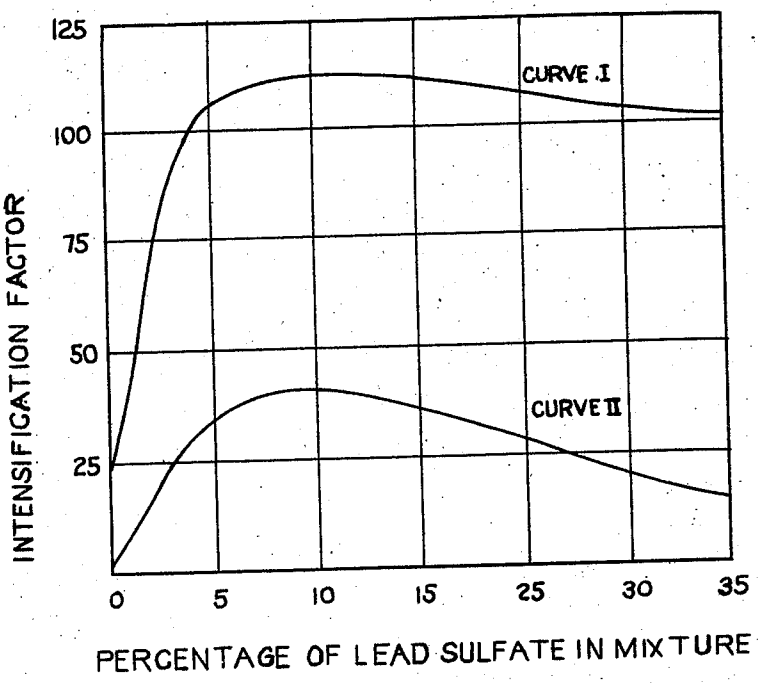
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PRODUCTION AND USE OF FLUORESCENT MATERIAL

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PRODUCTION AND USE OF FLUORESCENT MATERIALS

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The invention relates to layers or coatings which fluoresce under the stimulus of X-rays and gamma-rays, to fluorescent materials for use in X-ray screens, to photographic materials embodying such fluorescent screens and suitable for the production of X-ray and gamma-ray photographs, that is, so-called "radiographs," and to the production of such screens, fluorescent materials and X-ray sensitive photographic materials.

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 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 mixed crystals of substantially pure barium sulphate and substantially pure lead sulphate fluoresce under the influence of X-rays or gamma-rays to a very much greater degree than do either of such substances alone and that they may be employed as the fluorescent material in fluorescent screens. It has, further, been discovered that by appropriate methods, these mixed crystals can be prepared in a form such that when a screen incorporating them is subjected to the influence of X-rays generated at the kilovoltages employed for medical purposes and higher kilovoltages, e. g., 40–100 k. v. p. or more, the screen has a higher intensification factor than the known fluorescent screens incorporating calcium tungstate in similar quantity.

By the term "mixed crystals of barium sulphate and lead sulphate" is meant crystals which contain both these substances in solid solution and not merely a mixture of separate crystals of the substances. The term is not, however, intended to exclude the case in which there may be present in admixture with the mixed crystals a small proportion of separate crystals of one or both of these substances.

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 in the present invention, and it is preferable that the reagents should have an even higher degree of purity than is required by these standards. In particular, it is generally desirable that the reagents should be free from even minute amounts of iron, manganese, chromium and copper (and to a lesser degree, nickel, cobalt, silver, arsenic, antimony and silica) as these impurities tend to affect the fluorescent properties of the final product and frequently reduce its value for radiographic purposes. However, it is permissi-

ble 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 mixed crystals of substantially pure barium sulphate and substantially pure lead sulphate distributed in one of the 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 fluorescent layer may be carried on a single support layer, e. g., of paper or cellulose film, as a unit. In this case the fluorescent material may be incorporated in a carrier layer situated between the support layer and the emulsion layer, or may be incorporated in the emulsion layer or the support layer.

The invention also includes a method for the production of mixed crystals of substantially pure barium sulphate and substantially pure lead sulphate suitable for use as the fluorescent substance in an intensifying screen which comprises the step of firing a mixture of these substances at a temperature above about 600° C., and preferably above 700° C., e. g., 850–1050° C., or even higher, e. g., up to 1150° C.

