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(54) Phosphor-containing compositions and their use in X-ray photography.

(57) A composition of matter is described suitable for use as fluorescent screen in X-ray photography. The composition of matter comprises halide-containing phosphor particles and in order to improve the stability against moisture of these particles, a non-metal organic compound of the formula

$$R{-}X \text{ or } X{-}R'{-}X$$

wherein R and R' are organic groups preferably comprising at least 6 C-atoms, and not containing a reactive hydrogen as does X, and

X is a group containing a reactive hydrogen atom. The compound has a solubility of not more than 5 g in 100 ml of water at 15°C.

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Phosphor-containing compositions and their use in X-ray photography.

The present invention relates to phosphor-containing compositions of matter and more particularly to improved radiation conversion screens comprising halide containing phosphors and a process for producing such compositions and screens.

A first class of radiation conversion screens are X-ray intensifying screens containing fluorescent substances which are employed for absorbing X-rays and converting said rays into light to which silver halide of a photographic material is more sensitive than to direct X-ray exposure. These screens also called radiographic intensifying screens are customarily arranged inside a cassette, so that each side of a silver halide film, emulsion-coated on both sides, after the cassette has been closed is in intimate contact with an adjacent screen. In exposing the film the X-rays pass through one side of the cassette, through one entire intensifying (front) screen, through the light-sensitive silver halide film emulsion-coated on both sides and strike the fluorescent substances (phosphor particles) of the second (rear) intensifying screen. This causes both screens to fluoresce and to emit fluorescent light into at least the adjacent silver halide emulsion layer, which is inherently sensitive or spectrally sensitized to the light emitted by the screens.

A second class of radiation conversion screens are the so-called "fluoroscopic screens". Such screens have the function of producing a directly viewable image in correspondence with a pattern of penetrating radiation.

A third class of radiation conversion screens are fluorescent screens used in conjunction with a photocathode that emits photoelectrons under the influence of the fluorescent light of the screen. Such screens find application e.g. in image intensifier or image conversion tubes. In said tubes normally also a fluorescent screen is present which transforms the impact of fast moving electrons in light.

The commonly used X-ray intensifying screens comprise a support and a layer of fluorescent particles dispersed in a coherent film-forming macromolecular binder medium. Normally a protective coating is applied on top of the fluorescent layer to shield said layer from ambient influences e.g. moisture, air and mechanical abrasion.

Usually these protective coatings are composed of cellulose derivatives or synthetic polymers as described, e.g., in the United States Patent Specification 3,164,719 of Herbert Bauer, issued January 5, 1965.

Generally, layers comprising cellulosic derivatives are somewhat permeable to moisture and therefore more hydrophobic but also more costly synthetic polymers e.g. polymers containing fluorine atoms are applied to shield the phosphor layer from moisture.

The protection from moisture is required not only to prevent the fluorescent layer from staining but also to prevent water from adsorbing to the phosphor particles. Unlike calcium tungstate a broad class of halide containing phosphors is more or less hygroscopic and even small amounts of water reduce the fluorescent light-emitting power of the phosphor after a certain time so that the intensifying screen becomes useless in the long run.

So far one has only tried to remedy these defects as described in the United States Patent Specifications 3,164,719, already mentioned hereinbefore and 3,836,784 of Clayton W.Bates and Reichard A.Wallace, issued September 17, 1974, e.g. by mixing the phosphor particles with a hydrophobic polymeric binder or by coating the phosphor layer with a special protective highly water-impermeable layer. The hydrophobic polymers have to be used in rather large amounts, which reduces the light-emitting power of the screen.

The protective layers do not always have the desired mechanical strength and adherence to the phosphor layer and often require a high temperature coating procedure because of poor solubility of the polymers.

It is an object of the present invention to provide a composition of matter, which incorporates halide-containing phosphor particles, and wherein the phosphor particles are better protected against the influence of moisture and loss of fluorescence power.

It is more particularly an object of the present invention to provide better moisture-resistant radiation conversion screens incorporating particles of a halide-containing phosphor.

It is another object of the present invention to provide a process for preparing such screens having an improved stability with respect to their fluorescent light-emitting power.

In accordance with the present invention a composition of matter is provided, which composition includes halide-containing phosphor particles, which are admixed or combined in contact with or have reacted with at least one organic compound in such a way that the fluorescing power of the phosphor particles is less susceptible to the deleterious influence of humidity and wherein said organic compound is a non-metal organic compound corresponding to one of the following general formulae :

$$R\text{-}X \quad \text{and} \quad X\text{-}R^1\text{-}X$$

wherein :

R represents a monovalent organic group, preferably of at least 6 carbon atoms e.g. a hydrocarbon group,

R^1 represents a bivalent organic group, preferably of at least 6 carbon atoms e.g. a bivalent hydrocarbon group, with the proviso that these R and R^1 groups contain no reactive hydrogen such as contained in X, and

X represents a group containing reactive hydrogen, with which said compound by reacting with acetyl chloride is capable of splitting off chlorine therefrom in the form of hydrogen chloride in the circumstances of the test A below, e.g. mercapto, a primary or secondary amino group, carboxyl or hydroxyl, and wherein said compound at 15°C has a solubility of no more than 5 g in 100 ml of water.

In the formula $X\text{-}R^1\text{-}X$ the groups X may be the same or different chemical groups.

