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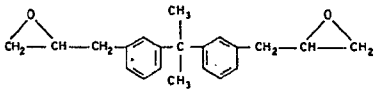
(71) Applicant
Ciba-Geigy A.G., CH-4002 Basel, Switzerland
(72) Inventors
Terence Richard John Bossomaier,
Peter Charles Sangway
(74) Agent
R. N. Matthews

(54) X-Ray Intensifying Screens

(57) Stabilization of X-ray intensifying screens against discoluration and hydrolysis of lanthanum or gadolinium oxyhalide phosphors is achieved by incorporating into the phosphor/binder formulation a compound containing free epoxy groups.

Suitable epoxy compounds include a substance with the formula:—



Other examples include gamma glycidoxy trimethoxy silane and dimethyl di(m-glycidoxy methyl phenyl)methane.

The oxyhalide may be activated by Tb, Tm or Yb and may be mixed with other phosphors. Plasticisers and organo-tin stabilisers for the formulation are given. Many binders are specified, preferably these should not react with the free epoxy groups.

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SPECIFICATION

X-Ray Intensifying Screens

This invention relates to phosphor screens for converting X-rays to visible or near visible radiation.

Screens which convert X-rays to visible or near visible radiation are of particular use in radiography in which patients are exposed to X-radiation which is then converted to light by a phosphor intensifying screen. The light emitted by the screen exposes an X-ray film which yields after development an X-ray picture of the exposed portion of the patient. In recent years it has been realised that patients should be exposed to as little X-radiation as possible because exposure to X-rays can cause organic damage in the tissues of the patient.

Recently great use been made of new lanthanum-oxy-halide phosphors in X-ray intensifying screens. These phosphors are more efficient than calcium tungstate which has been used in X-ray intensifying screens since 1896 and the use of such screens enables the exposure of the patient to X-rays to be considerably reduced. However it has been discovered that screens containing lanthanum-oxy-halide phosphors tend to discolour rapidly when in use and in particular when held in contact with an X-ray film, as often occurs in hospitals who like to keep their cassettes charged with unexposed film, ready for use.

Gadolinium-oxy-halides are similar to lanthanum-oxy-halides and whilst not much use has been made of these phosphors trials have shown that these phosphors offer much the same advantages as lanthanum-oxy-halide but also exhibit the same disadvantages.

In spite of intensive research into this discolouration defect the cause of it is not yet clearly known but it appears to be a complex reaction caused, in part at least, by the hydroscopic nature of the lanthanum-oxy-halide phosphors or gadolinium-oxy-halide phosphors, the nature of the binder and the presence of the X-ray film held in contact with the screen for a period of time. Such discolouration of screens containing these phosphors can reduce their effective speed to a quarter of the original speed and thus their advantage is lost.

Furthermore, under somewhat different conditions of use X-ray screens and in particular X-ray screens which contain lanthanum-oxyhalide or gadolinium-oxyhalide phosphors can lose speed due to a different defect which appears to involve only the phosphor. This is hydrolysis of the phosphor which is caused by water present in the phosphor layer due either to atmospheric moisture or aqueous cleaning fluid penetrating the protective layer of the screen. It is thought that quantities of halide or more surprisingly, the free halogen, released by hydrolysis may actually catalyse the discolouration of the binder or of compounds having migrated from the film.

However we have discovered a class of compounds which act to stabilise X-ray intensifying screens comprising lanthanum-oxy-halide phosphors or gadolinium-oxy-halide phosphors against discolouration and also against hydrolysis of the phosphor.

According to the present invention there is provided an X-ray intensifying screen which comprises in a fluorescent layer at least one lanthanum-oxy-halide phosphor of the general formula I:—

$$LaOX:Re \qquad I$$

where X is a halogen or mixture of halogens including Cl, Br, F.I. and Re is a rare earth activator or a mixture of rare earth activators and/or at least one gadolinium-oxy-halide of the general formula II:—

$$GaOX:Re \qquad II$$

where X and Re are as defined above and/or a mixed lanthanum-gadolinium-oxy-halide of the general formula III:—

$$GaLaOX:Re \qquad III$$

Where X and Re are as defined above, a binder, the phosphor or phosphors and as a stabiliser for the phosphor or phosphors a compound which has free epoxy groups.