In carrying out the method just described the lead and barium sulphates may be first formed by double decomposition from separate solutions, and the sulphates then mixed together in the desired proportions (e. g., by grinding together in a mortar) and subjected to the firing step to produce the fired, mixed crystals.

The optimum temperature of the firing treatment and the optimum duration of that treatment are inter-related and depend on the constitution of the material under treatment. By varying the conditions, products having intensification factors exceeding 30, 50 or even exceeding 100 may be prepared. For example, products having intensification factors exceeding 100 may be prepared by heating a mixture containing 5–20% of lead sulphate and 95–80% barium sulphate at about 1000° C. for about 1 to 2 hours. Somewhat longer periods of firing do not materially affect the characteristics of this product though exceptionally long periods of firing, e. g., ten hours or more, usually have a deleterious effect. The firing treatment appears to increase the fluorescent properties of the product up to a maximum value after which further firing is either ineffective or is definitely deleterious. It is desirable, therefore, to ascertain for any particular mixture the optimum firing time at any particular temperature and not to exceed this optimum time. At lower firing temperatures the fluorescent properties of the products do not usually reach so high a value as at the higher firing temperatures, and it may be further noted that the lower the firing temperature employed, the longer is the time necessary to obtain the optimum results.

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

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

During the firing operation some sintering of the mixture may occur and if this occurs it is desirable to grind the product in a mortar (if desired, wetted with water) before employing it for the production of a fluorescent screen.

As indicated above by employing a mixture containing 5 to 20% of lead sulphate and firing at temperatures of the order of 1000° C. for one to two hours, products may be obtained which have an intensification factor exceeding 100. This intensification factor, and others given elsewhere in this specification and in the claims, are determined by the following method. A uniform layer of the fluorescent material in powder form, having a thickness equal to 20 grams 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.

It may be noted that under similar test conditions powdered calcium tungstate as used in the production of a modern fast commercial X-ray intensifying screen has an intensification factor of about 75.

As an alternative to the method of producing the mixed crystals by firing as described above, the mixed crystals may be produced by the method, which is also within the invention, which comprises the simultaneous precipitation of the lead and barium sulphates from a single solution by simultaneous double decomposition. Such mixed crystalline precipitates have intensification factors which exceed 15 and may exceed 30 and which are far greater than those of precipitated lead sulphate or precipitated barium sulphate alone. Such co-precipitated mixed crystal material is very suitable as a substitute for the normal "baryta coating" for paper coated with X-ray sensitive silver halide emulsions.

In general, however, it is desirable, especially when separate screens of high intensification factors are required, to subject the mixed crystals made by simultaneous double decompositions to a firing treatment as described above before use. In one example of the method of producing the mixed crystals by double decomposition, a solution containing soluble salts of lead and barium in the desired proportions is added to an excess of a solution of a soluble sulphate or sulphuric acid and the precipitate is filtered off,

washed and dried. If desired, the precipitate may then be fired to obtain a product having still better fluorescent properties. The nitrates of lead and barium (and of strontium and calcium if used) may be used as the soluble salts in the original solution and the precipitation is preferably effected by interaction with an alkali sulphate under neutral or slightly acid conditions.

If nitrates are used the amount of free acid present during precipitation must be kept low preferably not exceeding one-tenth normal, or there will be a tendency during subsequent firing of the products for lead oxides to be formed, resulting in discoloured products of relatively low intensification factor. If barium and lead chlorides or the corresponding acetates are employed, more acid conditions are allowable, but not necessary. The grain size of the precipitate increases with increasing acidity. Whatever reagents are used, they should all be of the highest degree of purity obtainable. The precipitated product should be washed thoroughly.

A third method of preparing the mixed crystals which is also within the invention and which is of value where products of only very low lead sulphate content are required, is to treat pure dried barium sulphate (produced, for example, by double decomposition) with a solution containing the desired quantity of lead sulphate, to re-dry the barium sulphate without washing it, and then to fire the product.

The intensification factors of the unfired mixed crystals depend to a considerable extent on the particular lead and barium reagents chosen on the conditions such as concentration and temperature, during precipitation of the lead and barium sulphates and, both for the unfired and fired products, on the care exercised in removing any excess reagents and by-products of the reaction.

