Jan. 24, 1967 K. C. KENNARD ET AL 3,300,311

X-RAY INTENSIFYING SCREENS EMPLOYING A WATER SOLUBLE COPOLYMER OF ALKYL ACRYLATE AND ACRYLIC ACID

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Fig.1

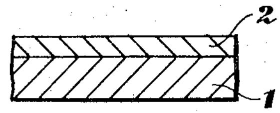


Fig.2

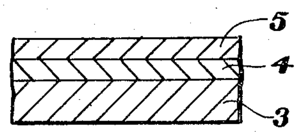


Fig.3

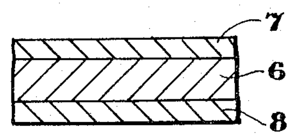


Fig.4

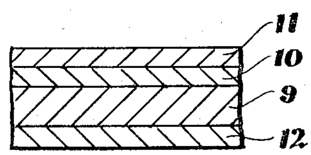


Fig.5

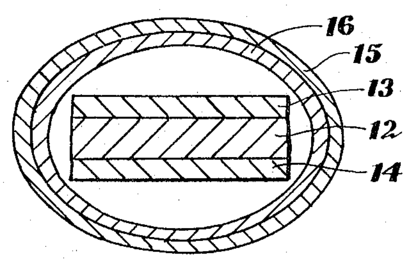
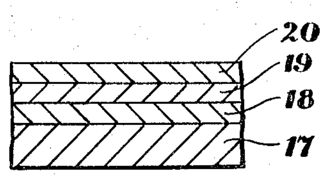


Fig.6



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X-RAY INTENSIFYING SCREENS EMPLOYING A WATER SOLUBLE COPOLYMER OF ALKYL ACRYLATE AND ACRYLIC ACID

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12 Claims. (Cl. 96—82)

The application is a continuation-in-part of Kennard et al. U.S. patent application Serial No. 223,377, filed September 13, 1962, and now abandoned.

This invention relates to X-ray intensifying screens, and more particularly to X-ray intensifying screens for use in X-ray photography.

It is common in the practice of X-ray photography to employ an intensifying screen in connection with the photographic element. The X-ray intensifying screen converts a portion of the X-ray radiation in the ultraviolet and visible light regions of the electromagnetic spectrum, thereby allowing the silver halide emulsion to more efficiently and accurately record the desired image. The X-ray screen most commonly used in industrial X-ray radiography has been lead foil, whereas in the medical and dental professions, the intensifying screen has generally comprised a support having a coating thereon of phosphor dispersed in a suitable vehicle or binder.

Although lead foil intensifying screens may produce satisfactory results, it is difficult to manufacture lead foil without surface irregularities which cause different densities in the X-ray photograph or plate. In addition, the thickness of lead foil is frequently not uniform, which also results in irregular densities in the film. It is difficult to determine whether such imperfections are caused by the lead foil or by the object being photographed.

Previous attempts to provide X-ray intensifying screens by coating a support with metallic lead or lead compounds have generally been unsuccessful because of the inability to discover a binder which allowed a high ratio of metallic lead or lead compound to binder, and did not introduce other problems, such as curling and brittleness.

As noted above, in the medical and dental professions, it has been common to employ in X-ray radiography an intensifying screen comprising a support having a coating thereon of a phosphor dispersed in a suitable binder. However, the screens previously known in the art have generally suffered from one or more disadvantages. Frequently, the binder employed does not allow a high phosphor-to-binder ratio, thereby necessitating a large number of coatings to achieve adequate intensification. Other binders have been susceptible of application only by the use of expensive organic solvents which may be toxic or inflammable. In some instances, when it is desirable to coat the intensifying screen directly adjacent the photographic emulsion, considerable difficulties are encountered in achieving a satisfactory bond between the two layers. The coating of the intensifying screen from an aqueous solution is preferable, but the few binders of the prior art which allow coating from aqueous solutions will not tolerate high phosphor-to-binder ratios. Still other binders have produced new problems, such as brittleness, difficulty of removal and problems of curling. It therefore appears desirable to provide binders for phosphors, metallic lead and lead compounds (generally referred to herein as "pigments") which are superior to those previously known in the art.

