphor and the support of the screen may reflect the radiation at the third wavelength. Thus, the radiation at the third wavelength, which is emitted when the phosphor is irradiated at the second wavelength, is not trapped by total internal reflection or by the support, but escapes from the screen and is efficiently collected by a photomultiplier tube with appropriate optics or by other photosensors which respond efficiently to the radiation at the third wavelength. Screens of this type are particularly useful for radiography and other applications in which a pattern of high energy radiation is absorbed by the phosphor, then released by scanning the screen with a laser beam that has a wavelength equal to that where the index of refraction of the phosphor and binder are matched and where the support of the screen has minimum reflectance. Ideally, the beam from the laser follows the path of the high energy radiation so that the resolution of the image from the screen is determined by the dimensions of the laser beam. The light released from the phosphor by the laser is collected by an appropriate photosensor, amplified, and the signal displayed on a cathode ray tube or recorded on an image recording medium to form the image. Appropriate phosphors comprise the barium alkaline earth metal fluorohalides of German Patent No. 2,951,516, German Patent No. 2,928,244, and other storage phosphors which have indices of refraction less than 1.75 in the visible region of the spectrum. The phosphor crystals are optionally activated to obtain the desired speed by any conventional method of activation. One method is the addition of a solution of a small amount (0.05 percent by weight) of the activating ion in a solvent, such as isopropanol, to a vigorously stirred solution of the isotropic host in a solvent, such as water, at very low temperatures (−30 to +20°C), followed by collection of the precipitated activated phosphor.

The substantially isotropic phosphors used in the invention generally have crystalline morphologies which are cubic or substantially cubic. The substantially isotropic phosphors useful in the invention generally have crystal sizes in the range from 1 to 50 microns, with the size range from 10 to 20 microns being preferred.

The novel x-ray intensifying screen includes any polymer having an index of refraction within 0.02 of the index of refraction of the phosphor over at least 80 percent of the emission spectrum.

The selection of the polymer for the novel x-ray intensifying screen is dependent on the index of refraction of the selected substantially isotropic phosphor at its emission wavelength. The index of refraction of the phosphor is determined by measuring the transmission spectra of the phosphor mixed with a series of Cargille liquids, as described in "The Particle Atlas", McCrone, Draftz and Delly, Ann Arbor Science Publishers, Inc., 1967, and determining the wavelength at which the index of refraction of the phosphor and the liquid match. A phosphor dispersion curve is obtained by plotting the wavelengths of maximum transmission for the series on the family of Cargille dispersion curves published in "The Particle Atlas" referred to above. The phosphor dispersion curve thus obtained is

used directly to find the index of refraction required for the polymer of the novel transparent x-ray intensifying screen.

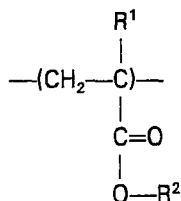
The polymer having the required index of refraction, i.e., an index of refraction within 0.02 of the refraction of the phosphor over at least 80 percent of its emission spectrum, comprises a single
 5 polymerized monomer, or the polymer comprises a mixture of two or more copolymerized monomers. 5
 Generally, the polymer comprises two copolymerized monomers, one of which, when polymerized,
 provides a polymer of higher index of refraction than required, and one which when polymerized,
 provides a lower index of refraction than required. The relative proportions of the two monomers are
 adjusted to provide the required refraction index. Calculated formulations are verified by measuring the
 10 transmission curve of a sample coating of the fluorescent composition of the novel intensifying screen 10
 on a spectrophotometer. A wavelength of maximum transmission which is less than that of the
 phosphor emission wavelength indicates that the refractive index of the polymeric binder is too low. A
 wavelength of maximum transmission which is greater than that of the phosphor emission wavelength
 indicates that the refractive index of the polymer is too high.

15 Monomers which, when polymerized, provide an index of refraction higher than that of the 15
 phosphor selected generally provide an index of refraction above 1.6, preferably in the range from 1.60
 to 1.75. Examples of monomers which, when polymerized, provide an index of refraction higher than
 that of the phosphor selected, and thus can be mixed with monomers having a lower index of refraction
 to become useful herein, include S-(1-naphthylmethyl) thioacrylate, naphthyl acrylate, 1-bromo-2-
 20 naphthylacrylate and naphthylmethacrylate. The preferred monomers is S-(1-naphthylmethyl)thio- 20
 acrylate.