The component sulphates may be present in the mixed crystals of barium sulphate and lead sulphate in widely varying relative proportions. However, it has been found that, in general, higher intensification factors are obtained when the proportion of barium sulphate is high and that of lead sulphate correspondingly low. Thus, for example, products obtained from processes giving a theoretical proportion of from 2 to 20% of lead sulphate in the mixed crystals have been found to give particularly good results. However, the proportion of lead sulphate may be even lower, e. g., 1% or less, or may be considerably higher, e. g., up to 40%, or the lead sulphate may form the major constituent.

The following examples illustrate the production of fluorescent materials according to this invention:

Example 1

235 gms. of "Analar" quality barium nitrate and 25.5 gms. of "Analar" quality lead nitrate are dissolved in 1 liter of hot distilled water. 150 gms. of "Analar" quality sodium sulphate (anhydrous) are dissolved in 1 liter of 0.01 normal "Analar" quality nitric acid. Both solutions are filtered hot and heated to about 90–95° C. The mixed barium lead nitrate solution is then added to the sodium sulphate solution and the resulting precipitate is digested at the same temperature for about five minutes. The barium-lead sulphate precipitate is then allowed to settle and is filtered off. It is then transferred to 1 liter of hot distilled water and stirred for about ten minutes. The residue is filtered off and the process repeated. The barium-lead sulphate is finally filtered off by means of a suction filter, sucked as dry as possible and then dried at 90–100° C. The barium-lead sulphate may be used in this condition or it may be fired in a porcelain or alumina crucible (preferably lined with calcium sulphate) at 1000–1050° C. and then ground in a mortar to a suitable fineness.

Instead of the 150 gms. of "Analar" quality sodium sulphate referred to above there may be employed 140 gms. of "Analar" quality ammonium sulphate.

Example 2

220 gms. of "Analar" quality barium chloride ($BaCl_2.2H_2O$) and 25.5 gms. of "Analar" quality lead nitrate are dissolved in 1 liter of hot distilled water. 150 gms. of "Analar" quality sodium sulphate are dissolved in 1 liter of 0.1–1.0 normal "Analar" quality hydrochloric acid. The solutions thus prepared are filtered hot, care being taken that no lead chloride crystallizes from the barium-lead solution. The barium-lead solution is added to the sodium sulphate solution, both solutions being maintained at 90–95° C. Barium-lead sulphate precipitates and the subsequent operations are similar to those set forth in Example 1.

Typical products prepared by the methods set forth in the foregoing two examples were found to have intensification factors as follows:

Unfired	Fired at 1,000–1,050° C. for—				
	½ hour	1 hour	2 hours	4 hours	6 hours
45	90	100	110	110	90

As stated above, the intensification factor of the mixed crystal products depends inter alia on the relative proportions of lead sulphate and barium sulphate present. The variation of intensification factor with composition is illustrated in the accompanying drawing in which curve I relates to a mixed crystal material which has been subjected to firing at 1000–1050° C. and curve II relates to a mixed crystal material which has not been subjected to the firing treatment.

Percentages of lead sulphate greater than 30% are not shown but it may be stated that with increase in the proportion of lead sulphate beyond this figure there is a general falling off of the curves.

X-ray or gamma-ray screens incorporating the fired barium sulphate/lead sulphate mixed crystal product may be prepared by dispersing the product 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 barium sulphate/lead sulphate mixed crystal product may be used to form a fluorescent layer in a unit comprising the silver halide emulsion and a single support layer as de-

scribed 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 and then with or without drying the product coating a gelatino-silver halide emulsion of the type commonly employed for radiographic purposes on the top of the fluorescent layer. Alternatively, the fluorescent material may be dispersed in the silver halide emulsion itself.

Other arrangements of the unit, in addition to those mentioned above in which the barium sulphate/lead sulphate mixed crystal product is located between the support and the sensitive layer or in the support or the emulsion 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, 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 barium sulphate/lead sulphate mixed crystal product in a strippable material, e. g. collodion, may be coatted 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.

Owing to the insolubility of the barium sulphate/lead sulphate mixed crystal product in the usual photographic developing and fixing baths, unless it is coated on the surface and removed in the manner described above, the lead and barium salts remain in the finished radiograph and although this is a disadvantage for some purpose, 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 employed in this invention possesses many advantages. Thus it can be readily prepared having a very high 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. Since it can readily be obtained in micro-crystalline form the screens containing it as the active ingredient yield radiographs of very good definition with very short exposures.

