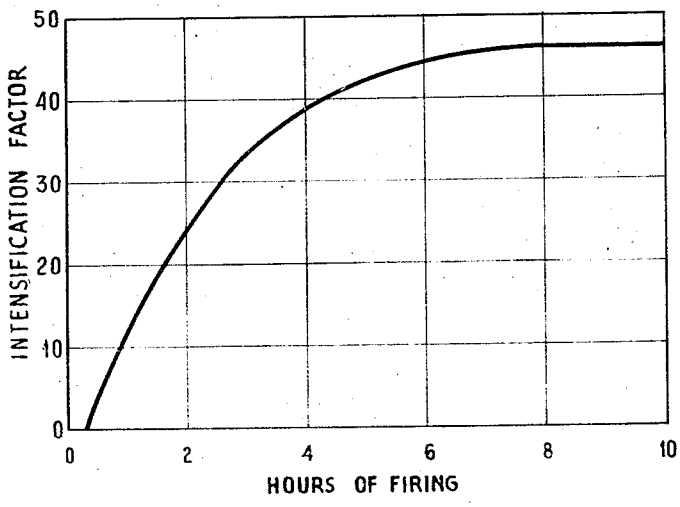
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MANUFACTURE AND USE OF FLUORESCENT MATERIAL

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MANUFACTURE AND USE OF FLUORESCENT MATERIALS

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This invention relates to the production of materials which fluoresce under the stimulus of X-rays and gamma-rays, to the production of fluorescent screens containing such materials, and to the production of photographic products embodying such fluorescent materials and suitable for the production of X-ray and gamma-ray photographs, that is, so-called "radiographs."

It is well known that X-rays and gamma-rays from radium and other radio-active materials are capable of forming latent images in silver halide emulsions and that it is possible therefore to make radiographs by interposing the article to be radiographed between a source of X-rays or of gamma-rays and a silver halide photographic emulsion.

It is also well known that the duration of the exposure necessary to produce a latent image in a silver halide emulsion can be reduced by making use of an intensifying screen which consists of a carrier or support bearing in layer form a substance, e. g., calcium tungstate or zinc sulphide, which fluoresces under the influence of X-rays or gamma-rays. In use, an intensifying screen is placed in contact with a silver halide photographic emulsion coated on a support and the combination is exposed to the rays with the result that the fluorescent light emitted by the screen forms a latent image in the emulsion more quickly than the rays alone could do.

The effectiveness of an intensifying screen may be defined by its "intensification factor." This is the factor by which the exposure time would have to be multiplied if no intensifying screen were used, in order to give an image in the developed emulsion of equal density to that obtained with the aid of the screen.

Intensifying screens are usually made as independent units and the same screen is used for many exposures. It has, however, been proposed to combine with a silver halide photographic emulsion on a transparent support a layer of material which fluoresces under the influence of X-rays, the layer being incorporated in or on the emulsion or embodied in the support. However, while such combinations of fluorescent and light-sensitive materials have certain advantages, they have not found favour in practice largely because of the difficulty and expense involved in the preparation of the known fluorescent substances which can be so employed and which, when used in such combinations, can only be employed for one exposure.

It is an object of this invention to provide a new fluorescent material. A further object of the invention is to provide fluorescent screens containing such fluorescent material and a still further object is to provide photographic materials containing such fluorescent material suitable for the production of radiographs. Another object of the invention is to provide processes for the production of the new fluorescent material.

It has now been discovered, and this forms the basis of the present invention, that if substantially pure crystalline barium sulphate is subjected to a firing treatment at temperatures of the order of 900 to 1150° C. for several hours, the product obtained is strongly fluorescent in the blue-violet and ultra-violet under the influence of X-rays or gamma-rays and may be used as the fluorescent substance in a fluorescent screen.

Such material has an intensification factor greater than 12 and, dependent on its purity and the firing conditions its intensification factor may be considerably greater, e. g., 50 or even more. These intensification factors and others given elsewhere in this specification and in the claims are determined by the following method. A layer of the fluorescent material in powder form, having a thickness equal to 20 gms. per square decimetre (i. e., sufficiently thick to give substantially the maximum emission of light from the surface of the layer) is placed behind and in contact with a normal type of blue-sensitive X-ray emulsion and exposed to X-rays generated at 100 k. v. p. and filtered through 2.5 mm. of copper. The intensification factor is defined as the ratio of the exposure necessary to produce a developed image of standard density in the absence of the fluorescent material to the exposure necessary to produce a developed image of the same density in the presence of the fluorescent material.