Monomers which, when polymerized, provide an index of refraction lower than that of the
 phosphor generally provide an index of refraction of up to 1.60, preferably in the range from 1.40 to
 1.60. Examples of monomers which, when polymerized, provide an index of refraction lower than that
 25 of the phosphor selected and thus are useful when mixed with monomers having a higher index of 25
 refraction, include copolymerizable ethylenically unsaturated monomers such as acrylates and
 methacrylates such as methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate, butyl
 methacrylate and cyclohexyl methacrylate; vinyl esters, amides, nitriles, ketones, halides, ethers,
 olefins, and diolefins as exemplified by acrylonitrile, methacrylonitrile, styrene, α -methyl styrene,
 30 acrylamide, methacrylamide, vinyl chloride, methyl vinyl ketone, fumaric, maleic and itaconic esters, 2- 30
 chloroethylvinyl ether, dimethylaminoethyl methacrylate, 2-hydroxyethyl methacrylate, N-vinyl-
 succinamide, N-vinylphthalimide, N-vinylpyrrolidone, butadiene and ethylene. Preferred monomers are
 acrylates and methacrylates, with cyclohexyl methacrylate being most preferred.

The proportion in which the above-described monomers having high refractive indices and low
 35 refractive indices are mixed varies widely to provide a polymer having the required index of refraction. 35
 The polymerized monomer having low refractive index preferably comprises from 5 to 100 mole
 percent of the resulting polymer, with the range from 15 to 80 mole percent being most preferred. The
 polymerized monomer having high refractive index preferably comprises from 0 to 95 mole percent of
 the resulting polymer, with the range from 20 to 85 mole percent being most preferred.

40 The preferred polymer of the novel intensifying screen comprises from 5 to 100 mole percent of 40
 recurring units having the formula:

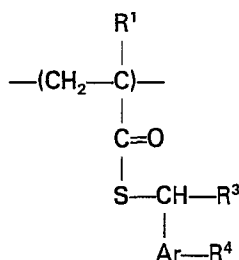


wherein:

45 R¹ is H or alkyl, preferably containing from 1 to 4 carbon atoms, such as methyl, ethyl, propyl, 45
 isopropyl, and butyl; and

R² is alkyl, preferably containing from 1 to 12 carbon atoms, such as methyl, ethyl, propyl and
 butyl; cycloalkyl, such as cyclopentyl and cyclohexyl; aryl preferably containing from 6 to 22 carbon
 atoms, such as phenyl, naphthyl, anthryl, perylenyl and acenaphthenyl; aralkyl, preferably containing
 from 5 to 20 carbon atoms, such as benzyl, phenylethyl, phenylpropyl, phenylbutyl, tolylbutyl and
 50 naphthylmethyl or aryl substituted with alkyl, preferably containing from 1 to 20 carbon atoms, such as 50
 methyl, ethyl, isopropyl and hexyl; alkoxy, preferably containing from 1 to 20 carbon atoms, such as
 methoxy and ethoxy; or a heterocyclic group, preferably a 5 to 7-membered ring which may be
 saturated, such as pyrrolidonyl, morpholinyl, piperidinyl, tetrahydrofuryl, dioxanyl and quinaldinyl, or
 unsaturated, such as pyrrolyl, isoxazolyl, imidazolyl, isothiazolyl, furazanyl and pyrazolinyl.

55 A preferred polymer of the novel x-ray intensifying screen further comprises from 0 to 95 mole 55
 percent of recurring units having the formula:



wherein:

Ar is arylene, preferably containing from 6 to 22 carbon atoms, such as phenylene, naphthylene, anthrylene; perylenylene and acenaphthenylene;

5 R¹ is H or alkyl as described for R¹

R³ is H, alkyl, aryl, or aralkyl as described for R² above; and

5

10 R⁴ is H, alkyl, preferably containing from 1 to 20 carbon atoms such as methyl, ethyl, isopropyl, and hexyl; alkoxy, preferably containing from 1 to 20 carbon atoms, such as methoxy and ethoxy; amino; halogen such as chloride and bromide; sulphide, sulphoxide; sulphonate; or a heterocyclic piperidinyl, tetrahydrofuryl, dioxanyl and quinaldinyl, or unsaturated, such as pyrrolyl, isoxazolyl, imidazolyl, isothiazolyl, furazanyl and pyrazolynyl.

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The monomers may be prepared by heating the appropriate mercaptan, such as 1-(naphthylmethyl)-mercaptan with 0—20% molar excess of bicycloheptene carbonyl chloride in an organic solvent, such as methylene chloride, at a temperature of 30—50°C, while an acid-accepting amine, such as diisopropylethylamine is slowly added to the mixture. The product is distilled under conditions favourable to the splitting off of cyclopentadiene, such as vacuum distillation at 200—300°C, resulting in a good yield of the monomers such as S-(1-naphthylmethyl)thioacrylate.