Test A

Stoichiometric amounts of acetyl chloride and of the organic compound to be examined are dissolved in anhydrous benzene and refluxed herein for 24 h in the presence of a stoichiometric amount of pyridine. The pyridinium chloride formed is separated from the cooled reactive mixture (20°C) by filtering or centrifuging. If pyridinium chloride crystals happen to be contained in the cooled reaction mixture, the compound meets the demand, viz. to be usable as a stabilising agent in the present invention.

If the organic compound to be examined is a primary or secondary amine, pyridine may be omitted from the reaction mixture and the chlorides corresponding with these amines form in the reaction.

Pyridine is normally used as hydrogen chloride scavenger in alcoholysis (see John H.Billman and Elisabeth S.Cleland in Methods of Synthesis in Organic Chemistry - Edward Brothers, Inc. Ann Arbor, Mich., U.S.A. (1951) 78. The use of pyridine as condensing agent in the preparation of acid anhydrides starting from a carboxylic acid chloride and a carboxylic acid has been described by Wagner and Zook, Synthetic Organic Chemistry - John Wiley and Sons (1953) 558.

Suitable non-metal organic compounds are non-metal organic compounds according to the above general formulae wherein X is a mercapto group, a primary or secondary amino group, a carboxyl group or a hydroxyl group, which is linked to an aliphatic group or aromatic nucleus.

The invention includes compositions of matter as hereinbefore defined wherein (an) organic compound(s) having said effect of stabilising the phosphor against the influence of moisture (is) are present at the surfaces of the phosphor particles. Such compound(s) is (are) applied to or deposited on the phosphor particles, or result from a reaction with such phosphor particles e.g. after it (they) has (have) been dissolved in a liquid medium and then brought in dissolved state into contact with the phosphor particles.

The invention includes compositions of matter as hereinbefore defined wherein the phosphor particles bearing one or more organic compounds affording protection against moisture are dispersed in a binder.

The invention also includes any intensifying screen consisting of or incorporating a layer formed wholly or in part of a composition of matter according to the invention as above defined, with or without any one or more of the optional features above or hereinafter referred to.

A preferred optional feature resides in the employment as agent for the purposes of reducing the adverse effects of moisture on the phosphor, of an organic compound or a combination of such compounds whose potential protective power satisfies a certain test. This test (hereafter called the "Standard Test") has been devised for the purpose of assessing the level of effectiveness of any selected organic compounds for phosphor protection in accordance with the invention and is as follows :

Standard test

(1) An X-ray image intensifying screen (Screen A) is prepared from the following composition :

terbium-activated lanthanum oxybromide phosphor	100 g
organic substance (compound or combination of organic compounds) to be tested	0.5 g
poly(vinyl-n-butyral) containing 12% by weight of non-acetalized vinyl alcohol units and having an average molecular weight of 50,000	12.5 g
ethylene glycol monomethyl ether	48 g

by ball-milling to reduce the particle size to 7 NS Hegman Fineness measured with a Hegman gage as specified in ASTM 1210, filtering the resulting dispersion, de-aerating it and applying the composition to a baryta-coated paper of 290 g per m2 at a coverage of 500 g/m2.

(2) A second X-ray image intensifying screen (screen B) is prepared in the same way as screen A except that the organic substance to be tested is omitted.

(3) Screen A is treated with moisture by applying onto the phosphor layer of the screen a wet circular piece of filter paper having a dry weight of 1.355 g, a dia-

meter of 15 cm and a water content of 3100 g, airtightly enclosing the screen A together with the applied filter paper in a polyethylene bag, keeping the bag for 64 h at 60°C in a ventilated cabinet and then removing the screen from the bag, removing the filter paper and drying the screen in air for 30 min at 80°C.

(4) The screens A and B (the former having been moisture-treated as above described) are subjected to an X-ray exposure while the phosphor layers are in contact with distinct areas of the same silver halide emulsion layer of a photographic material having a transparent emulsion layer support and the exposed photographic material is developed, the X-ray exposure and development being such that in the area of the emulsion layer which was in contact with screen B a spectral density of at least 1.00 above inherent fog is obtained; and the composition of the silver halide material and the development being such that gradually increasing exposures of the silver halide emulsion area in contact with screen B would give a silver image density versus log exposure curve having a gamma value (maximum gradient of the characteristic curve) of 3;

(5) the densities D_A and D_B obtained in the areas of the emulsion layer, which were exposed in contact with screens A and B are measured;

(6) the actual loss of fluorescent light-emitting power of the moisture-treated screen A is computed on the basis of the spectral densities D_A and D_B measured in step 5 above and the gamma value 3.

An organic compound or combination of organic compounds is regarded as satisfying the above Standard Test if the result of the determination in step 6 is that the fluorescent light-emitting power of screen A incorporating that compound or combination of compounds is at least

25% of that of the non-moisture treated screen B. In the most preferred embodiment of the invention the organic compound(s) affording the moisture protection is (are) such that when such compound(s) is (are) used in screen A in the Standard Test the fluorescent light-emitting power of screen A is at least 65% and most preferably at least 75% of that of the non-moisture treated screen B.

If screen B in the Standard Test were to be moisture-treated like screen A before being subjected to the exposure and development moisture treated screen B would show a fluorescent power of less than 10% relative to that of the non-moisture treated screen B.

As already indicated a mixture or combination of organic stabilizing compounds can be employed in any one screen composition.