By the expression "substantially pure" is meant that the purest obtainable reagents should be employed to produce the product. Reagents having at least the degree of purity defined in the book "'Analar' Standards for Laboratory Chemicals," formulated and issued jointly by The British Drug Houses Ltd., and Hopkin & Williams Ltd., and published in 1934, may be employed and it is preferable that the reagents should have an even greater degree of purity than is required by these standards. In particular it has been found that the presence, even in minute amounts, of iron, manganese, chromium and copper, and to a lesser degree, nickel or cobalt impairs the fluorescent properties of the prod-

uct. However, it is permissible for there to be present in the fluorescent materials of this invention a considerable proportion, e. g., 10%, 20% or even more of the closely related pure calcium and pure strontium sulphates, and the expression "substantially pure" is to be understood with this qualification. It may be noted that since it is desirable for a fluorescent screen material to be highly resistant to moisture, an unduly large proportion of calcium or strontium sulphate is undesirable.

The invention includes X-ray or gamma-ray sensitive material for radiography which comprises one or more support layers, at least one silver halide emulsion layer and substantially pure crystalline barium sulphate which has been fired as described distributed in one of the above layers or in a carrier layer attached to one of the support or silver halide emulsion layers to form an intensifying screen which will fluoresce under the stimulus of X-rays or of gamma-rays and so effect exposure of the emulsion layer. The material may be made in the form of a bi-pack in which the silver halide emulsion layer is carried on one support and the intensifying screen is carried in or on another support layer. Alternatively the emulsion layer and the screen may be carried on a single support layer, e. g., of paper or cellulose film, as a unit. In this case the fluorescent material is preferably incorporated in a carrier layer situated between the support layer and the emulsion layer, or is incorporated in the emulsion or in the support layer.

The substantially pure crystalline barium sulphate to be subjected to firing to produce the fluorescent material of this invention may be made by any suitable method. A most convenient method is to form the barium sulphate as a precipitate by double decomposition between a solution of a soluble barium salt, e. g., barium nitrate, and an excess of sulphuric acid or of a solution of an alkali sulphate, e. g., sodium sulphate or other colourless soluble sulphate. Preferably the precipitated barium sulphate is washed with a dilute solution of sulphuric acid or pure distilled water before use. It is important, of course, that the purest obtainable reagents be used throughout, e. g., "Analar" reagents.

The firing operation is conveniently carried out in pure air in a muffle furnace, the barium sulphate being contained in a crucible composed of an inert material or lined with an inert material. Thus, for example, the barium sulphate may be fired in an electrically heated furnace in a crucible lined with pure calcined calcium sulphate or in an alumina crucible.

The duration of the firing treatment in order to obtain the optimum results depends, inter alia, on the temperance of that treatment. In general, it may be noted that at any given firing temperature, increases in time of firing increase the fluorescent properties of the product up to a maximum after which further firing either has no effect or is definitely deleterious. Also, it may be noted that the lower the firing temperature the longer is the time necessary to obtain the optimum results. In general, at lower firing temperatures the fluorescent properties of the product are not usually so good as at the higher firing temperatures.

By way of example, it may be stated that when pure precipitated barium sulphate is fired at temperatures of 1000 to 1060° C. the intensification factor of the product increases with time of firing of the barium sulphate and reaches a value of about 40–50 after 6 to 10 hours firing. The accompanying drawing illustrates the variation of intensification factor with time of firing at 1050° C. in a particular case.

If desired, the barium sulphate may be fired in the presence of a flux, e. g., magnesium sulphate or sodium sulphate, which is afterwards dissolved out.

During the firing operation some sintering of the barium sulphate may occur and if so it is desirable to grind the product to a fine powder preferably wetted with water before employing it for the production of a fluorescent screen.

Whilst in the production of an intensifying screen as a separate unit intended, in use, to be placed next to a photographic element, it is desirable that the intensification factor of the barium sulphate material should be as high as possible, this is not so important where the intensifying screen is included with a support and photographic emulsion as a unitary element. In this latter case barium sulphate material having an intensification factor of only 12–15 is often useful, though material of higher intensification factor, e. g., 20–30 or more may obviously be employed in such unitary products. Substantially pure crystalline barium sulphate which has not been subjected to the special firing treatment of this invention has negligible intensifying properties, and never approaches an intensification factor as high as 12.