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20 The starting material, bicycloheptene carbonyl chloride, may be prepared by stirring cyclopentadiene with a 0—20% molar excess of acryloyl chloride and an organic solvent, such as methylene chloride, at a reduced temperature, such as -70 to -85°C, and allowing the mixture to warm slowly to room temperature. The acid chloride product may be isolated by distillation.

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A further description of the monomers may be found in our co-pending U.K. Patent Application No. (AND/238403) which has the same filing date as the present application and claims

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25 priority from U.S. Serial No. 238403. It is noted that throughout the specification and claims the terms "alkyl", "aryl" and "arylene" include substituted alkyl, aryl and arylene, such as methoxyethyl, chlorophenyl and bromonaphthyl.

25

Examples of polymers useful for the novel x-ray intensifying screen include:

30 poly[1-naphthyl methylmethacrylate-co-S-(1-naphthylmethyl)thioacrylate];

poly[1-naphthylmethyl methacrylate-co-1-bromo-2-naphthylacrylate];

30

poly[S-(1-naphthylmethyl)thioacrylate-co-benzyl methacrylate];

poly[S-(2-naphthylmethyl)thioacrylate-co-benzyl methacrylate]; and

poly[t-butyl methacrylate].

35 In an especially preferred embodiment, the polymer of the novel intensifying screen comprises from 5 to 100 mole percent of a polymerized co-polymerizable naphthylmethyl methacrylate

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monomer, and from 0 to 95 mole percent of a polymerized copolymerizable naphthylmethyl thioacrylate monomer. In a still further embodiment, the polymer comprises from 5 to 100 mole percent of polymerized 1-naphthylmethyl methacrylate and from 0 to 95 mole percent of polymerized S-(1-naphthylmethyl)thioacrylate.

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40 The x-ray intensifying screen which contains a substantially isotropic phosphor, which is excited by x-rays and substantially transparent to light emitted by the phosphor, and a polymeric binder carefully selected so as to match, within 0.02, the index of refraction of the phosphor, is highly transparent. The intensifying screens of the invention generally exhibit a mean free path for light scatter greater than one millimeter, preferably greater than 3 millimeters, for phosphor:binder ratios of 2.5 or larger. This highly transparent screen material allows the use of relatively thick screens which absorb more of the incident x-ray beam, and thus results in higher speed. Further, the increased absorption of x-rays decreases quantum mottle and allows improvement in overall image quality. Further still, the polymeric binder protects the fragile phosphors from physical damage.

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50 The support for the x-ray intensifying screen of the invention includes any material having an index of refraction equal to or up to 0.05 units higher than the index of refraction of the phosphor at its wavelength of maximum emission, and having a reflection optical density of at least 1.7 to light emitted by the phosphor. Suitable support materials include polymeric materials such as Lucite (poly(methylmethacrylate)); Elbite (tourmaline); Formica (poly(urea)formaldehyde resin); polyolefins such as polyethylene and polypropylene; polycarbonates; cellulose acetate; cellulose acetate butyrate; poly(ethylene terephthalate); glass such as Corning Fotoform glass having 80 percent of its area

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covered with holes 0.381 mm deep and 0.127 mm in diameter; and metal such as black anodized aluminium. "Lucite" and "Formica" are Registered Trade Marks.

The required reflection optical density of 1.7 to light emitted by the phosphor is provided by the use of support materials which are inherently darkly coloured materials which have been dyed or pigmented during manufacture to provide a uniform dark colour throughout, or materials which have undergone a surface treatment such as coating with a dye, pigment or dyed or pigmented material, anodizing in the case of metals, or a combination of the above surface treatments.

A preferred support having both the required optical density and the required index of refraction may be a conventional support material having a thin polymeric layer on the surface on which the fluorescent composition is to be applied. This thin polymeric layer comprises a polymer having an index of refraction equal to or up to 0.05 units higher than the index of refraction of the phosphor at its wavelength of maximum emission, and a finely divided pigment such as carbon in an amount sufficient to produce an optical density of 1.7 to light emitted by the phosphor.

The x-ray intensifying screen of the invention comprising a highly transparent screen material having high speed and a light-absorbing support having the required reflection optical density, gives high contrast and resolution. The use of a support which has the same or very slightly higher (up to 0.05 higher) index of refraction compared to that of the phosphor layer decreases the flare of the image and increases contrast.

The mixture comprising the fluorescent composition of the novel intensifying screen is preferably prepared by combining a substantially isotropic phosphor in the form of a free-flowing powder with a polymerizable monomer or mixture of copolymerizable monomers which, when polymerized, exhibit the required index of refraction. The useful phosphor to monomer ratio varies widely, but preferable ranges are from 50:50 to 90:10 by weight, and more preferably in the range from 70:30 to 80:20 by weight. Generally, the phosphor to monomer ratio is maximized, resulting in a honey-like, viscous mixture, which is capable of being poured. The resulting mixture is optionally degassed to remove trapped air bubbles.