Preferably use is made of at least one organic compound, which is colourless and upon reaction with the phosphor yields a colourless hydrophobic reaction product at the surface of the phosphor particles.

A first class of suitable organic compounds for use according to this invention comprises organic compounds wherein reactive hydrogen is directly bound to sulphur, e.g. in thiols. Preferably thiols are used that contain a hydrocarbon group of at least 6 carbon atoms. Such thiols including aliphatic as well as aromatic representatives have been described by Arthur I.Vogel, Textbook of Practical Organic Chemistry, Longmans 3rd ed. (1959) p. 502. Very good results are obtained with 1-n-dodecanethiol (laurylmercaptan).

A second class of organic compounds for use according to this invention are organic compounds that contain the reactive hydrogen in an amino group, i.e. primary or secondary amines. Preferably aliphatic primary or secondary amines are used that contain a hydrocarbon group of at least 8 carbon atoms. Especially good results are obtained with 1-n-dodecylamine (laurylamine).

A third class of organic compounds for use according to this invention are organic compounds that contain the reactive hydrogen in a carboxyl group. Preferably aliphatic carboxylic acids are used that contain a hydrocarbon group of at least 6 carbon atoms. Very good results are obtained with dodecanoic acid (lauric acid), but aliphatic carboxylic acids containing more than one carboxyl group are considered too, e.g. hexadecylenesuccinic acid and octadecylsuccinic acid.

A fourth class of organic compounds for use according to this invention are organic compounds that contain the reactive hydrogen in a hydroxyl group, which is preferably linked to a hydrocarbon group of at least 6 carbon atoms, such as e.g. in lauryl alcohol, p-t-amylphenol and isohexadecyl alcohol.

The hydrocarbon groups as referred to hereinbefore may comprise substituents that do not enhance the water-solubility of the organic compounds beyond the already given value. Suitable substituents rendering the compounds more hydrophobic are halogen atoms, e.g. fluorine, chlorine and bromine, such as e.g. in p-bromophenol and perfluorocaprylic acid.

The above mentioned organic compounds can be used in combination with metal-organic compounds that are described as stabilisers for halide-containing phosphor particles in the DE-OS 2,710,497.

To be mentioned in that respect are, e.g., organotin compounds and organobismuth compounds. Many of them are known as hydrogen chloride or hydrogen bromide scavenger or are known for the slowdown of thermal degradation of poly(vinyl chloride). Examples of such compounds are triphenylantimony, triphenylbismith and tetraphenyltin.

A preferred class of stabilizing organometal compounds for use in combination with the organic compounds according to the present invention corresponds to the following formula :

$$R_mSnX_{4-m}$$

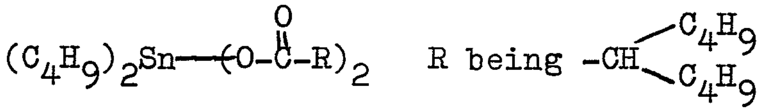
wherein :

R is a hydrocarbon group, e.g. an alkyl group,

X is one to three electronegative substituents e.g. oxygen in substituted form as in an alkoxy or in a carboxylate group, or is an electronegative sulphur substituent or a water-repelling sulphur-containing substituent linked through sulphur to the tin atom e.g. a thioether, a mercaptide or xanthate group, and

m is 1, 2, or 3, excluding X being three, two or one halogen atom(s) when m is 1, 2 or 3 respectively.

Examples of such compounds are dibutyltin bis(oxo-octylthioglycolate), also called dibutyltin S,S'-bis(n-octylmercapto acetate) and



$$(C_4H_9)_2Sn\text{—}(O\text{-}\overset{O}{\overset{\|}{C}}\text{-}R)_2 \quad R \text{ being } \text{-}CH\begin{smallmatrix}C_4H_9\\C_4H_9\end{smallmatrix}$$

described as stabilizing agent for polyvinyl chloride by D.H.Solomon, The Chemistry of Organic Film Formers, John Wiley & Sons, Inc. New York, p.175 to 177 (1967), and dibutyltin maleate, dibutyltin lauryl mercaptide, and di(n-octyl)-tin S,S'-bis(iso-octylmercapto acetate) described by Kirk-Othmer, Encyclopaedia of Chemical Technology, 2nd compl. revised edition, Vol. 21, p.390 (1965) and in J.Polymer Sci. Part A, Vol. 2 (1964) 1801-1813.

A composition of matter of the present invention comprises halide-containing phosphor particles, preferably inorganic halide-containing phosphor particles, by admixture combined with (a) said organic stabilizing substance(s) optionally in a binder medium.

In one process for preparing a composition of matter according to the present invention the halide-containing phosphor particles are allowed to come in intimate contact with the organic stabilizing substance(s) in an organic liquid medium wherein said substance(s) dissolve and thus treated particles are separated out and dried.

In one process for preparing a radiation conversion screen according to the present invention the halide-containing phosphor particles are dispersed in an organic liquid medium in the presence of (a) dissolved binding agent(s) and at least one dissolved organic stabilizing substance. According to one embodiment the dispersing proceeds in a ball-mill.

Preferably the organic stabilizing substance(s) is (are) combined by admixture with the halide-containing phosphor particles in a selected phosphor binder layer combination in an amount sufficient to maintain the fluorescent light-emitting power of the layer in a moisture treatment as defined above for screen (A) at a level of at least 25% and preferably at a level of at least 75% of the level before said treatment.