X-ray or gamma-ray screens incorporating the fired barium sulphate may be prepared by dispersing the fired barium sulphate in any suitable carrier, e. g., a solution of a cellulose derivative or of a colourless synthetic resin, and then casting the resulting dispersion to form a film, or coating on a paper or other support. Gelatin and other hydrophilic colloids may also be used as carriers. A screen produced in this way may be used in the usual manner of X-ray intensifying screens, i. e., it may be placed in contact with a silver halide emulsion and the emulsion and the screen exposed to X-rays, the fluorescent light emitted by the screen producing a latent image in the emulsion more rapidly than the X-rays alone.

Alternatively, the fired barium sulphate may be used to form a fluorescent layer in a unit comprising the silver halide emulsion and a single support layer as described above. This may, for example, be effected by dispersing the fluorescent product in a colloid carrier (e. g., a cellulose derivative, a colourless synthetic resin, a solution of gelatin or the like), coating the dispersion on a support by any of the usual coating methods employed in the photographic industry, drying the product and then coating a gelatino-silver halide emulsion of the type commonly employed for radiographic purposes on the top of the fluorescent layer, or the fluorescent barium sulphate may be dispersed in the photographic silver halide emulsion itself before it is coated on its support.

Other arrangements of the unit, in addition to those mentioned above in which the fired barium sulphate is located between the support and the sensitive layer or in the support, are possible, but it is necessary to take into account the opacity of the fluorescent layer both to visible light and to X-rays and gamma-rays. For example, the fluorescent layer may be on the face of the emulsion, in which case the support is preferably transparent to visible light as well as to the rays and the emulsion is preferably

exposed to rays passing through the support. Further, if the support is very thin and transparent to visible light and to the rays, the fluorescent layer may be on the back of the support. When the fluorescent layer is coated on the face of the emulsion or on the back of the support, it may be suspended in a carrier soluble in water or dilute alkali or other solvent which does not attack the emulsion or support for example, fish glue, or an acid resin, which will permit the ready removal of the fluorescent layer before or during processing of the emulsion.

Again, the fluorescent layer may be of such a character that it can be stripped, in the wet or dry condition, from the assembly. Thus for example a layer of the fired barium sulphate in a strippable material, e. g., collodion, may be coated on to the surface of the emulsion remote from the support, and the layer may be removed before processing so that the finished radiograph can be viewed by reflected light if the support is not transparent or by transmitted light if the support is transparent.

When the fluorescent layer is coated on the silver halide emulsion layer there may, if desired, be a second emulsion layer on the opposite side of the support, the support being of course, in this case, transparent both to the rays and to visible light and thin.

Owing to the insolubility of the fired barium sulphate in the usual photographic developing and fixing baths, unless it is coated on the surface and removed in the manner described above, it remains in the finished radiograph and although this is a disadvantage for some purposes, it is of no importance where the support is opaque, for example of paper, and the radiograph is viewed by reflected light.

The fluorescent material of this invention possesses many advantages as the active fluorescent material in an X-ray or gamma-ray intensifying screen. Thus it gives a screen having a satisfactory intensifying factor and unlike zinc sulphide it is effective not only with X-rays generated at relatively low peak kilovoltages, but also with X-rays generated at high peak kilovoltages such as are used for the radiography of thick and/or very dense objects. Further, since it can readily be obtained in microcrystalline form screens containing it as the active ingredient yield radiographs of very good definition.

Again, since barium sulphate is a cheap material (compared, for example, with calcium tungstate) and unlike zinc sulphide has no deleterious effect on silver halide photographic emulsions, it can be economically employed, as indicated above, as an element in a unitary product containing both emulsion and fluorescent screen, and used for a single exposure. Also screens made in accordance with the present invention are highly resistant to deleterious action on their fluorescent properties by water.

What I claim is:

1. Fluorescent barium sulphate material consisting essentially of substantially pure crystalline barium sulphate having an intensification factor of at least 12 and obtainable by heating substantially pure crystalline barium sulphate at a temperature of 900–1150° C. for a period of at least 1 hour.

2. Fluorescent barium sulphate material consisting essentially of substantially pure barium sulfate having an intensification factor of at least 20 and being substantially identical with that obtainable by heating substantially pure crystalline barium sulfate at a temperature of 900–1150° C. for a period of several hours.

3. Fluorescent barium sulphate material consisting essentially of substantially pure crystalline barium sulphate having an intensification factor of at least 12 and obtainable by heating substantially pure crystalline barium sulphate at a temperature of 1000 to 1060° C. for six to ten hours.