The mixture optionally further comprises from 0.001 to 1.0 percent by weight, preferably from 0.1 to 0.5 percent by weight of a photoinitiator such as 4,4'-bis-chloromethyl benzophenone, benzoin methyl ether, or benzoyl peroxide. It is noted that further additional components are optionally included in the mixtures of the novel process. For example, resins, stabilizers, surface active agents and mould release agents serve to improve film formation, coating properties, adhesion of the mixture to the support, separability of the mixture from non-support materials, mechanical strength and chemical resistance.

The mixture is coated onto the support to a pre-determined thickness by techniques well-known in the art, such as roll coating, brush coating, solvent coating or slide-hopper coating. One method of coating the mixture comprises pouring the mixture onto the desired support, covering it with a cover sheet, such as a glass cover sheet, having appropriate spacers to produce a predetermined coating thickness, and spreading the mixture by applying pressure to the cover sheet to the limit of the spacers.

The optimum coating thickness of the phosphor-monomer mixture depends upon such factors as the use to which the coating will be put, the speed desired, the degree of image quality desired, the phosphor selected, the monomer or monomer mixture employed, the phosphor to monomer ratio and the nature of other components which may be present in the coating. Useful coating thicknesses for use in preparing x-ray intensifying screens are from 25 to 2500 microns, with coating thicknesses of from 400 to 1200 microns being preferred. The preferred coating coverage likewise varies widely between 110 and 5400 g/m², with the range from 540 to 2200 g/m² being preferred.

The coating, comprising a monomer or mixture of monomers and a phosphor, is preferably polymerized at a temperature of 20—30°C by irradiation with a may be used. Other methods of polymerization are similarly used. Such methods include thermal polymerization, polymerization by electron beam radiation and polymerization by high energy gamma irradiation.

After polymerization, the polymerized mixture is preferably cooled to room temperature or below, and any cover sheet used to spread the coated mixture and establish coating thickness is removed. In some cases, release is gently initiated, by inserting a blade between the support and the cover sheet to separate the support from the coated polymerized mixture, until Newton's rings are observed at the initiation site. The cover sheet is then lifted away, optionally further cooling the cover sheet briefly, for example, with powdered dry ice. Further cooling should be carefully undertaken however, as overcooling the cover sheet is likely to shatter the polymerized, coated screen mixture.

The resulting polymer has an index of refraction within 0.02 of the index of refraction of the phosphor over 80 percent of its emission spectrum, thus maintaining a high degree of transparency to the light emitted by the excited phosphor. The polymer protects the phosphor from mechanical damage, and, if hydrophobic, from damage caused by moisture.

The process of the invention thus provides a highly transparent x-ray intensifying screen having satisfactory speed, high contrast and high resolution. Further the process as described provides a relatively inexpensive and straightforward method of manufacturing high speed, high resolution x-ray intensifying screens without the addition of reflecting pigments.

The following preparations and examples are included for a further understanding of the invention.

Preparation 1

The phosphor RbI:TI (0.0004 mole TI/mole RbI) was prepared by adding a solution of 0.33 g of thallos acetate in 500 ml of isopropanol at a rate of 36 ml/min to a vigorously stirred solution of 636 g rubidium iodide in 460 g of water. The temperature of the isopropanol solution was maintained at -29°C , and the temperature of the aqueous solution was maintained at about 15°C . 200 g of the precipitated rubidium iodide phosphor was collected, carefully removing all of the supernatant isopropanol-water mixture, which was reserved for recovery of unprecipitated rubidium iodide to be used in subsequent preparations. (Any supernatant isopropanol-water mixture remaining with the precipitated phosphor can contaminate the precipitated phosphor with further precipitation of a phosphor differing in composition, and cause unwanted scattering of light in the resulting fluorescent composition). The precipitated thallium-activated RbI phosphor, being free of supernatant isopropanol-water mixture, was then washed twice with isopropanol in a high speed, food-processing blender, and the precipitate collected on glass filter paper after each washing. The phosphor was vacuum dried and bottled. The speed of the RbI:TI (0.0004) thus prepared was about equal to that of KI:TI, and speeds between 6 and 7 times greater than that of DuPont No. 501 commercial CaWO_4 phosphor were obtained in the x-ray powder test described in U.S. Patent No. 3,668,142, previously referred to herein.