One object of our invention is to provide X-ray intensifying screens. Another object of our invention is to provide a support having a coating thereon of phosphors, metallic lead or a lead compound dispersed in a binder. A further object of our invention is to provide a support having a coating thereon of phosphor, metallic lead or a lead compound dispersed in a binder, which coating has a high ratio of pigment to binder. Still another object of our invention is to provide a photographic element comprising a support, a silver halide emulsion layer, and a layer thereover comprising phosphor, metallic lead or a lead compound dispersed in a binder. Another object of our invention is to provide a photographic element comprising a support having coated on one side a gelatino-silver halide emulsion, and on the other side, an X-ray intensifying screen comprising a phosphor metallic lead or a lead compound dispersed in a binder. Another object of our invention is to provide an X-ray sensitive photographic element enclosed in an opaque support having a coating thereon of phosphor, metallic lead or a lead compound dispersed in a binder. Other objects of our invention will appear herein.

These and other objects of our invention are accomplished by a support having a coating thereon of a compound selected from the group consisting of a phosphor, metallic lead or a lead compound dispersed in a copolymer of an alkyl acrylate and acrylic acid as binder. We have found that the phosphors, metallic lead and lead compounds may be dispersed in this polymeric binder in a high ratio of pigment-to-binder, thereby providing excellent X-ray intensifying screens. The screens prepared in accordance with our invention may be coated directly onto a photographic emulsion and are easily removed with water.

Various methods of utilizing the X-ray screens of our invention are shown in FIGS. 1–5. FIG. 1 shows a separate screen comprising a support **1** having an X-ray intensifying screen **2** coated thereon in accordance with our invention. FIG. 2 shows a support **3** having a gelatino-silver halide emulsion coated thereon **4**, and a coating over the gelatino-silver halide emulsion of an X-ray intensifying screen **5** in accordance with the invention. FIG. 3 shows a support **6** having a gelatino-silver halide coating **7** on one side thereof, and on the reverse side, an X-ray intensifying screen **8** in accordance with our invention. FIG. 4 shows a support **9** having a gelatino-silver halide coating thereover **10** and X-ray intensifying screens in accordance with our invention coated thereover **11**, and on the reverse side of the support, **12**. FIG. 5 shows a support **12** having coated on each side thereof a gelatino-silver halide emulsion, **13** and **14**, enclosed in an opaque support **15** having an X-ray intensifying screen **16** thereon in accordance with our invention. FIG. 6 shows a support **17** having a gelatino-silver halide coating thereon **18**, a stripping layer **19** and an X-ray intensifying screen **20** coated thereover.

Our invention will be further illustrated by the following examples. Examples 1–4 illustrate an X-ray intensifying screen comprising a support having a coating thereon of a phosphor dispersed in a copolymer of ethyl acrylate and acrylic acid.

Example 1

To 1098 cc. of an aqueous 8.2% solution of the ammonium salt of a copolymer composed of 80% ethyl acrylate and 20% acrylic acid was added 525 cc. of distilled water, 18 cc. of a 16% aqueous solution of sodium oleyl methyl taurine (OMT), 9 cc. of 2-methyl-2,4-pentanediol, 4.5 g. of 1,4-butanediol diglycidyl ether hardener in 10 cc. of acetone diluted to 100 cc. with distilled water and 600 g. of calcium tungstate obtained as Radelin Phosphor, color T–5, from the U.S. Radium Corporation. The mixture was thoroughly agitated with a Manton-Gaulin type LP colloid mill set at 0.01 inch. After mixing, the disperseion was then coated onto two polystyrene supports at the rate of 30 cc./ft.^{2} (approximately 10 grams/ft.^{2} of phosphor and 1.5 g./ft.^{2} of polymer) and one of the supports was given a second coating the same as the first to form a screen of approximately 20 g./ft.^{2} of phosphor and 3 g./ft.^{2} of polymer. Both supports were then overcoated with 50 milligrams/ft.^{2} of a gelatin protective coating. The X-ray intensifying screens thus obtained were found to be flexible and the coating of the phosphor was uniform. The ability of these screens to intensify X-ray radiation for photographic purposes is shown in Table 1.

Example 2

The procedure of Example 1 was followed except that 600 g. of barium lead sulfate phosphors, obtained as Du pont Luminescene Chemical No. 513, from E. I. du Pont de Nemours Company, Wilmington, Delaware, was substituted for the calcium tungstate of Example 1 to prepare an X-ray intensifying screen having 10 g./ft.^{2} of the phosphors. The screen thus obtained was tested for its ability to increase the sensitivity of photographic emulsions to X-ray radiation. The results are shown in Table 1.

