May 9, 1950 J. H. SCHULMAN ET AL 2,506,749

X-RAY SENSITIVE SCREEN

Filed May 27, 1948

FIG. 1

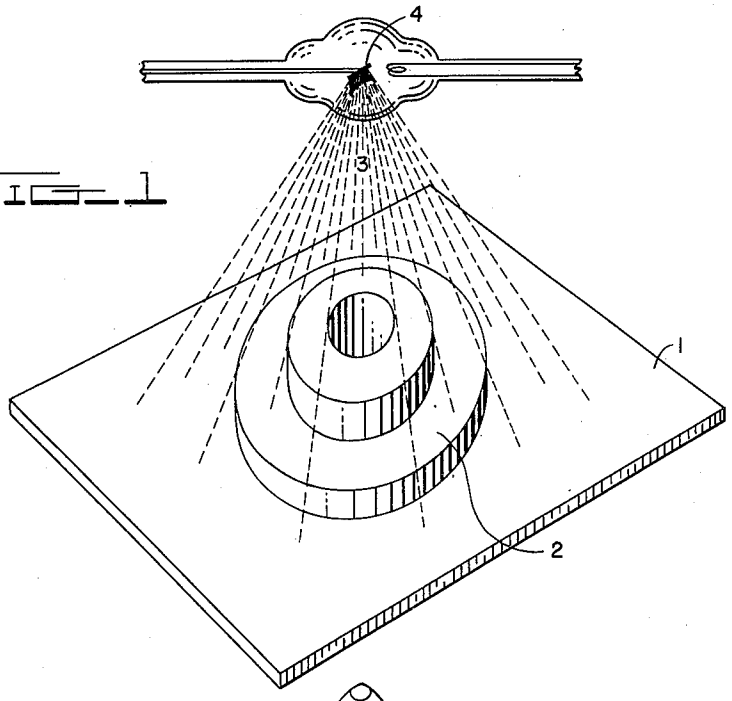
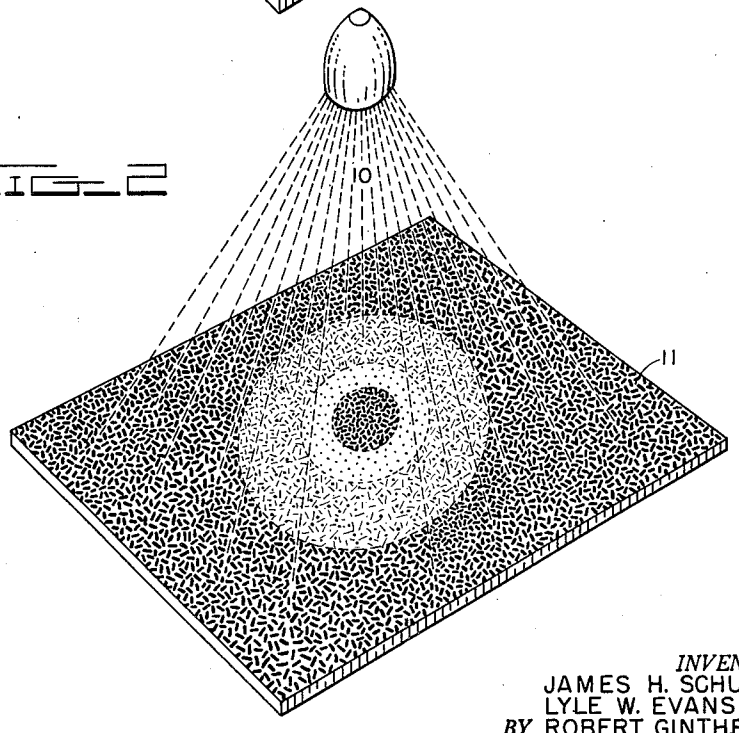


FIG. 2



INVENTORS
JAMES H. SCHULMAN
LYLE W. EVANS
BY ROBERT GINTHER
M. D. Hayes
ATTORNEY

Patented May 9, 1950 2,506,749

UNITED STATES PATENT OFFICE

2,506,749

X-RAY SENSITIVE SCREEN

James H. Schulman, Washington, D. C., Lyle W. Evans, Emporium, Pa., and Robert Ginther, Washington, D. C.

