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FLUORESCENT SUBSTANCES

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This invention consists in improvements in fluorescent substances, more particularly substances suitable for the production of fluorescent screens for X-ray purposes.

For the production of intensifying screens, such as are used in X-ray photography, it is necessary to have a substance which will fluoresce under the stimulation of X-rays and emit rays which affect the usual X-ray sensitive emulsions. It has long been known that a number of substances will fluoresce in the desired manner, but during the last twenty or thirty years calcium tungstate has been the only substance which has been successfully employed in practice for the manufacture of intensifying screens for X-rays, the fluorescent light emitted by calcium tungstate when stimulated by X-rays being very actinic to the usual X-ray emulsions, the colour of the emitted rays being mainly in the short wave region of the spectrum.

Among other substances which will fluoresce in the desired manner is suitably prepared zinc sulphide. It has long been known that, under the stimulation of X-rays, suitably prepared zinc sulphide will emit a bright blue fluorescence which is very actinic to the normal X-ray emulsions, and intensifying screens produced from zinc sulphide when properly prepared can be made faster than those produced from calcium tungstate, that is shorter times of exposure are required. The practical application of such zinc sulphide is described in two papers in the British Journal of Radiology, "A new and much more rapid intensifying screen allowing great alterations in Radiographic Technique" by Levy and West, Vol. VI, No. 62, page 85 and "A new fluorescent screen for visual examination" by Levy and West, Vol. VI, No. 67, page 404.

It is well known that the colour of the rays emitted by zinc sulphide when fluorescing is modified by the addition of cadmium sulphide and in the case of intensifying screens small proportions of cadmium sulphide can be added to blue fluorescing zinc sulphide without destroying the actinic character of the fluorescence. When referring to these compounds it has been usual to include zinc-cadmium sulphides under the generic term "zinc sulphide" and we wish it to be understood that where the term "zinc sulphide" is used hereafter in this specification and claims it is intended to include both simple zinc sulphide and zinc-cadmium sulphide.

All screens containing zinc sulphide produced up to the present have disadvantages in common which limit their use in intensifying screens for X-ray photography. They all display the phenomenon of after-phosphorescence, that is the screens emit radiations which affect the normal X-ray emulsions even after the stimulation with X-rays has been discontinued. They also display the phenomenon of persistence of latent image, which is a more or less temporary increase of their sensitivity to X-rays which occurs locally at those parts influenced by the X-rays so that when the screen has been employed for one exposure and is used again after an interval for a second exposure, a latent image of the former exposure persists in the screen. Secondary images due to both phenomena are liable to be reproduced together with the record obtained at a second exposure. These phenomena, limit the use of such screens in practice, for example for use in hospitals, as they can only be employed satisfactorily when fairly long intervals of time elapse between two exposures.

It is an object of the present invention to produce a fluorescent substance containing fluorescent zinc sulphide in which the after-phosphorescence and latent image phenomena are such (e. g. are of such short duration and/or low intensity) that they will not interfere with the repeated use of the screen in a series of exposures.

According to the present invention a fluorescent substance suitable for the production of screens for X-ray purposes comprises fluorescent zinc sulphide in a high state of purity, an activator (for example silver), and a proportion of not more than one part of nickel in five hundred thousand parts of zinc sulphide whereby undesirable after-phosphorescence and the retention of latent image are eliminated. It is further found that the action of nickel is still obtained when the zinc sulphide has cadmium sulphide mixed with it in order to modify the fluorescence.

Experience has shown that it is desirable to produce the zinc sulphide in a very high state of purity since many substances, if present even in minute traces, act as "poisons" and inhibit the production of suitable fluorescence. On the other hand it is desirable to add a small quantity of an activating substance to modify the qualities of the fluorescence produced. A suitable substance for use in accordance with the present invention is silver.

In applying the invention the zinc sulphide is carefully purified and then the activator, e. g. silver and the nickel are added and the whole heated to a very high temperature, for example 1200–1300° C. The nickel may be added in any convenient form but is preferably added as a

soluble salt, such as nickel chloride, and should be distributed as uniformly as possible before heating.