The amount of organic stabilizing substance or mixture of stabilizing substances suitable for a practically useful increase in stability against moisture of the applied halide-containing phosphor particles can be determined by simple tests.

Effective amounts of organic stabilizers, e.g. with regard to lanthanum oxybromide phosphors, are in the range of 0.05 to 10 g per 100 g of phosphor. More hygroscopic phosphors such as cesium iodide phosphors may be used in conjunction with higher amounts of stabilizer(s).

In the production of a radiation conversion screen according to the present invention the dispersion may be coated and dried on a permanent support, e.g. a cardboard or resin sheet, or coated on a temporary support to form a self-supporting sheet later on. The solvent(s) used in the preparation of the coating composition is (are) normally evaporated under reduced pressure. An ultrasonic treatment can be applied to improve the packing density and to perform the de-aeration of the phosphor-binder combination. Before the optional application of a protective coating the phosphor-binder layer may be calendered to improve the packing density (i.e. the number of grams of phosphor per cm^3 of dry coating).

Self-supporting screens of this invention can also be prepared by means of "hot-pressing", excluding the use of solvent(s) in the manufacture of the screens.

To provide high X-ray efficiency it is preferably that a minimum amount of binder be employed in the fluorescent layer. However, the less binding agent the more brittle the layer, so that a compromise has to be made. The thicker the fluorescent layer of a screen, the higher its intensification, but the image sharpness is decreased accordingly so that a balance between speed and definition has to be sought. Suitable binders for use in the preparation of the fluorescent layers are, e.g., a cellulose acetate butyrate, polyalkyl (meth)acrylates, e.g. polymethyl methacrylate, a polyvinyl-n-butyral, a copoly(vinyl acetate/vinyl chloride) and a copoly(acrylonitrile/butadiene/styrene) or a copoly(vinyl chloride/vinyl acetate/vinyl alcohol) or mixtures thereof. The preferred binders are halogen-free polymers or copolymers.

Optionally, a light-reflecting layer is provided between the fluorescent layer and its support to enhance the exposure of the silver halide emulsion material.

To the phosphor-containing layer a protective coating may be applied preferably having a thickness in the range of 5 to 25 µm and being composed of any film-forming polymeric material that is photographically inert towards a silver halide emulsion layer.

Polymeric materials suitable for that purpose include, e.g., cellulose derivatives e.g. cellulose nitrate, cellulose triacetate, cellulose acetate propionate, cellulose acetate butyrate, polyamides, polystyrene, polyvinyl acetate, polyvinyl chloride, silicone resins, poly (acrylic ester) and poly(methacrylic ester) resins, fluorinated hydrocarbon resins, and mixtures of the foregoing materials. Representative examples of various individual members of these binder materials include the following resinous materials : poly(methyl methacrylate), poly(n-butyl methacrylate), poly(isobutyl methacrylate), copolymers of n-butyl methacrylate and isobutyl methacrylate, copolymers of vinylidene fluoride and hexafluoropropylene, copolymers of vinylidene fluoride and trifluorochloroethylene, copolymers of vinylidene fluoride and tetrafluoroethylene, terpolymers of vinylidene fluoride, hexafluoropropylene and tetrafluoroethylene, and poly(vinylidene fluoride).

According to a special embodiment the outer face of the screen intended for contact with the photographic silver halide emulsion material contains a solid particulate material that has a static friction coefficient (μ) at room temperature (20°C) of less than 0.50 on steel.

Antistatic substances may be applied to the screen to reduce the risk of electrical potential differences resulting in sparking. For example, the screens are treated with the "ANTI-STAT" 6 spray, which leaves on odourless transparent antistatic deposit. ANTI-STAT is a trade name of Braun Laboratories Div. Barrett Chemical Co. Inc., Philadelphia, Pa., U.S.A.

At least a part of the halide-containing phosphor particles in the present composition of matter are preferably halide-containing rare-earth metal compounds, in which the host metal of the phosphor is a rare-earth metal and the activator consists of one or more other rare-earth metals. For example, these phosphors contain yttrium, gadolinium, lanthanum, or cerium as a host metal and at least one of the metals of the group of terbium, europium, dysprosium, thulium, samarium and ytterbium as activator metal.

Preferred phosphors of this class correspond to one of the following general formulae :

$$La_{(1-n)}Tb_{n}^{3+}OX$$

wherein X is halogen such as e.g. chlorine, bromine, or fluorine, and n is from 0.006 to 0.0001, the halogen being present preferably in the range of between about the stoichiometric amount and about 2.5 percent differing therefrom; or

$$La_{(1-w-y)}OX:Tb_{w}Yb_{y}$$

wherein X is chlorine or bromine

w is 0.0005 to 0.006 mole of the oxyhalide, and
y is 0.00005 to 0.005 per mole of the oxyhalide.

Cerium may replace lanthanum in an amount described in the U.K.Patent Specification 1,247,602 filed October 9, 1969 by General Electric and Co.

The preparation of terbium-activated lanthanum oxychloride and lanthanum oxybromide phosphors emitting visible light is described, e.g., in U.K.Patent Specification 1,247,602 mentioned hereinbefore, the French Patent Specifications 2,021,398 and 2,021,399 both filed October 23, 1969 by General Electric and Co, and the published German Patent Applications (DE-OS) 1,952,812 filed October 21, 1969 and 2,161,958 filed December 14, 1971 both by General Electric and Co. Suitable lanthanum oxychloride-fluoride phosphors are described in the published German Patent Application (DE-OS) 2,329,396 filed June 8, 1973 by Siemens A.G.