Preparation 2

The phosphor KI:TI (0.0003 mole TI/mole KI) was prepared by adding a solution of 0.4 g thallos acetate in 1.6 litres of isopropanol at -29°C to a solution of 800 g potassium iodide in 600 g distilled water at 15°C with vigorous stirring. The temperature of the reaction solution was maintained at about 14°C . The rate of addition was 35 ml/min. The crystals of the precipitated phosphor were free from defects and had cubic morphology with crystal sizes in the range from 10—20 microns. The speed of the phosphor, measured after precipitation, washing, and drying, by the method used in U.S. 3,668,142 was about seven times that of commercial calcium tungstate.

Preparation 3

A mixture of 66 g of cyclopentadiene and 500 ml of methylene chloride was stirred with 90 g of acryloyl chloride at dry ice temperature (-78.5°C) and allowed to warm slowly to room temperature over 24 hours. The reaction product was then distilled. The resulting bicycloheptane carbonyl chloride thus obtained was allowed to react with 1-(naphthylmethyl)mercaptan and refluxed in methylene chloride (b.p. $40-41^{\circ}\text{C}$) while one equivalent of diisopropylethylamine was slowly added to the mixture. The product was vacuum distilled, using a 250°C oil bath, under which conditions the cyclopentadiene split off, giving S-(1-naphthylmethyl)thioacrylate in good yield. A thin-layer chromatograph (50:50 hexane/ether, silica gel) of the resulting product indicated an R_f value of 0.69 to 0.72.

Preparation 4

1-naphthylmethyl methacrylate was prepared by catalytic transesterification of an excess quantity of methyl methacrylate with the alcohol 1-naphthyl methanol. The by-product, methanol, was continuously removed by azeotropic distillation and/or use of molecular sieves, thus pulling the reversible reaction towards completion. When the reaction was essentially complete, the excess methyl methacrylate was removed by distillation at atmospheric pressure. A small amount (from 5 to 25%) of the unreacted higher alcohol 1-naphthyl methanol remained in the resulting 1-naphthylmethyl methacrylate.

Preparation 5

In an alternative synthesis of 1-naphthylmethyl methacrylate, 1-(chloromethyl)naphthalene is treated with one equivalent of potassium methacrylate in dimethyl sulphoxide. The potassium methacrylate employed is either previously isolated or formed *in situ* from potassium hydroxide and methacrylic acid. The reaction is continued at 70°C for 30 minutes. The resulting 1-naphthylmethyl methacrylate is isolated in 93—98% yield, virtually free from contaminants.

Preparation 6

Aluminium plates were anodized in 12—15 percent H_2SO_4 at 70°C and 12—14 amperes/ft². The porous deposit was treated with aluminium Black BK dye (a registered trademark of Sandoz Colors and Chemicals) and then sealed with hot water or nickel acetate solution. The resulting support exhibited an optical density of 2.34 when overcoated with a mixture of rubidium iodide and polymer having matched indexes of refraction. Although the index of refraction of anodized aluminium is not precisely known, it is thought to be about 1.76, which is less than 0.05 units higher than that of rubidium iodide at 425 nm, the region of maximum emission.

Example 1

A mixture of 100 g of thallium-activated potassium iodide phosphor (0.0003), as prepared in

Preparation 2, and 40 g of a 4:1 mixture of S-(1-naphthylmethyl)thioacrylate, as prepared in Preparation 3, and 1-naphthylmethyl methacrylate, as prepared in Preparation 4, containing 0.3 percent by weight of 4,4'-bis-chloromethyl benzophenone was degassed under vacuum. A portion of the mixture was photopolymerized between two glass sheets to form an unsupported screen, and released. The unsupported screen was placed in a Cary 17 spectrophotometer and its optical density was measured using an unsupported screen containing only photopolymerized polymer (lacking the phosphor) as a reference. The optical density of the unsupported screen was used to calculate the mean free path of light through the screen. The mean free path was calculated to be at least 2.3 mm.

Another portion of the mixture was coated at different thicknesses on a black anodized aluminium support as prepared in Preparation 6, and photopolymerized under glass cover sheets. Radiographs were made by exposing Lo-Dose film in contact with these experimental supported screens as back screens with 70 kVp x-rays. A control radiograph was made by likewise exposing Lo-Dose film in contact with a DuPont Par Speed Intensifying screen in order to obtain the relative speeds of the experimental screens. The difference in speed was calculated through the known density vs. log exposure curve for Lo-Dose film from the densities which resulted in the exposed and developed films. The following results were obtained.