It is found that the addition of the nickel reduces the intensity of the fluorescence to a certain extent but that provided it is present in very minute quantities the intensity of the fluorescence is only slightly reduced compared to that obtained without the addition of the nickel. Any reduction in intensity is, however, more than compensated for by the fact that with screens made with the substances in accordance with the present invention the after-phosphorescence phenomena are of such a nature and/or of such short duration that after the normal interval between exposures they will not affect the usual X-ray sensitive emulsions.

As an example of the method of producing the fluorescent substances containing zinc and sulphur in accordance with the present invention, highly purified zinc sulphide (or zinc-cadmium sulphide) is prepared in known manner and a very small proportion of nickel is added to the precipitate itself. The exact moment of addition being immaterial provided it is prior to the heating of the sulphide. The activating substance, e. g. silver, is also added prior to the heating. The whole is then heated to a high temperature of approximately 1200–1300° C. in the usual manner. This heating step may be conducted, if desired, in the presence of a fusible salt such as sodium chloride.

The precise amount of nickel added is limited by the permissible reduction in fluorescence. About one part by weight of metallic nickel in one million parts by weight of zinc sulphide is found to be suitable. Higher proportions of nickel may be employed but it is found that one part in five hundred thousand is about the maximum proportion permissible, since any material excess over this will reduce the fluorescence to an undesirable extent. In practice just sufficient of nickel is added to give the desired effect. A proportion of nickel as low as one part in three million or even less may be employed but if too little nickel is added the actinic nature and/or duration of the after-phosphorescence and latent image is not sufficiently depressed.

Provided the correct amounts of nickel are added it is found that intensifying screens prepared from the substances in accordance with the invention reduce the time of exposure necessary as compared with the usual calcium tungstate screens, and in addition do not suffer to any appreciable extent from the disadvantages due to actinic after-phosphorescence and latent image which have been characteristics of all zinc sulphide intensifying screens previously produced.

Although the substances described are particularly suitable for use in the production of intensifying screens they may be employed for other purposes including the production of screens for visual examination with X-rays, for cathode ray tubes and the like.

We claim:—

1. A fluorescent screen for X-ray purposes made up from fluorescent material free from undesirable after-phosphorescence and the retention of latent image and containing fluorescent zinc sulphide obtained by precipitation in a high degree of purity as the essential fluorescent component and a proportion of not more than one part of nickel in five hundred thousand parts of zinc sulphide as the component which acts to eliminate the after-phosphorescence and retention of latent image.

2. A fluorescent screen for X-ray purposes made up from fluorescent material free from undesirable after-phosphorescence and the retention of latent image and containing fluorescent zinc sulphide obtained by precipitation in a high degree of purity as the essential fluorescent component and a proportion of nickel between one part in five hundred thousand and one part in three million parts of zinc sulphide as the component which acts to eliminate the after-phosphorescence and retention of latent image.

3. A fluorescent screen for X-ray purposes made up from fluorescent material free from undesirable after-phosphorescence and the retention of latent image and containing fluorescent zinc sulphide obtained by precipitation in a high degree of purity as the essential fluorescent component, a small proportion of an activator for activating the fluorescent properties of the zinc sulphide, and a proportion of not more than one part of nickel in five hundred thousand parts of zinc sulphide as the component which acts to eliminate the after-phosphorescence and retention of latent image.

4. A fluorescent screen for X-ray purposes made up from fluorescent material free from undesirable after-phosphorescence and the retention of latent image and containing fluorescent zinc sulphide obtained by precipitation in a high degree of purity as the essential fluorescent component, a small proportion of silver as a material for activating the fluorescent properties of the zinc sulphide and a proportion of not more than one part of nickel in five hundred thousand parts of zinc sulphide as the component which acts to eliminate the after-phosphorescence and retention of latent image.

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