Preferably in each formula X is bromine or chlorine.

Examples of suitable rare earth activating agents are thullium, ytterbium, terbium and cerium.

Examples of specific gadolinium-and-lanthanum-oxy-halides are:—

$$La_{(0.998)}OBr:Tm_{(0.002)}$$
$$La_{(0.999)}OBr:Tb_{(0.0008)}Yb_{(0.0002)}$$
$$Gd_{(0.998)}OCl:Tm_{(0.002)}$$

Other phosphors may also be present in the fluorescent layer for example barium fluoro-chloride, barium strontium sulphate and calcium tungstate.

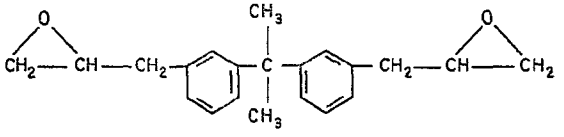
It is important that the stabiliser comprises free epoxy groups and does not cross-link with the binder thus losing its free epoxy groups.

Suitable binders for the phosphor are cellulose esters for example cellulose acetate, cellulose triacetate, cellulose acetate butyrate, cellulose nitrate, polyvinyl compounds for example polyvinyl chloride and polyvinyl butyral and copolymer of vinyl compounds, solvent-soluble polyesters and polycarbonates. Preferably acrylate and methacrylate compounds for example homo or co-polymers of ethyl acrylate, butyl acrylate, butyl methacrylate and methyl methacrylate are used as the binder.

Preferably as a high proportion of phosphor to binder as possible should be present in the fluorescent layer while ensuring that the fluorescent layer has adequate strength and does not crack after some usage. Suitably the proportion of phosphor to binder used in the fluorescent layer is from 40 phosphor to 1 of binder to 4 of phosphor to 1 of binder, the ratios being by weight.

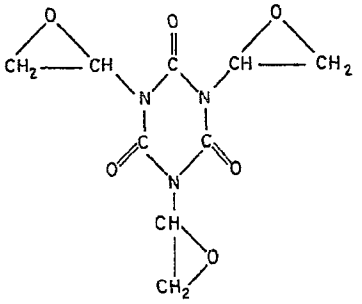
Many types of epoxy compounds can be used as the stabilising agent but preferably non-polymeric epoxy compounds are used. Most preferably the epoxy compounds should be non-volatile and soluble in organic solvents, for example ketones, aliphatic esters and aromatic hydrocarbons, to enable them to be incorporated in the fluorescent layer.

Examples of suitable epoxy compounds are glycidyl bisphenol compounds for example the compound of formula IV:—



IV

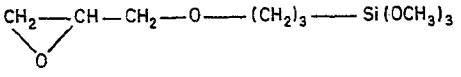
Other suitable epoxy compounds are glycidyl isocyanurates for example the compound of formula V:—



V

Other epoxy compounds which also help to plasticise the layer are of use for example epoxidised soya bean oil such as the commercially available plasticiser made by Röhm and Haas and marketed as Paraplex G62.

A particularly suitable class of epoxy compounds are epoxy silanes. An example of an epoxy silane is gammaglycidoxy trimethoxy silane which has the formula VI:—



VI

Epoxy silanes are of particular use as they can be reacted with the surface of the phosphor in the presence of moisture. In effect the silane functional group bonds to the surface of the phosphor leaving the free epoxy groups close to the surface of the phosphor.

X-ray intensifying screens usually comprise a self-supporting support base there being present thereon in order, a light reflecting layer or light absorbing layer (optional), a fluorescent layer and a protective layer. The light-reflecting layer (if present) usually comprises particles of a light reflecting substance e.g. baryta, calcium carbonate, magnesium carbonate, magnesium oxide or titanium dioxide in a polymeric binder. Alternatively a light reflecting support base containing for example one or more of the just-mentioned light-reflecting pigments may be used or the base may be a voided base containing many trapped air cavities, such bases being highly reflective. The light-absorbing layer if present usually comprises carbon black particles in a binder. In order to protect the surface of the fluorescent layer a protective layer which is usually a transparent polymeric substance is coated onto the fluorescent layer. If the self-supporting support used is transparent for instance if polyester is used it is not necessary for a light reflecting layer to be present between the base support and the fluorescent layer. In this case the light reflective layer (if used) may be present on the side of the base support distal to the fluorescent layer or separate light reflecting means may be used in conjunction with the intensifying screen.