	Screen Thickness (Microns)	Screen Coverage (g/m ²)	Relative Speed PAR=100*	10 Micron Lead Test Object Resolution	
20	405	655	175	3.15 l/mm	20
	750	1215	265	2.24—2.5	
	1115	1810	325	2.0	

*DuPont Par Speed Intensifying Screen

Example 2

A mixture of 35.5 g of the thallium-activated rubidium iodide phosphor (0.0004) as prepared in Preparation 1 and 10 g of a 60:40 mixture of 1-naphthylmethyl methacrylate and 1-bromo-2-naphthylacrylate containing 0.3 percent 4,4'-bis-chloromethyl benzophenone was spread on a black anodized aluminium support and covered with a glass sheet while being photopolymerized. When polymerization was complete, the glass sheet was released. The resulting transparent screen was 500 microns thick and had a coverage of 89 g of phosphor per square foot. Radiographs made with this screen as a back screen with Lo-Dose Film at 70 kVp gave a relative radiographic speed (calculated as in Example 1) of 255 compared to 285 for a DuPont Hi-Plus Screen with Lo-Dose Film. When a bone and bead test object was employed in the same comparison, better image quality was obtained with the transparent screen.

Example 3

A mixture of 250 g of the thallium-activated rubidium iodide and 65 g of a 3:1 mixture of 1-naphthylmethyl methacrylate and S-(1-naphthylmethyl)-thioacrylate which also contained 0.3 percent by weight of 4,4'-bis-chloromethyl benzophenone was degassed under vacuum and then coated three ways: (1) on black anodized aluminium support, (2) on reflective aluminium support on an optically flat surface, and (3) on no support (self-supporting film). All three coatings were of equal thickness and were photopolymerized. Radiographs were made with these three screens, together with the DuPont Hi-Plus screen, using Lo-Dose Film, 70 kVp x-rays and a 20 μ lead bar test object. The resolution of the radiographs was as follows:

45	Hi-Plus Screen	4.0 l/mm	
	Black Aluminium Support	4.0 l/mm	45
	Reflective Aluminium Support	1.8 l/mm	
	Unsupported	1.8 l/mm	

The resolution of the screen having a black support showed a dramatic increase both over the resolution of the screen having a reflective support and over that of the unsupported screen.

Example 4

A mixture of 136.8 g of thallium-activated rubidium iodide (0.0004), 40.0 g of a 3:1 mixture of 1-naphthylmethyl methacrylate containing up to 25 percent 1-naphthylmethanol and S-(1-naphthylmethyl) thioacrylate, and 0.3 percent by weight of 4,4'-bis-chloromethyl benzophenone was degassed under vacuum. The mixture was then coated on a support consisting of inlaid strips of black polished Formica, black anodized aluminium, black Corning Fotoform glass having 80 percent of its area covered with holes, 0.127 mm in diameter and 0.381 mm deep, and dark blue tourmaline in a matrix of black Lucite plastic. The mixture was spread evenly across the support so that the different types of support were coated with an equal thickness of the mixture. A glass cover sheet was placed on the

mixture, and the mixture was photopolymerized. The cover sheet was removed, and the reflection optical densities of the different areas were measured. A 70 kVp radiograph of a 10 micron lead bar resolution test object was made using the screen as a back screen with DuPont Lo-Dose film. The radiograph made using this transparent screen was compared with a control radiograph made with Lo-Dose film and using an opaque Hi-Plus screen. Radiographic speed was determined as in Example 1. The results obtained were as follows:

	<i>Support</i>	<i>Refractive Index nd</i>	<i>Reflection Optical Density</i>	<i>Radio-graphic Speed</i>	<i>Resolu-tion (l/mm)</i>	
10	Lucite	1.49	2.25	315	2.5—2.8	10
	Fotoform Glass	—	1.87	250	3.15	
	Tourmaline	1.64	2.57	250	3.15	
	Formica	1.65	2.17	245	3.15—3.55	
	Black Anodized Aluminium	1.76	2.34	245	3.55	
15	Hi-Plus Screen Control (opaque)	—	—	285	3.55	15

The results indicated that the optimum combination of speed and resolution were obtained when the fluorescent composition mixture was coated on a black anodized aluminium surface for the particular transparent phosphor-polymer combination selected. Further, the results showed that the transparent screen having a black anodized aluminium support exhibited resolution equal to and radiographic speed nearly equal to the conventional opaque control screen; however, the transparent screen of the invention displayed less quantum mottle than the conventional opaque screen.

Example 5

A mixture of 180 g of finely powdered $Ba_{.94}Sr_{.06}FCl:Eu$ (0.006) phosphor and 51 g of a blend of benzyl methacrylate and 1-naphthylmethyl methacrylate (approximately 50:50 by weight) was degassed under vacuum and spread on a black anodized aluminium support. A glass cover sheet was placed on top of the layer and the mixture was polymerized by irradiation with an ultraviolet lamp with substantial emission at 365 nm through the glass. After the glass was removed, the area of the layer and the weight were recorded. Coverage of the screen was calculated as 915 g/m² of phosphor. The mean free path for 380 nm radiation was measured spectrophotometrically as 304 microns.