The screens prepared in accordance with Examples 1 and 2 were used in conjunction with standard Royal Blue Medical X-Ray Film, commercially available from the Eastman Kodak Company, and were compared to the results obtained without using any intensifying screen. In each test, the screens were placed both on the front and the back of the film, and the film was exposed to 80 kv.-X-ray and developed for 5 minutes in Kodak Rapid X-ray Developer. The results are shown in Table 1:

TABLE 1

Active Ingredient in X-ray Intensifying Screen	Amount of Active Ingredient, g./sq. ft.	Relative Speed
$CaWO_4$	20	35.0
$CaWO_4$	10	20.0
$BaSO_4/PbSO_4$	10	30.0
None		2.5

The comparative data set out in the above table clearly show that the X-ray intensifying screens in accordance with our invention efficiently increase the sensitivity of the photographic emulsion to X-ray exposure.

Example 3

The screen obtained in accordance with Example 1, containing 20 g./ft.^{2} of $CaWO_4$ phosphor and 3 g./ft.^{2} of copolymer, was coated with a silver bromoiodide gelatin emulsion (having a relative speed of 2 when no intensifying screen was employed), exposed to 80 kv.-X-ray exposure with no external screen, developed 5 minutes in Kodak Rapid X-ray Developer, and was found to have a relative speed of 20.

Example 4

A baryta paper was coated with a barium lead sulfate phosphor dispersed in an aqueous solution of the ammonium salt of the copolymer of 80% ethyl acrylate and 20% acrylic acid so that the resulting paper contained a coating of 10 g./ft.^{2} of phosphor and 1.5 g./ft.^{2} of copolymer to provide an X-ray intensifying screen. A light sensitive gelatin-silver bromoiodide emulsion was coated over the intensifying screen. In a control film, the silver bromoiodide emulsion was coated directly on the baryta-coated paper. The integral X-ray film with intensifying screen and a control film were tested by exposing with no additional screen and with a separate intensifying screen composed of baryta-coated paper having a coating thereon of barium lead sulfate dispersed in the ammonium salt of copolymer of 80% ethyl acrylate and 20% acrylic acid at the rate of 10 g./ft.^{2} of phosphor and 1.5 g./ft.^{2} of copolymer. The tests were carried out by exposing each film to 80 kv.-X-ray and development for 5 minutes in Kodak Rapid X-ray Developer. The results are shown in Table 2.

TABLE 2

Photographic Element	Auxiliary Screen	Relative Speed
Control	None	2
Do	$BaSO_4/PbSO_4$	32
Emulsion coated over $BaSO_4/PbSO_4$ screen.	None	47
Do	$BaSO_4/PbSO_4$	100

The results set out in Table 2 show that the integral X-ray emulsion and intensifying screen is superior to the same X-ray emulsion and intensifying screen when used as a nonintegral photographic X-ray element.

Example 5 demonstrates an X-ray intensifying screen comprising a support having a coating thereon of lead oxide dispersed in an alkyl acrylate-acrylic acid copolymer.

Example 5

825 g. of a 9.12% solution of the sodium salt of a copolymer composed of 80% ethyl acrylate and 20% acrylic acid was combined with 367 ml. of distilled water, 15 ml. of a 17% aqueous solution of OMT, 7.5 ml. of 2-methyl-2,4-pentanediol and the mixture was agitated with the addition of 1602 grams of lead oxide (obtained as Red Lead, Dry, High-Oxide, from the National Lead Company, Depew, New York). The suspension was milled three times in a Manton-Gaulin colloid mill, Type LP, and 83 ml. of a 4.51% solution of 1,4-butanediol diglycidyl ether hardener was added thereto. The dispersion was coated onto a paper support containing a black pigment to give an equivalent of 16.9 g./ft.^{2} of lead. The coating obtained had excellent uniformity and X-ray photographs produced with this screen were indistinguishable in quality from those produced by the best lead foil. Assigning a relative speed of 100 to high quality lead foil, the speed obtained with the intensifying screen obtained in accordance with this example had a relative speed of 85. The slightly slower speed obtained with the intensifying screens in accordance with this example is of small practical significance.

The active ingredients which we may employ in the X-ray intensifying screens in accordance with our invention broadly include phosphors, metallic lead and lead compounds. These pigments may be incorporated in a ratio to binder of 1:1 to 1000:1, or preferably within a range of 5:1 to 300:1. A ratio of pigment-to-binder of 5:1 to 160:1 is especially good.