The preparation of lanthanum oxyhalides activated with terbium and ytterbium is described, e.g., in the published German Patent Application (DOS) 2,161,958 mentioned hereinbefore.

Oxyhalides of lanthanum and gadolinium activated with thulium are described, e.g., for use in radiographic intensifier screens in the United States Patent Specification 3,795,814 of Jacob G.Rabatin, issued March 5, 1974.

An ultraviolet-emitting phosphor is barium fluoride chloride activated with europium(II) as described, e.g., in the French Patent Specification 2,185,667 filed May 23, 1973 by Philips Gloeilampenfabrieken N.V. According to an embodiment the present composition of matter is a composition wherein at least a part of said phosphor particles consists of said barium fluoride chloride.

An X-ray image intensifier screen employing rather hygroscopic sodium-activated cesium iodide is described in the United States Patent Specification 3,836,784, already mentioned hereinbefore. According to an embodiment the present composition of matter is a composition wherein at least a part of the phosphor particles is sodium-activated cesium iodide.

The thickness of the supported fluorescent layer may vary within a broad range but is preferably in the range of 0.05 to 0.5 mm.

The coverage of the phosphors is, e.g., in the range of approximately 200 to 800 g/sq.m and preferably approximately 300 to 600 g/sq.m.

The image sharpness obtainable with a fluorescent screen-silver halide material system can be improved considerably by incorporating a fluorescent light-absorbing dye, called "screening dye" herein, into the fluorescent screen material, e.g. into the fluorescent layer or into a layer adjacent thereto e.g. into a subjacent anti-reflection layer. As the oblique radiation covers a large path in the screen material, it is attenuated by the screening dye or dyes to a greater extent than the radiation impinging normally. The term "screening dye" used herein includes dyestuffs (i.e. coloured substances in molecularly divided form) as well as pigments.

Diffuse radiation reflecting from the support of the fluorescent screen material can be mainly attenuated in an anti-reflection layer containing the screening dyes subjacent to the fluorescent layer.

The screening dye need not to be removed from the fluorescent screen material and may therefore be any dye or pigment absorbing in the emission spectrum of the fluorescent substance(s). Thus black substances such as carbon black particles of an average size of 0.15 to 0.60 µm incorporated in said anti-reflection layer or the phosphor layer yield quite satisfactory results.

The screening dye(s) is (are) preferably used in the fluorescent layer e.g. in an amount of at least 0.5 mg per sq.m. When used in the anti-reflection layer, however, the amount of said dye(s) is not limited.

A suitable screening dye for use in the fluorescent screens emitting in the green range (500 to 600 nm) of the visible spectrum is, e.g., Neozapon Fire Red (C.I. Solvent Red 119), an azochromium rhodamine complex. Other suitable screening dyes are C.I. Solvent Red 8, 25, 30, 31, 32, 35, 71, 98, 99, 100, 102, 109, 110, 118, 124 and 130.

The non-self-supporting phosphor-binder composition may be coated on a wide variety of supports, e.g. cardboard and plastic film, e.g. polyethylene terephthalate film. A support used in a fluorescent screen of the present invention may be coated with (a) subbing layer(s) to improve the adherence of the fluorescent coating thereto.

Screens according to the present invention may be used in conjunction with light-sensitive silver halide materials emulsion-coated on one or both sides of the support.

The following examples illustrate the present invention.

Example 1

Preparation of screen A

A mixture consisting of 100 g of terbium-activated lanthanum oxybromide phosphor, 0.5 g of lauric acid as stabilizing compound, 12.5 g of poly(vinyl-n-butyral) still containing 12% by weight of non-acetalized vinyl alcohol units and having an average molecular weight of 50,000, and 48 g of ethylene glycol monomethyl ether were ball-milled to a fineness of grind corresponding with 7 NS Hegman fineness of grind measured with the Hegman gauge as specified in ASTM D1210. The dispersion obtained was filtered and after de-aeration coated onto a baryta-coated paper of 290 g per sq.m at a coverage of 500 g per sq.m to form said screen A.

Preparation of screen B

The X-ray image intensifying screen (B) was manufactured as described for screen (A) with the difference that the stabilizing compound was omitted from the composition of the screen.

Moisture treatment

The moisture treatment of screens (A) and (B) proceeded by covering congruently the phosphor coating of each of the screens (A) and (B) with a wet circular piece of filter paper having a weight of 1.355 g in dry state, a diameter of 15 cm, and a water content of 3.100 g. Subsequently, the covered screens (A) and (B) were separately packed air-tight in a polyethylene bag and kept at 60°C for 64 h in a ventilated cabinet. The screens (A) and (B) were removed then from the bag and after removal of the filter paper dried in the air for 30 min at 80°C.

X-ray exposure and development

The thus moisture-treated screens (A) and (B) and a screen (B^1) which was like screen B but was untreated with moisture, were exposed to X-rays in contact with a CURIX RP1 film (Curix is a trade mark of the Applicant for a medical X-ray film). The exposure was effected to such a degree that after development for 23 s at 35°C in Agfa-Gevaert's hardening developer G 138 containing hydroquinone and 1-phenyl-3-pyrazolidinone as developing agents and glutaraldehyde as a hardener the area of the silver halide material exposed in contact with the untreated screen (B^1) showed a transmission spectral density of 1.82 above fog. After gradually increasing exposures with screen (B^1) of the above film material and said development of the film as described a silver image with a gamma (γ) of 3 is obtained.