Again, since the fluorescent material is cheap to produce and unlike zinc sulphide has no tendency to affect silver halide emulsions delteriously 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 only. Also screens made in accordance with the present invention are highly resistant to deleterious action on their fluorescent properties by water especially if the fluorescent material consists mainly of barium sulphate.

What we claim is:

1. Process for the production of material adapted to fluoresce strongly under the influence of X-rays and gamma-rays which comprises forming mixed crystals of substantially pure barium sulphate and substantially pure lead sulphate.

2. Process for the production of material adapted to fluoresce strongly under the influence of X-rays and gamma-rays which comprises forming and precipitating mixed crystals of substantially pure barium sulphate and substantially pure lead sulphate by the simultaneous double decomposition of soluble salts of barium and lead contained in a single solution by treatment of such solution with a solution containing sulphate ions.

3. Process for the production of material adapted to fluoresce strongly under the influence of X-rays and gamma-rays which comprises forming mixed crystals of substantially pure barium sulphate and substantially pure lead sulphate by heating a mixture of the said substantially pure sulphates to a temperature of 600–1150° C. for a period of at least half an hour.

4. Process according to claim 3, wherein the mixture is heated with a water-soluble flux and the said flux is thereafter dissolved out.

5. Process for the production of material adapted to fluoresce strongly under the influence of X-rays and gamma-rays which comprises forming and precipitating mixed crystals of substantially pure barium sulphate and substantially pure lead sulphate by the simultaneous double decomposition of soluble salts of barium and lead contained in a single solution by treatment of such solution with a solution containing sulphate ions, and thereafter subjecting the product to a heat treatment at 600–1150° C. for a period of at least half an hour.

6. Fluorescent material consisting essentially of mixed crystals of substantially pure barium sulphate and substantially pure lead sulphate.

7. Fluorescent material consisting essentially of mixed crystals of substantially pure barium sulphate and substantially pure lead sulphate, the proportion of the lead sulphate in the mixed crystals being from 2–20% by weight.

8. Fired fluorescent material consisting essentially of mixed crystals of substantially pure barium sulphate and substantially pure lead sulphate, the proportion of the lead sulphate in the mixed crystals being from 2–20% by weight, said material having an intensification factor exceeding 50.

9. Fired fluorescent material consisting essentially of mixed crystals of substantially pure barium sulphate and substantially pure lead sulphate, the proportion of the lead sulphate in the mixed crystals being from 2–20% by weight, said material being substantially identical with that obtainable by heating the mixed crystals to a

temperature of 600 to 1150° C. for a period of at least one-half hour.

10. A screen adapted to fluoresce under the influence of X-rays and gamma-rays which comprises a support and a layer which comprises essentially mixed crystals of substantially pure barium sulphate and substantially pure lead sulphate.

11. A screen, adapted to fluoresce under the influence of X-rays and gamma-rays which comprises a support and a layer which comprises essentially mixed crystals of substantially pure barium sulphate and substantially pure lead sulphate, the proportion of the lead sulphate in the mixed crystals being from 2–20% by weight.

12. A screen adapted to fluoresce under the influence of X-rays and gamma-rays which comprises a support and a layer which comprises essentially fired mixed crystals of substantially pure barium sulphate and substantially pure lead sulphate the proportion of the lead sulphate in the mixed crystals being from 2–20% by weight, said mixed crystals being substantially identical with those obtainable by heating the mixed crystals to a temperature of 600 to 1150° C. for a period of at least one-half hour.

13. 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 mixed crystals of substantially pure barium sulphate and substantially pure lead sulphate.

14. 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 mixed crystals of substantially pure barium sulphate and substantially pure lead sulphate, the proportion of the lead sulphate in the mixed crystals being from 2–20% by weight, and the whole combined to form a unitary product.

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DISCLAIMER

2,289,997.—*Frank Forster Renwick* and *Hardwicke Slingsby Tasker*, Ilford, England. PRODUCTION AND USE OF FLUORESCENT MATERIALS. Patent dated July 14, 1942. Disclaimer filed November 23, 1944, by the assignee, *Ilford Limited.*

Hereby enters this disclaimer to claims 1, 2, 6, and 7 of said patent.

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