In the X-ray intensifying screen of the present invention the fluorescent layer may comprise particles of a single phosphor or a mixture of phosphors.

The X-ray intensifying screen of the present invention may be prepared by dispersing the phosphor particles in a solution of a suitable binder. The phosphor dispersion is then coated on a suitable stable base and dried. The protective layer may then be coated on the dried phosphor layer.

A suitable coating weight of the phosphor or mixed phosphors in the fluorescent layer is from 2—20 g/dm^2. The prepared amount of epoxy compound in the fluorescent layer is from 0.1 to 1.5% by weight of the coating weight of phosphor and most preferably from 0.3 to 1.2%.

Suitable base materials are card, cellulose esters, for example cellulose triacetate, polyesters, for example polyethylene terephthalate and in particular so-called voided polyester as described in B.P. 1415686 and white pigmented polyester or cellulose triacetate.

Suitable reflective layers, which may be present between the usually opaque base and the fluorescent layer, are a layer containing titanium dioxide (or the other white pigments just mentioned) or a metallic layer for example a thin film of aluminium or silver evaporated on to the base.

The protective layer may be of any of the usual polymeric compounds employed for this purpose for example cellulose acetate, cellulose nitrate or polymethyl methacrylate

There may be present in the fluorescent layer a plasticiser for example triphenyl phosphate, tricresyl phosphate, dialkyl phthalates, dimethyl glycol phthalate alkyl adipates and polyester plasticisers. Also epoxidised soya bean oil may be used as a plasticiser as well as a stabiliser.

Another class of stabiliser which may be present in the fluorescent layer of the X-ray intensifying screen of the present invention is a dialkyl tin compound for example dibutyl tin dioctyl (thioglycollate).

There may be present in at least one of the phosphor layers, protective layers or light-reflecting layers acutance dyes or pigments which help to increase the sharpness of the image.

It is to be understood that a light-reflecting layer which comprises light reflective particles in a polymeric binder may be cast first on to the dimensionally stable support before the fluorescent layer is case on to this support. If the base support is transparent the fluorescent layer may be coated on to the other side of the support to the light reflecting layer. The preferred base is polyester and it is usually required that the polyester base is comparatively thick compared with a base used for photographic purposes that is to say the base used should be in the region of 0.025 cm.

The medical X-ray films used in the examples comprised a subbed polyethylene terephthalate base coated on each side with a layer of a gelatino silver iodobromide emulsion containing 1.6% iodine and having a silver coating weight of 38 mg/dm^2 and a gelatin coating weight of 40 mg/dm^2 on each side and also a gelatin supercoat having a coating weight of 12 mg/dm^2 on each emulsion layer. The silver halide crystals were heterodispersed polyhedral in habit.

The X-ray films used in the examples also contained the usual addenda such as sensitising agents, stabilising agents, polyethylene oxide compounds and optical sensitising dyes.

The following Examples will serve merely to illustrate the invention.

Example 1

Preparation of Stabilised Screen, A

100 g of a thulium activated lanthanum oxybromide phosphor, 5 g of cellulose acetate polymer and 0.3 g of the epoxy compound, monomeric diglycidyl ether of bis-phenol A are dispersed in 25 g of acetone, 4.5 g of ethyl acetate and 4.0 g of dimethyl phthalate. The suspension of phosphor particles in the organic solution of the polymeric binders and other additives is then milled in a ball-mill for 24 hours to achieve adequate dispersion of the phosphor. The dispersion is coated on to a subbed polyethylene terephthalate support layer and dried thoroughly to produce a coated weight of 500 g/m^2.

A 15% solution by weight of cellulose acetate in acetone is applied to this phosphor layer and dried thoroughly to produce a 25 μm thick continuous layer which protects the phosphor layer.

Preparation of Unstabilised Control Screen, B

Screen B is prepared exactly as screen A except that the epoxy compound is omitted from the formulation of the coating solution.