The transmission spectral densities obtained with the moisture-treated screens (A) and (B) were 1.76 and zero above fog respectively.

The actual loss in fluorescence power of screen (A) was computed as follows :

Δ density (ΔD) = 1.82 - 1.76 = 0.06

Δ log exposure ($\Delta \log E$) $= \frac{\Delta D}{\gamma} = \frac{0.06}{3} = 0.02$

antilog 0.02 = 1.05 ; 1/1.05 = 0.95

100% - 95% = 5%.

A usable result was also obtained by replacing lauric acid by a same amount of 1-n-dodecylamine.

Example 2

Preparation of screen I

- 5 g of a 40% by weight solution in toluene of ELVACITE 2044 (ELVACITE 2044 is a trade name of E.I. du Pont de Nemours & Co. (Inc.), Wilmington, Del., U.S.A., for a poly-n-butyl methacrylate)
- 100 g of LaOBr: 0.02 Tb: 0.0005 Yb phosphor particles

prepared according to published German Patent Specification 2,161,958,

- 0.5 g of the stabilizing compound : laurylmercaptane, and
- 251.2 g of toluene were ball-milled for 4 h, whereupon a further amount of 10.5 g of ELVACITE 2044 (trade name) was added and ball-milling was continued up to a Hegman fineness of grind of 7 NS (average phosphor particle size 7 µm) measured with the Hegman gauge as specified in ASTM D1210.

The dispersion obtained was coated at a coverage of 500 g per sq.m of phosphor on a subbed polyethylene terephthalate support and dried.

Preparation of screen II

Screen II was prepared in the same way as described for screen I with the difference, however, that the stabilizing compound was omitted from the composition.

Moisture treatment

Circular pieces of screen I and screen II each of them having a diameter of 15 cm were separately covered congruently with a wet circular piece of filter paper having a weight of 1.355 g in dry state, a diameter of 15 cm, and a water content of 3.100 g. Each of the thus covered screens was packed air-tight separately in a polyethylene bag and kept at 60°C in a ventilated cabinet for 64 h. Subsequently, the covered screens were removed from the polyethylene bag and the pieces of screens I and II after separation from the filter paper were dried in the air for 30 min at 80°C.

X-ray exposure and development

The moisture-treated screens I and II and an untreated screen II' were exposed to X-rays in contact with a CURIX (trade mark) RP1 film. The exposure was effected to such a degree that after development for 23 s at 35°C in Agfa-

Gevaert's hardening developer G 138 containing hydroquinone and 1-phenyl-3-pyrazolidinone as developing agents and glutaraldehyde as a hardener the area of the silver halide material exposed in contact with the untreated screen II' showed a transmission spectral density of 1.25 above fog.

Computed from the difference in density obtained with the moisture-treated screen I and non-moisture-treated screen II' the actual loss in fluorescence power of screen I was 7.9 %.

Example 3

Preparation of screen P

A mixture consisting of 100 g of terbium-activated lanthanum oxybromide phosphor, 0.5 g of lauryl alcohol as stabilizing compound, 12.5 g of poly(vinyl-n-butyral) still containing 12% by weight of non-acetalized vinyl alcohol units and having an average molecular weight of 50,000 and 48 g of ethylene glycol monomethyl ether were ball-milled to 7 NS Hegman fineness of grind measured with the Hegman gauge as specified in ASTM D1210. The dispersion obtained was filtered and after de-aeration coated onto a baryta-coated paper of 290 g per sq.m at a coverage of 150 g of phosphor per sq.m to form screen P.

The phosphor layer was overcoated with a protective coating from a 7.5% solution in ethylene glycol monomethyl ether of cellulose acetate butyrate having a degree of substitution (DS) of acetyl 1.31 and a DS of butyryl of 1.51. The dried protective coating had a coating weight of 10 g per sq.m.

Preparation of screen Q

The X-ray image intensifying screen Q was manufactured as described for screen P with the difference that the stabilizing compound was omitted from the composition of the screen.

Preparation of screen R

The X-ray image intensifying screen R was manufactured as described for screen P with the difference that before coating the oxybromide phosphor dispersion was mixed with a calcium tungstate phosphor dispersion prepared as described for the lanthanum oxybromide phosphor dispersion of screen P with the only difference that the oxybromide phosphor was replaced by a same amount of calcium tungstate. The calcium tungstate phosphor dispersion was added in an amount such that the final dispersion contained the oxybromide phosphor and calcium tungstate phosphor in a ratio of 1:2.

The phosphor mixture dispersion was coated on the same support as described for screen P at a phosphor mixture coverage of 150 g of terbium-activated lanthanum oxybromide phosphor and 300 g of calcium tungstate per sq.m.

Moisture treatment

The moisture treatment of screens P, Q and R proceeded by incubation in a cabinet having inside an atmosphere of 85% relative humidity at 20°C. Said incubation treatment was effected for a period of 2 weeks. After that period the fluorescence power of screen Q was completely lost and screen P showed randomly distributed spots and small craters. Screen R did not show any trace of deterioration. When screens P and R were X-ray exposed in contact with separate strips of the same silver halide emulsion film the developed film strip exposed in combination with screen P showed more than 100 white spots per sq.dm whereas the developed film strip which was exposed in contact with screen R did not show any spots at all and was evenly blackened.

