Jan. 24, 1967 K. C. KENNARD ET AL 3,300,310

X-RAY INTENSIFYING SCREENS EMPLOYING AQUEOUS ETHYL ALCOHOL-SOLUBLE NYLON BINDERS

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Fig. 1

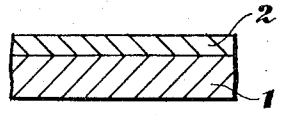


Fig. 2

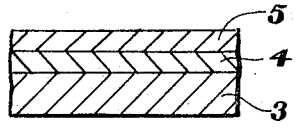


Fig. 3

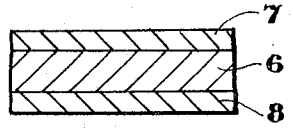


Fig. 4

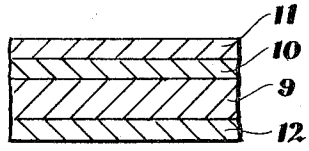


Fig. 5

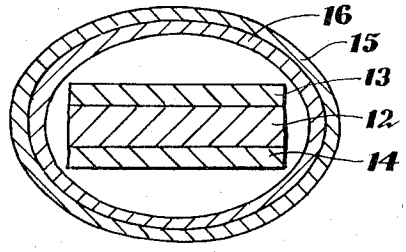
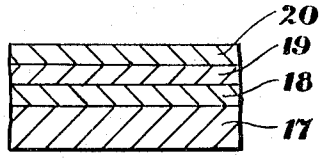


Fig. 6



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X-RAY INTENSIFYING SCREENS EMPLOYING AQUEOUS ETHYL ALCOHOL-SOLUBLE NYLON BINDERS

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9 Claims. (Cl. 96—82)

This 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 into 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 aqueous ethyl alcohol soluble nylon as binder. We have found that the phosphors, metallic lead and lead compounds may be dispersed in aqueous ethyl alcohol soluble nylon 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 an aqueous alcohol solution.

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 which demonstrate the use of aqueous ethyl alcohol soluble nylon as binder for lead oxide and lead powder.

Example 1

500 grams of a 5% solution of a nylon resin, soluble in 20% aqueous ethyl alcohol, obtained as Zytel 61

resin from E. I. du Pont and Company, Wilmington, Delaware, was stirred in a Waring Blendor with the addition of 750 grams of the lead oxide (obtained as Red Lead, Dry, High-Oxide, from the National Lead Company, Depew, New York). The dispersion was coated on cellulose acetate film base to give an equivalent of 21.5 g./ft.^{2} of lead. The X-ray intensifying screens obtained had excellent uniformity. Assigning a relative speed of 100 to the results obtained with a high quality lead foil, the speed obtained with the same emulsion using the intensifying screen prepared in this example had a relative speed of 85. The slightly slower speed obtained with the intensifying screen of this example is of small practical significance.

Example 2

300 grams of the 5% solution of soluble nylon resin described in Example 1 were stirred in a Waring Blendor with the addition of 2,400 grams of lead powder, obtained as MD201 from the Metals Disintegrating Company, Elizabeth, New Jersey, and ground to a particle size of 3–8 microns. The stirring was continued at a moderate rate with a magnetic stirrer during the coating. The dispersion was coated on a cellulose acetate film base to give 57 g./ft.^{2} of lead. This resulted in a ratio of 160:1 of lead powder to nylon resin. The relative speed of a photographic film when the intensifying screen of this example is employed is substantially equal to that when lead foil is substituted for the screen.

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 the aqueous ethyl alcohol soluble nylon 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 binders disclosed herein to provide highly satisfactory X-ray intensifying screens in accordance with our invention. 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 nylons which we employ as a binder in the X-ray intensifying screens in accordance with the invention comprise those which are soluble in aqueous ethyl alcohol solution, such as 80% ethanol-20% water. The soluble nylon may be employed with good results as a binder for the phosphors, metallic lead and lead compounds with particularly satisfactory results being achieved when lead oxide (PbO and Pb_3O_4) and finely divided metallic lead powder are employed.

X-ray intensifying screens in accordance with our invention may be prepared by incorporating the phosphor, metallic lead or lead compound in the aqueous ethyl alcohol soluble nylon binder 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 aqueous ethyl alcohol. 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 coated from aqueous solution, said layer comprising an active ingredient selected from the group consisting of phosphors, metallic lead and lead compounds dispersed in aqueous ethyl alcohol-soluble nylon binder, the weight ratio of active ingredient to binder being at least 1:1.

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 layer coated from an aqueous solution, said layer comprising an active ingredient selected from the group consisting of phosphors, lead compounds and metallic lead dispersed in aqueous ethyl alcohol-soluble nylon binder, the weight ratio of active ingredient to binder being at least 1:1.

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, said intensifying layer being coated from aqueous solution and comprising an active ingredient selected from the group consisting of phosphors, lead compounds and metallic lead dispersed in aqueous ethyl alcohol-soluble nylon binder, the weight ratio of active ingredient to binder being at least 1:1.

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 a layer thereon coated from aqueous solution, said layer comprising an active ingredient selected from the group consisting of phosphors, lead compounds and metallic lead dispersed in aqueous ethyl alcohol-soluble nylon binder, the weight ratio of active ingredient to binder being at least 1:1.

5. An X-ray intensifying screen comprising a support having a layer thereon coated from aqueous solution, said layer containing an active ingredient selected from the group consisting of phosphors, lead compounds and metallic lead dispersed in an aqueous ethyl alcohol-solible nylon binder, the weight ratio of active ingredient to binder being from 1:1 to 1000:1.

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

7. Claim 5 wherein the active ingredient is Pb_3O_4 and the weight ratio of Pb_3O_4 to binder 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 5:1 to 300:1.

9. A film pack for recording X-ray radiation comprising a photographic element including a support having coated thereon a photographic silver halide emulsion layer which is sensitive to X-ray radiation, and an X-ray intensifying screen coated from aqueous solution and comprising a supported coating of an active ingredient selected from the group consisting of phosphors, lead compounds and metallic lead dispersed in a nylon binder soluble in 20 percent aqueous ethanol solution, the weight ratio of active ingredient to binder being at least 1:1, said screen being substantially coextensive with said silver halide emulsion layer, and said intensifying 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.

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