4. An X-ray fluorescent screen comprising a support and a layer which fluoresces under the influence of X-rays comprising substantially pure crystalline barium sulphate having an intensification factor of at least 20 obtainable by heating substantially pure crystalline barium sulphate at a temperature of 900–1150° C. for a period of several hours.

5. An X-ray sensitive screen assembly for radiography which comprises a silver halide photographic emulsion and a support for the emulsion in combination with a screen layer containing substantially pure crystalline barium sulphate having an intensification factor exceeding 12 which will fluoresce under the stimulus of X-rays or gamma-rays and produce a latent image in the photographic emulsion and is obtainable by heating substantially pure crystalline barium sulfate at a temperature of 900 to 1150° C. for a period of several hours.

6. An X-ray sensitive element for radiography which comprises a silver halide photographic emulsion, a support for the emulsion and a screen layer containing substantially pure crystalline barium sulphate having an intensification factor exceeding 20 substantially identical with that obtainable by heating substantially pure crystalline barium sulfate at a temperature of 900–1150° C. for a period of several hours, which will fluoresce under the stimulus of X-rays or gamma-rays and produce a latent image in the photographic emulsion, the whole combined to form a unitary product.

7. An X-ray sensitive element for radiography which comprises a silver halide photographic emulsion, a support for the emulsion and, between the emulsion and the support, a screen layer containing substantially pure crystalline barium sulphate having an intensification factor exceeding 12, which will fluoresce under the stimulus of X-rays or gamma-rays and produce a latent image in the photographic emulsion and is obtainable by heating substantially pure crystalline barium sulfate at a temperature of 900 to 1150° C. for a period of several hours.

8. An X-ray sensitive element for radiography which comprises a silver halide photographic emulsion, and a support for the emulsion which support contains incorporated in it a screen layer containing substantially pure crystalline barium sulphate having an intensification factor exceeding 12 which will fluoresce under the stimulus of X-rays or gamma-rays and produce a latent image in the photographic emulsion and is obtainable by heating substantially pure crystalline barium sulfate at a temperature of 900 to 1150° C. for a period of several hours.

9. An X-ray sensitive element for radiography which comprises a silver halide photographic emulsion, a support for the emulsion and, coated on an outer surface of the assembly of emulsion and support, a screen layer containing substantially pure crystalline barium sulphate having an intensification factor exceeding 12 which will fluoresce under the stimulus of X-rays or

gamma-rays and produce a latent image in the photographic emulsion and is obtainable by heating substantially pure crystalline barium sulfate at a temperature of 900 to 1150° C. for a period of several hours.

10. An X-ray sensitive element according to claim 9 wherein the barium sulphate screen layer is capable of ready removal from the assembly after the emulsion has been exposed.

11. An X-ray sensitive element for radiography which comprises a silver halide photographic emulsion, and a support for the emulsion, which emulsion contains incorporated in it a screen layer containing substantially pure crystalline barium sulphate having an intensification factor exceeding 12, which will fluoresce under the stimulus of X-rays or gamma-rays and produce a latent image in the photographic emulsion and is obtainable by heating substantially pure crystalline barium sulfate at a temperature of 900 to 1150° C. for a period of several hours.

12. Process for the production of barium sulphate material adapted to fluoresce strongly under the influence of X-rays and gamma-rays, which comprises heating substantially pure crystalline barium sulphate at 900–1150° C. for a period of at least one hour.

13. Process for the production of barium sulphate material adapted to fluoresce strongly under the influence of X-rays and gamma rays which comprises heating substantially pure crystalline barium sulphate at 900–1150° C. for a period of 6–10 hours.

14. Process for the production of barium sulphate material adapted to fluoresce strongly under the influence of X-rays and gamma-rays which comprises forming substantially pure crystalline barium sulphate by double decomposition between a solution of a pure barium salt in water and a solution in water of a compound selected from the group consisting of sulphuric acid, alkali metal sulphates and other soluble colourless sulphates, drying the product and thereafter heating it to 900–1150° C. for a period of at least one hour.

15. Process for the production of barium sulphate material adapted to fluoresce strongly under the influence of X-rays and gamma-rays which comprises heating substantially pure crystalline barium sulphate in admixture with a water-soluble salt acting as a flux at 900–1150° C. for a period of several hours and thereafter dissolving out said water-soluble flux.

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