Test of Stability to Prolonged Contact with Film—Test I (Discolouration Test)

Screen A and screen B are placed together in a radiographic cassette with a sheet of a medical X-ray film in contact equally with screen A and screen B and the cassette is closed. The cassette used is of any type intended for containing intensifying screens and film in a light-tight container during exposure to X-rays and had been shown to withstand the conditions involved in this test without itself producing adverse effects on any intensifying screen contained within the cassette.

The cassette containing screens A and B in contact with the medical X-ray film is then placed within an incubator at a temperature of 52 °C and at a relative humidity of 66%. These conditions are maintained for twenty-one days but the X-ray film was changed for a new one every day. The following test for loss of radiographic sensitivity or speed was carried out every seven days.

Radiographic Speed Measurement

After incubation in contact with an X-ray film, screens A and B are removed from the incubation cassette and allowed to equilibrate to ambient conditions. The treated screens A and B are tested

together with an untreated control screen C which has been produced identically to screen B but has not been incubated or kept in contact with X-ray film. Screens A, B and C are placed in contact with a medical X-ray film and are irradiated with X-rays to produce a uniform fluorescent light exposure of the film by each screen in area it covers. The duration and intensity of the irradiation is adjusted to produce an optical transmission density (D_C) to visible light of 1.6 to 2.0 above fog for the area of the medical X-ray film in contact with screen C when the film has been developed and fixed in the recommended manner to produce a known contrast G in the region of density 1.0 to 2.0 above fog.

The transmission densities of the film areas exposed to screens A and B are also measured (D_A and D_B). The loss of radiographic sensitivity (ΔS) of the screens is then calculated as follows with negative figures indicating a speed loss,

$$\Delta S_A = \frac{(D_A - D_C)}{\bar{G}}, \quad \Delta S_B = \frac{(D_B - D_C)}{\bar{G}}$$

This parameter is equal to the $\log_{10}$ (change in fluorescent emission).

Radiographic speed losses after	*Incubation time (days)* 7	14	21	*Visual appearance after 21d treatment*
ΔS_A	−0.05	−0.10	−0.17	slightly stained, off-white
ΔS_B	−0.14	−0.29	−0.49	heavily stained, light brown

Example 2

Preparation of Stabilised Screen, E

100 g of a thulium activated lanthanum oxybromide phosphor, 18 g of a 23% by weight solution of cellulose nitrate in acetone, 4.2 g of dibutyl phthalate, 0.3 g of epoxy compound monomeric diglycidyl ether of bis-phenol A are milled together in a ball-mill for eight hours. A further 16 g acetone, 5 g ethyl acetate and 2 g ethyl lactate are added and the mixture is milled for a further sixteen hours to achieve adequate dispersion of the phosphor in the binder solution. This dispersion is coated on to a subbed polyethylene terephthalate substrate and dried thoroughly to produce a coated weight of 500 g/m².

A 15% solution by weight of cellulose acetate in acetone is applied to this phosphor layer and dried thoroughly to produce 25 μm thick continuous layer which protects the phosphor layer.

Preparation of Unstabilised Control Screen, F

Screen F is prepared exactly as screen E except that the epoxy compound omitted from the formulation of the coating solution.

Test of Stability to Prolonged Contact with Film—Test I (Discolouration Test)

The test described for Example 1 is carried out for screens E and F in the same manner as for A and B.

Radiographic Speed Measurement

The treated screens E and F are compared with an untreated control screen H which has been produced identically to F but has not been incubated or kept with film. The test is carried out in the same manner as the comparison of the radiographic speed of treated screens A and B to screen C as described in Example 1.

Radiographic speed losses after	*Incubation time (days)* 7	14	21	*Visual appearance after 21d treatment*
S_E	−0.11	−0.18	−0.24	stained, pale yellow
S_F	−0.13	−0.23	−0.30	stained, light straw colour

Example 3

Preparation of Stabilised Screen, J

100 g of thulium activated lanthanum oxybromide, 0.3 g of the epoxy compound tri-N-glycidyl isocyanurate, 28 g of a 30% by weight solution of a copolymer of butyl methacrylate and methyl methacrylate (10:1 parts by weight) in acetone are milled together in a ball-mill for eight hours. A further 18 g of acetone is then added and the mixture milled for 16 hours to achieve adequate dispersion and complete dissolution of the stabiliser. The dispersion is coated on to a subbed polyethylene terephthalate support layer and is dried thoroughly to give coatings of 500 g/m² layer weight.