The ratio of the intensification factors of screens P and R was 1:1.

WHAT WE CLAIM IS :

1. A composition of matter including halide-containing phosphor particles, which are admixed or combined in contact with or have reacted with at least one organic substance such that the fluorescence power of said phosphor particles is less liable to be adversely affected by moisture, wherein said organic compound is a non-metal organic compound corresponding to one of the following general formulae :

$$R\text{-}X \quad \text{and} \quad X\text{-}R^1\text{-}X$$

wherein :

R represents a monovalent organic group,

R^1 represents a bivalent organic group, with the proviso that these R and R^1 groups contain no reactive hydrogen such as contained in X, and

X represents a group containing reactive hydrogen, said compound upon reacting with acetyl chloride being capable of splitting off chlorine in the form of hydrogen chloride in the circumstances of the test A described hereinbefore, said compound having a solubility at 15°C of no more than 5 g in 100 ml of water.

2. A composition according to claim 1, wherein the phosphor particles bearing one or more of said organic substances affording protection against moisture are dispersed in a binder.

3. A composition of matter according to any of claims 1 and 2 which includes halide-containing phosphor particles by admixture combined with at least one said organic substance, wherein said substance when used in the circumstances of the following test is capable of maintaining the fluorescent light-emitting power of the test-phosphor to a level of at least 25% of its original fluorescent light-emitting power, said test comprising the following steps :

(1) the production of X-ray image intensifying screens (A) and (B),

(2) a moisture treatment of screen (A),

(3) an X-ray exposure of said screens (A) and (B) in contact with distinct areas of a photographic silver halide emulsion material and the development of said material,

(4) the measurement of the spectral densities obtained in the areas of said material that have been exposed in contact with said screens (A) and (B), and

(5) the computation of the actual loss of fluorescent light-emitting power of the moisture-treated screen (A) in comparison with screen (B) from the spectral density results obtained in step (4),

- the production of the X-ray image intensifying screen (A) proceeding as follows :

100 g of terbium-activated lanthanum oxybromide phosphor, 0.5 g of the substance to be tested, 12.5 g of poly(vinyl-n-butyral) containing still 12% by weight of non-acetalized vinyl alcohol units and having an average molecular weight of 50,000 and 48 g of ethylene glycol monomethyl ether are ball-milled to a fineness of grind corresponding with 7 NS Hegman measured with the Hegman gauge as specified in ASTM D1210, whereupon the dispersion obtained is filtered and after deaeration coated onto a baryta-coated paper of 290 g

per sq.m at a coverage of 500 g per sq.m to form said X-ray image intensifying screen A,

- the production of the X-ray image intensifying screen (B) proceeding as described for screen (A) with the difference that the substance to be tested is left out of the composition of the screen,
- the moisture treatment of screen (A) proceeding by covering congruently the phosphor coating of screen (A) with a wet circular piece of filter paper having a weight of 1.355 g in dry state, a diameter of 15 cm and a water-content of 3.100 g, thereupon air-tight packing the thus covered screen (A) in a polyethylene bag and keeping the thus packed covered screen (A) at 60°C for 64 h in a ventilated cabinet followed by the removing of said screen (A) from the bag and after removal of the filter paper drying at the air at 80°C for 30 min,
- X-ray exposure of the thus treated screen (A) and untreated screen (B) proceeding while having said screens with the phosphor coating in contact with the silver halide emulsion layer side of a same photographic silver halide emulsion material with transparent base, the X-ray exposure and the subsequent development of the silver halide material being such that with screen (B) a spectral density of at least 1.00 above inherent fog is obtained in the silver halide material area contacting screen (B); the silver halide material and development are such that after gradually increasing exposures with screen (B) a silver image is obtained whose density versus log exposure curve has a gamma value of 3;
- the measurement of the transmission spectral densities D_A and D_B proceeding in the areas of the developed silver halide emulsion material that during the exposure have been in contact with screens (A) and (B) respectively;

- the computing of the actual loss of fluorescent light-emitting power of the moisture treated screen (A) in comparison with screen (B) proceeding on the basis of the spectral density results D_A and D_B and the gamma 3.

4. A composition of matter according to any of claims 1 to 3, wherein said composition has the form of an X-ray image fluorescent screen, which comprises in a layer containing a binding agent halide-containing phosphor particles in admixture or combined in contact with said organic compounds.

5. A composition of matter according to any of claims 1 to 4, wherein said organic compound is an organic compound wherein the reactive hydrogen atom is linked directly to a sulphur atom, or which compound contains the reactive hydrogen atom in an amino group, a carboxyl group or a hydroxyl group.

6. A composition according to any of the claims 1 to 5, wherein at least a part of the halide-containing phosphor particles are halide-containing rare-earth metal compounds in which the host metal of the phosphor is a rare-earth metal and the activator consists of one or more other rare-earth metals.

7. A composition according to claim 6, wherein the host metal is yttrium, gadolinium, lanthanum or cerium and the activator metal is at least one of the metals of the group of terbium, europium, dysprosium, thulium, samarium and ytterbium.