Any phosphor may be employed in accordance with our invention to produce high quality X-ray intensifying screens. Typical phosphors include calcium tungstate, barium lead sulfate (crystals containing both barium and lead atoms), zinc sulfide, and magnesium tungstate.

The metallic lead powder which we incorporate in the X-ray intensifying screens of our invention advantageously has a particle size of 1–100 microns, and preferably is 3–8 microns.

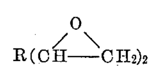
Any lead compound may be incorporated in the binder of the invention to provide highly satisfactory X-ray intensifying screens. Typical lead compounds include lead oxides (e.g., PbO and Pb_3O_4), both the organic and inorganic salts of lead, such as lead carbonate, lead oxylate and tetraalkyl lead. Lead oxide, as well as lead carbonate, produce especially good results.

When the X-ray intensifying screens of our invention contain lead oxide as the active ingredient, it is sometimes desirable to coat such screens with an aqueous acidic solution, such as aqueous sulfuric acid. When screens containing lead oxide are employed with a photographic emulsion in one integral element, it may be advantageous to separate the layer containing lead oxide from the photographic emulsion with the support, a stripping layer or a protective layer, e.g., gelatin.

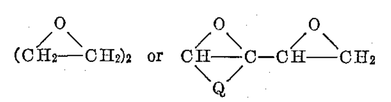
The alkyl acrylate-acrylic acid copolymers, which we employ as the binder in accordance with our invention, may be prepared by copolymerizing a mixture of an alkyl acrylate and acrylic acid according to the method described in Houck et al. U.S. patent application Serial No. 139,313, filed September 19, 1961. The alkyl acrylates which may be employed include those from methyl up to and including decyl. The copolymers which are useful herein are the water soluble ammonium and alkali metal salts made up of 50–90 mole percent alkyl acrylate and 50–10 mole percent acrylic acid. These copolymers provide highly satisfactory binders for phosphors, metallic lead and lead compounds.

The copolymers of ethyl acrylate and acrylic acid, especially those composed of 80% mole percent ethyl acrylate and 20% acrylic acid, produce excellent results. When alkyl acrylate-acrylic acid copolymer binders are employed, we have found that particularly good results are obtained with calcium tungstate, barium lead sulfate, lead oxide (PbO and Pb_3O_4) and lead carbonate. When lead oxide is employed as the active agent in the X-ray intensifying screen, we prefer to employ the sodium salt of the copolymer.

The copolymers of alkyl acrylate and acrylic acid employed in accordance with our invention are preferably hardened with a cross linking agent. One highly satisfactory cross-linking agent is a bisepoxide compound of the type described in Allen et al. U.S. patent application Serial No. 752,402, now U.S. Patent No. 3,047,394, which may have one of the following formulas:



where R is a hydrocarbon group or a chain consisting of hydrocarbon groups connected by either linkages:



where Q represents 2 hydrogen atoms or the nonmetallic atoms necessary to complete a hydrocarbon nucleus. Examples of some of the bisepoxides compounds which are useful include bis(2,3-epoxypropyl) ether, vinyl cyclohexanedioxide, ethylenebiglycidyl ether, bis(epoxypropoxyethyl) ether, hydroquinone bisglycidyl ether, resorcinol bisglycidyl ether, diepoxybutane, diepoxyhexane, and other compounds having a formula corresponding to one of those given above. Still other hardening agents which may be employed in the alkyl acrylate-acrylic acid copolymers include aziridinyl azines, containing at least 2 aziridinyl groups therein of the type described in Yudelson U.S. Patent 3,017,280, issued January 16, 1962.

X-ray intensifying screens in accordance with our invention may be prepared by incorporating the phosphor, metallic lead or lead compound in a copolymer of alkyl acrylate-acrylic acid, and coating the mixture onto any suitable support, such as baryta-coated paper, cellulose ester film base, polystyrene or metal foil. The support may be given one coating or a plurality of coatings to vary the amount of active ingredient as desired. We have found that 5–50 grams of active ingredient per square foot of support provides highly satisfactory intensifying screens; however, the rate may be varied widely to provide the desired intensification.