A 15% solution by weight of cellulose acetate in acetone is applied to this phosphor layer and dried thoroughly to produce a 25 μm thick continuous layer which protects the phosphor layer.

Preparation of Unstabilised Control Screen, K

Screen K is prepared in an identical manner to screen J except that the epoxy compound is omitted from the formulation of the coating dispersion.

Test of Stability to Contact with Film—Test I (Discolouration Test)

The screens J and K are subjected to the same test I as is outlined for screen A and B in Example I.

Test of Stability to Moisture—Test II (Phosphor Hydrolysis Test)

Screens J^1 and K^1 prepared identically to J and K are placed together in an air-circulating temperature and humidity controlled oven which is set at 60°C and 95% relative humidity. The samples are tested for loss of radiographic sensitivity or speed every seven days.

Radiographic Speed Measurement

Screens, J, K, J^1 and K^1 are removed from their respective test conditions and are allowed to equilibrate to ambient conditions. The loss of radiographic sensitivity or speed of each screen relative to screen L is determined as in Example 1.

Incubation time—Test I

Loss of Radiographic Sensitivity after	*7d*	*14d*	*21d*	*28d*	*35d*	*Visual appearance after 35d*
ΔS_J	0	−0.04	−0.06	−0.17	−0.26	pale yellow
ΔS_K	−0.02	−0.05	−0.26	−0.43	−0.52	light brown

Incubation time—Test II

Loss of Radiographic Sensitivity after	*7d*	*14d*	*21d*	*28d*	*35d*
$\Delta S_J 1$	0	−0.04	0	−0.04	−0.04
$\Delta S_K 1$	0	0	0	>−1.5	>−1.5

Example 4

Preparation of Stabilised Screen, M

100 g of thulium activated lanthanum oxybromide, is conditioned at room temperature and 80% relative humidity for 5 hours. A solution of 0.3 g epoxy compound γ-glycidoxypropyl-trimethyoxy-silane (Union Carbide Silane A187) dissolved in 25 g of acetone is added and the suspension of phosphor is refluxed for 1 hour before distilling off the acetone from the phosphor under reduced pressure. This procedure causes the stabiliser to become absorbed to and in part chemically reacted with the surface.

28 g of a 30% by weight solution of a copolymer of butyl methacrylate and methyl methacrylate (10:1 parts by weight) in acetone is milled in a ball-mill together with the treated phosphor for 8 hours. A further 18 g of acetone is then added and the mixture milled for a further 16 hours to achieve adequate dispersion. The dispersion is coated on to a subbed polyethylene terephthalate support layer and is dried thoroughly to give coatings of 500 g/m² layer weight.

A 15% solution by weight of cellulose acetate in acetone is applied to this phosphor layer and dried thoroughly to produce a 25 μm thick continuous layer which protects the phosphor layer.

Preparation of Unstabilised Control Screen, N

Screen N is prepared in an identical manner to screen M except that the stabiliser treatment is not applied to the phosphor and no further stabiliser addition is made to the formulation.

Test of Stability to Contact with Film—Test I (Discolouration Test)

The screens M and N are subjected to the same test 1 as is outlined for screen A and B in Example 1.

Test of Stability to Moisture—Test II (Phosphor Hydrolysis Test)

Screens M^1 and N^1 prepared identically to M and N are subjected to the same test II as is outlined for screens J^1 and K^1 in Example 3.

Radiographic Speed Measurement

Screens M, N, M^1 and N^1 are removed from their respective test conditions and are allowed to equilibrate to ambient conditions. The screens are tested as described in Example 1 by comparison with screen P which has been prepared in the same manner as screens N and N^1 but which has not been exposed to either of the test conditions. The loss of radiographic sensitivity or speed or each screen relative to screen P is determined as in Example 1.