8. A composition according to any of claims 6 and 7, wherein the rare-earth metal compound corresponds to one of the following formulae :

$$La_{(1-n)}Tb_n^{3+}OX$$

wherein X is halogen such as e.g. chlorine, bromine, or fluorine, and n is from 0.006 to 0.0001,

or

$$La_{(1-w-y)}OX: Tb_wYb_y$$

wherein X is chlorine or bromine

w is 0.0005 to 0.006 mole of the oxyhalide, and

y is 0.00005 to 0.005 per mole of the oxyhalide.

9. A composition according to any of claims 1 to 8, wherein said rare-earth metal compound is a terbium-activated lanthanum oxybromide phosphor.

10. A composition according to any of claims 1 to 9, wherein the phosphor particles and the organic compound are present in a binding agent consisting of a halogen-free polymer or copolymer.

WHAT WE CLAIM IS :

1. A composition of matter including halide-containing phosphor particles that are halide-containing rare-earth metal compounds in which the host metal of the phosphor is a rare-earth metal and the activator consists of one or more other rare-earth metals, and wherein said particles are admixed or combined in contact with or have reacted with at least one organic substance such that the fluorescence power of said phosphor particles is less liable to be adversely affected by moisture, characterized in that said organic compound is a non-metal-organic compound corresponding to one of the following general formulae :

$$R\text{-}X \text{ and } X\text{-}R^1\text{-}X$$

wherein :

R represents a monovalent organic group,

R^1 represents a bivalent organic group, with the proviso that these R and R^1 groups contain no reactive hydrogen such as contained in X, and

X represents a group containing reactive hydrogen, said compound upon reacting with acetyl chloride being capable of splitting off chlorine in the form of hydrogen chloride in the circumstances of the test A described hereinbefore, said compound having a solubility at 15°C of no more than 5 g in 100 ml of water.

2. A composition according to claim 1, wherein the phosphor particles bearing one or more of said organic

substances affording protection against moisture are dispersed in a binder.

- the computing of the actual loss of fluorescent light-emitting power of the moisture treated screen (A) in comparison with screen (B) proceeding on the basis of the spectral density results D_A and D_B and the gamma 3.

4. A composition of matter according to any of claims 1 to 3, wherein said composition has the form of an X-ray image fluorescent screen, which comprises in a layer containing a binding agent halide-containing phosphor particles in admixture or combined in contact with said organic compounds.

5. A composition of matter according to any of claims 1 to 4, wherein said organic compound is an organic compound wherein the reactive hydrogen atom is linked directly to a sulphur atom, or which compound contains the reactive hydrogen atom in an amino group, a carboxyl group or a hydroxyl group.

6. A composition according to claim 5 wherein said non-metalorganic compound is a thiol that contains a hydrocarbon group of at least 6 carbon atoms, an aliphatic primary or secondary amine that contains a hydrocarbon group of at least 8 carbon atoms, an aliphatic carboxylic acid that contains a hydrocarbon group of at least 6 carbon atoms, or a compound containing a hydroxyl group linked to a hydrocarbon group of at least 6 carbon atoms.

7. A composition according to any of claims 1 to 6, wherein the host metal of the phosphor is yttrium, gadolinium, lanthanum or cerium and the activator metal of the phosphor is at least one of the metals of the group of terbium, europium, dysprosium, thulium, samarium and ytterbium.

8. A composition according to claim 7, wherein the rare-earth metal compound corresponds to one of the following formulae :

$$La_{(1-n)}Tb_n^{3+}OX$$

wherein X is halogen such as e.g. chlorine, bromine, or fluorine, and n is from 0.006 to 0.0001,

or

$$La_{(1-w-y)}OX\colon Tb_wYb_y$$

wherein X is chlorine or bromine

w is 0.0005 to 0.006 mole of the oyxhalide, and

y is 0.00005 to 0.005 per mole of the oxyhalide.

9. A composition according to any of claims 1 to 8, wherein said rare-earth metal compound is a terbium-activated lanthanum oxybromide phosphor.

10. A composition according to any of claims 1 to 9, wherein the phosphor particles and the organic compound are present in a binding agent consisting of a halogen-free polymer or copolymer.

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EUROPEAN SEARCH REPORT

Application number
EP 78 20 0054
0000961

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
	DE - A - 2 304 150 (SIEMENS A.G.) * Claims 1-3; figure * --	1,2,4, 5,10
	DE - B - 1 271 542 (SIEMENS A.G.) * Claims 1,2,6; column 1, lines 1-7 * --	1,2,4, 5,10
	US - A - 3 649 329 (F.R.TAUBNER et C. F.CHENOT) * Claim 1, column 2, lines 10-22 * --	1,2,5, 10
P	FR - A - 2 344 618 (AGFA-GEVAERT) Corresponding to DE - A - 2 710 497 mentioned in the description of the examined application. * Claims 1,4-9,13,16,21,22 * ----	1-10

CLASSIFICATION OF THE APPLICATION (Int. Cl.²)

G 03 C 5/17
C 09 K 11/02
C 09 K 11/46
C 09 K 11/24
C 01 F 17/00

TECHNICAL FIELDS SEARCHED (Int.Cl.²)

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C 09 K 11/46
C 09 K 11/02

CATEGORY OF CITED DOCUMENTS

X: particularly relevant
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L: citation for other reasons

&: member of the same patent family,
corresponding document

☒ The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	15-08-1978	DECANNIERE

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