The screen was used as a back screen with a 58 g/ft² $Gd_2O_2S:Tb$ (on a highly reflecting support) front screen to make 70 kVp radiographs of a standard "bone and bead" test object with Kodak X-Omat R x-ray film. The control for the image quality evaluations was made with both front and back $Gd_2O_2S:Tb$ screens. The speed of the control was 400 and the resolution was 2.24 l/mm. The transparent back screen gave a speed of 350 and a resolution of 2.24 l/mm. The mottle of both radiographs was judged about equal, but the sharpness and bead visibility were superior in the transparent screen radiograph.

Examples 1 to 5 above illustrate the invention.

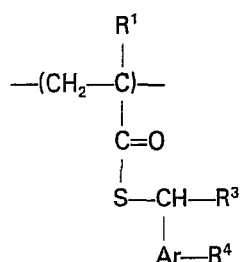
Claims

1. An x-ray intensifying screen comprising a support having thereon a fluorescent composition comprising at least one substantially isotropic phosphor which is excited by x-rays and substantially transparent to light emitted by said phosphor in a polymer having an index of refraction within 0.02 of the index of refraction of said phosphor over at least 80 percent of the emission spectrum of said phosphor, and wherein said support has an index of refraction up to or equal to 0.05 units higher than the index of refraction of said phosphor and a reflection optical density of at least 1.7 to light emitted by said phosphor.

2. A screen as claimed in Claim 1 comprising from 50 to 90 percent by weight of the phosphor and from 10 to 50 percent by weight of the polymer.

3. An x-ray intensifying screen comprising a support having thereon a fluorescent composition comprising:

- a) from 50 to 90 percent by weight of a substantially isotropic phosphor which is excited by x-rays and substantially transparent to the light emitted by said phosphor; and
- b) from 10 to 50 percent by weight of a polymer, wherein said polymer has an index of refraction within 0.02 of the index of refraction of said phosphor over at least 80 percent of the emission spectrum of the phosphor, said polymer comprising:
 - i) from 5 to 100 mole percent of a polymerized copolymerizable ethylenically unsaturated monomer; and
 - ii) from 0 to 95 mole percent of recurring units having the formula:



wherein:

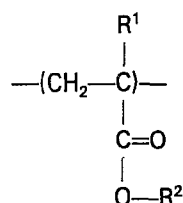
Ar is arylene;

R¹ is H or alkyl;

5 R² is H, alkyl, aryl, or aralkyl; and

R⁴ is H, alkyl, alkoxy, amino, halogen, sulphide, sulphoxide, sulphonate or heterocyclyl; said support having an index of refraction equal to or up to 0.05 units higher than the index of refraction of said phosphor, and having a reflection optical density of at least 1.7 to light emitted by said phosphor.

4. A screen as claimed in Claim 3 wherein the polymerized copolymerizable ethylenically unsaturated monomer of i) has recurring units having the formula: 10

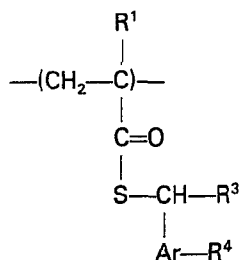


wherein:

R¹ is H or alkyl; and

R² is alkyl, cycloalkyl, aryl, aralkyl or aryl substituted with alkyl, alkoxy or heterocyclyl.

15 5. A screen as claimed in Claim 3 or Claim 4, wherein the recurring units of the formula: 15



are derived from a naphthylmethyl thioacrylate monomer.

6. A screen as claimed in Claim 3 or Claim 4, wherein said polymer comprises:

20 a) from 5 to 100 mole percent of recurring units derived from a naphthylmethyl methacrylate monomer; and

b) from 0 to 95 mole percent of recurring units derived from a naphthylmethyl thioacrylate monomer.

7. A screen as claimed in Claim 6, wherein said naphthylmethyl methacrylate monomer is 1-naphthylmethyl methacrylate and wherein said naphthylmethyl thioacrylate monomer is S-(1-naphthylmethyl)thioacrylate. 25

8. A screen as claimed in any one of the preceding claims wherein said phosphor is an alkali metal compound.

9. A screen as claimed in Claim 8 wherein said phosphor is RbI:Tl or KI:Tl.

10. A screen as claimed in any one of the preceding claims wherein said support comprises a black anodized aluminium surface. 30

11. A screen as claimed in Claim 1 substantially as hereinbefore described in any one of Examples 1 to 5.

12. A process for making an x-ray intensifying screen comprising the steps of:

A) coating a mixture comprising:

35 i) a substantially isotropic phosphor which is excited by x-rays and substantially transparent to light emitted by said phosphor; and

ii) at least one copolymerizable monomer or mixture of monomers, said monomer or mixture of monomers, when polymerized, having an index of refraction within .02 of the

index of refraction of said phosphor over at least 80 percent of the emission spectrum of said phosphor,

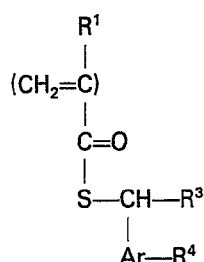
on a support having an index of refraction equal to or up to 0.05 units higher than the index of refraction of said phosphor and having a reflection optical density of at least 1.7 to light emitted by said phosphor; and

B) polymerizing said mixture coated on said support to produce a polymer comprising recurring units of said monomer or monomer mixture.

13. A process as claimed in Claim 12 wherein the mixture comprises from 50 to 90 percent by weight of the phosphor and from 10 to 50 percent by weight of the monomer or monomer mixture.

14. A process as claimed in Claim 12 or Claim 13 wherein the monomer or monomer mixture comprises:

- a) from 5 to 100 mole percent of at least one ethylenically unsaturated monomer, and
b) from 0 to 95 mole percent of at least one copolymerizable monomer having the formula:



15 wherein:

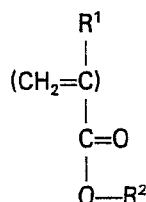
Ar is arylene;

R¹ is H or alkyl;

R³ is H, alkyl, aryl, or aralkyl; and

R⁴ is H, alkyl, alkoxy, amino, halogen, sulphide, sulphoxide, sulphonate or heterocyclyl.

15. A process as claimed in Claim 14 wherein the ethylenically unsaturated monomer of a) has the formula:



wherein:

R¹ is H or alkyl; and

R² is alkyl, cycloalkyl, aryl, aralkyl or aryl substituted with alkyl, alkoxy, or heterocyclyl.

16. A process as claimed in Claim 15 wherein the ethylenically unsaturated monomer of a) is a naphthylmethyl methacrylate monomer.

17. A process as claimed in any one of Claims 14 to 16 wherein the monomer of b) is a naphthylmethyl thioacrylate monomer.

18. A process as claimed in any one of Claims 12 to 17 wherein said mixture further comprises from .001 to 1.0 percent by weight of a photoinitiator.

19. A process as claimed in Claim 18 wherein said polymerization step (B) is effected by irradiation with near-ultraviolet light.

20. A process as claimed in Claim 12 substantially as hereinbefore described in any one of

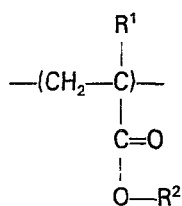
Examples 1 to 5.

21. A fluorescent composition comprising:

a) from 50 to 90 percent by weight of a substantially isotropic phosphor which is excited by x-rays and substantially transparent to light emitted by said phosphor; and

b) from 10 to 50 percent by weight of a polymer having an index of refraction within 0.02 of the index of refraction of said phosphor over at least 80 percent of the emission spectrum of said phosphor, said polymer comprising:

i) from 5 to 99 mole percent of recurring units having the formula:



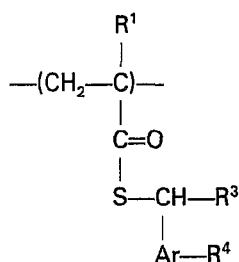
wherein:

R¹ is H or alkyl; and

R² is alkyl, cycloalkyl, aryl, aralkyl or aryl substituted with alkyl, alkoxy, or heterocyclyl; and

5 ii) from 1 to 95 mole percent of recurring units having the formula:

5



wherein:

Ar is arylene;

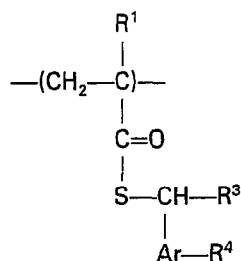
R¹ is H or alkyl;

10 R³ is H, alkyl, aryl, or aralkyl; and

R⁴ is H, alkyl, alkoxy, amino, halogen, sulphide, sulphoxide, sulphonate or heterocyclyl.

10

22. A fluorescent composition as claimed in Claim 1, wherein the recurring units of the formula:



are derived from a naphthylmethyl thioacrylate monomer.

15 23. A fluorescent composition as claimed in Claim 21, wherein said polymer comprises: 15

a) from 5 to 99 mole percent of recurring units derived from a naphthylmethyl methacrylate monomer; and

b) from 1 to 95 mole percent of recurring units derived from a naphthylmethyl thioacrylate monomer.

20 24. A fluorescent composition as claimed in Claim 21 substantially as hereinbefore described in 20 any one of Examples 1, 3 and 4.