Incubation time—Test I

Loss of Radiographic Sensitivity after	*7d*	*14d*	*21d*	*28d*	*35d*	*Visual Appearance after 35d*
ΔS_M	0	−0.03	−0.10	−0.19	−0.26	light yellow
ΔS_N	−0.02	−0.05	−0.26	−0.43	−0.52	brownish

Incubation time—Test II

Loss of Radiographic Sensitivity after	*7d*	*14d*	*21d*	*28d*	*35d*
$\Delta S_M 1$	0	0	0	−0.01	−0.06
$\Delta S_N 1$	0	0	0	>−1.5	>−1.5

These Examples show that epoxy compounds serve to stabilise X-ray screens of the present invention against discolouration and against hydrolysis of the phosphor.

Claims

1. An X-ray intensifying screen which comprises in a fluorescent layer at least one lanthanum-oxy-halide phosphor of the general formula I:—

$$LaOX:Re \qquad I$$

where X is a halide and Re is a rare earth activator and/or at least one gadolinium-oxy-halide of the general formula II:—

$$GaOX:Re \qquad II$$

where X and Re are as defined above and/or a mixed lanthanum-gadolinium-oxy-halide of the general formula III:—

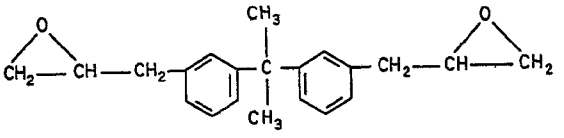
$$GaLaOX:Re \qquad III$$

where X and Re are as defined above, a binder for the phosphor or phosphors and as a stabiliser for the phosphor or phosphors a compound which comprises free epoxy groups.

2. An X-ray intensifying screen according to Claim 1 wherein the epoxy compound is a non-volatile compound which is soluble in organic solvents.

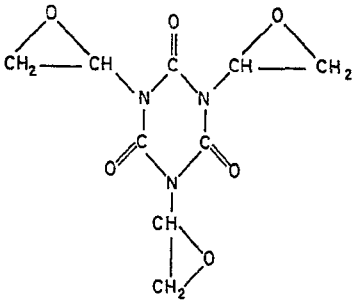
3. An X-ray intensifying screen according to Claim 2 wherein the epoxy compound is a glycidyl bisphenol resin.

4. An X-ray intensifying screen according to Claim 3 wherein the glycidyl bisphenol resin is the compound of the formula:—



5. An X-ray intensifying screen according to Claim 2 wherein the epoxy compound is a glycidyl isocyanurate.

6. An X-ray intensifying screen according to Claim 5 wherein the glycidyl isocyanurate is the compound of the formula:—



7. An X-ray intensifying screen according to claim 2 wherein the epoxy compound is an epoxidised soya bean oil.

8. An X-ray intensifying screen according to claim 2 wherein the epoxy compound is an epoxy silane.

9. An X-ray intensifying screen according to claim 8 wherein the epoxy silane is gammaglycidoxy trimethoxy silane.

10. An X-ray intensifying screen according to any one of claims 1—9 wherein the coating weight of the phosphor or mixed phosphors in the fluorescent layer is from 2 to 20/dm^2.

11. An X-ray intensifying screen according to claim 10 wherein amount of epoxy compound present in the fluorescent layer is from 0.1 to 1.5% by weight of the coating weight of the phosphor.

12. An X-ray intensifying screen according to claim 11 wherein the amount of epoxy compound present is from 0.3 to 1.2% by weight of the phosphor coating weight.

13. An X-ray intensifying screen according to any one of claims 1—12 which also comprises in the fluorescent layer a plasticiser.

14. An X-ray intensifying screen according to claim 13 wherein the plasticiser is triphenyl phosphate, tricresyl phosphate, a dialkyl polyester plasticiser or a dialkyl phthalate.

15. An X-ray intensifying screen according to any one of claims 1 to 14 which also comprises in the fluorescent layer a dialkyl tin compound.

16. An X-ray intensifying screen according to claim 15 wherein the dialkyl tin compound is dibutyl tin dioctyl (thioglycollate).

17. An X-ray intensifying screen which comprises a self-supporting support base, optionally a light-reflecting or light-absorbing layer, a fluorescent layer as defined in any one of claims 1 to 16 and a protective layer.

18. An X-ray intensifying screen according to claim 1 substantially as hereinbefore described with reference to the foregoing examples.

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