The X-ray screens of our invention may be utilized as a separate screen or as an integral screen, that is, as a separate distinct layer of a photographic element comprising a silver halide emulsion coated onto a support. The screens in accordance with our invention may be coated directly over the photographic emulsion, on the opposite side of the support from the photographic emulsion, or on both sides. Intermediate layers, such as stripping layers, may be coated between the X-ray emulsion and the intensifying screen. Further, the X-ray intensifying screens may be removable, for example, with stripping or washing with water. Suitable stripping layers which may be employed include unhardened gelatin and cellulose ether phthalate.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

We claim:

1. An X-ray intensifying screen composed of a support having a layer thereon comprising a compound selected from the group consisting of phosphors, metallic lead and lead compounds dispersed in a water soluble copolymer composed of 50 to 90 mole percent alkyl acrylate and 50 to 10 mole percent acryllic acid, said layer being coated from aqueous solution.

2. An integral photographic film and X-ray intensifying screen composed of a support having a gelatino silver halide emulsion thereon, and a separate distinct second layer comprising an active ingredient selected from the group consisting of phosphors, lead compounds and metallic lead dispersed in a water-soluble copolymer composed of 50 to 90 mole percent alkyl acrylate and 50 to 10 mole percent acrylic acid, said second layer being coated from aqueous solution.

3. A photographic element composed of a support having a photographic emulsion thereon, a stripping layer coated over the photographic emulsion, and an X-ray intensifying layer on the stripping layer comprising an active ingredient selected from the group consisting of phosphors, lead compounds and metallic lead dispersed in a water-soluble copolymer composed of 50 to 90 mole percent alkyl acrylate and 50 to 10 mole percent acrylic acid, said intensifying layer being coated from aqueous solution.

4. A photographic element composed of a support having a gelatino silver halide emulsion coated on at least one side thereof, said support being enclosed in an envelope opaque to visible radiation but transparent to X-ray radiation, said envelope having coated on at least one side thereof an X-ray intensifying layer comprising an active ingredient selected from the group consisting of phosphors, lead compounds and metallic lead dispersed in a water-soluble copolymer composed of 50 to 90 mole percent alkyl acrylate and 50 to 10 mole percent acrylic acid, said intensifying layer being coated for aqueous solution.

5. An X-ray intensifying screen comprising a support having an X-ray intensifying layer thereon comprising an active ingredient selected from the group consisting of phosphors, lead compounds and metallic lead dispersed in a hardened, water soluble binder which is the salt of a copolymer composed of 50–90 mole percent alkyl acrylate and 50–10 mole percent acrylic acid, the ratio of active ingredient to binder being from 1:1 to 1000:1, said intensifying layer being coated from aqueous solution.

6. Claim 5 wherein the active ingredient is calcium tungstate and the weight ratio of calcium tungstate to binder is from 5:1 to 300:1.

7. Claim 5 wherein the active ingredient is a barium lead sulfate phosphor containing both barium and lead atoms in the crystal, and the weight ratio of barium lead sulfate to copolymer is from 5:1 to 300:1.

8. Claim 5 wherein the active ingredient is metallic lead powder having a particle size of 1–100 microns, and the weight ratio of metallic lead powder to binder is from 5:1 to 300:1.

9. Claim 5 wherein the active ingredient is lead oxides; the salt of the copolymer is an alkali metal salt; and, the weight ratio of lead oxide to copolymer is from 5:1 to 300:1.

10. Claim 5 wherein the active ingredient is Pb_3O_4; the salt of the copolymer is an alkali metal salt; and, the weight ratio of Pb_3O_4 to copolymer is from 5:1 to 300:1.

11. Claim 5 wherein the active ingredient is lead carbonate and the weight ratio of lead carbonate to binder is from 5:1 to 300:1.

12. A film pack for recording X-ray radiation comprising a photographic element including a support having thereon a photographic silver halide emulsion coating which is sensitive to X-ray radiation, and X-ray intensifying screen comprising a supported layer of an active ingredient selected from the group consisting of phosphors, lead compounds and metallic lead dispersed in a binder essentially consisting of a water-soluble copolymer which is a salt of an alkyl acrylate and acrylic acid copolymer containing 50–90 mole percent alkyl acrylate and 50–10 mole percent acrylic acid, said screen being substantially coextensive with said silver halide emulsion coating, and said layer and said photographic element being positioned in overlying relationship and enclosed in an envelope opaque to visible radiation but transparent to X-ray radiation, said layer being coated from aqueous solution.

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