Application May 27, 1948, Serial No. 29,607

7 Claims. (Cl. 250—71)

(Granted under the act of March 3, 1883, as amended April 30, 1928; 370 O. G. 757)

1

This invention relates to the use of non-photographic chemical materials in the detecting and recording of high frequency radiation, such as X-ray and gamma ray radiation, and their applications to radiography and diffraction.

Certain materials, generically referred to as "phosphors," have been widely used for this purpose in X-ray work in conjunction with photographic plates or film.

In this latter capacity they emit actinic radiation as a direct result of simply being irradiated with X-rays and thereby augment the photochemical reduction brought about as primarily a function of the X-rays. Thus they act as "intensifiers" in that they reduce the amount of X-ray energy required for adequate film blackening and consequently the requisite exposure time or tube current. It may be pointed out that the phenomenon here involved is properly referred to as "fluorescence," rather than "phosphorescence" even though the radiation emitted is not necessarily visible. This is because the "luminescence" (broad usage) continues only during the period of exposure to X-rays whereas "phosphorescence" is a phenomenon operative after the primary radiation has ceased.

Another example of a "phosphor" is the "fluoroscopic screen" which is made of a closely related luminescent material differing only in that its emits radiation falling within the visible range of the spectrum and thus does away with the need for a photographic operation when only observation is desired.

Some phosphor materials after treatment with X-rays exhibit to varying degrees a true phosphorescence or after-glow in either the visible or invisible range. Recently phosphors have been developed in which the after-glow (which happens to be visible) can be retained for a considerable period of time, particularly at low temperatures. The radiation rate of these phosphors is increased by raising the temperature and also by subjecting the material to infrared radiation.

Thus it is seen that the prior art of phosphor materials is limited to cases where the luminescence is a direct result of the primary irradiation, whether said luminescence be concurrent with (fluorescent) or subsequent to (phosphorescent) said irradiation. In other words the phenomenon of luminescence follows immediately and necessarily as a result of the original excitation, and further treatment of any kind is one affecting only the rate of luminescent decay.

2

The present invention involves, on the other hand, not a process for altering the rate of the emission of absorbed radiant energy, but rather for permanently altering the physical nature of the affected materials (to which we shall apply, broadly, the term "phosphors") by means of one type of radiation in such a way that their characteristics under certain other radiations are clearly altered.

It is the general object of this invention to provide a method for detecting by means of one type of radiation the permanent changes brought about in certain phosphor materials by means of another type of radiation.

Another object is to provide a method of permanently affecting certain materials by X-ray or gamma ray radiation so that the effect can at any later time be detected by subsequent ultra-violet radiation treatment.

It is the particular object of the invention to provide a new and improved radiographic or diffraction technique wherein certain non-photographic phosphor material is permanently affected by X-ray or gamma ray radiation, differentially, according to the intensity of the transmitted or diffracted beam so as to form a "shadowgraph" (radiographic image) or diffraction pattern on the affected phosphor material, and subsequently irradiating said material with ultra-violet radiation to bring out said shadowgraph or pattern, negatively, through visible fluorescence of the unaffected portion of the screen.

The present invention consists in the process of treating certain phosphor materials with high-frequency radiation having a wave length between 0.001 Å. and 500 Å. such as X-rays or gamma rays, and thereby decreasing their luminescence under subsequent radiation treatment with a given ultra-violet radiation, said materials being strongly luminescent in the visible range under said ultra-violet radiation prior to exposure to said high-frequency radiation; in other words, the process of destroying some of the "ultra-violet luminescent responsivity" by means of X-rays. In all cases the material is originally visibly fluorescent under the particular ultra-violet radiation used.

In our co-pending application, Serial No. 29,606, filed of even date herewith, we have disclosed a type of phosphor material and a technique embodying its usage, in which ultra-violet responsivity is created by treatment with X-rays. Whether or not a material is originally

luminescent or non-luminescent under ultra-violet radiation may depend on the wavelength of said radiation. Thus, it is necessary to know the effect of a particular ultra-violet radiation on a particular phosphor prior to its exposure to X-irradiation, and to bring out the effect of said irradiation with the same ultra-violet radiation after exposure. Although there is probably for every phosphor an optimum ultra-violet wavelength at which the intensity of contrast is a maximum, any radiation under which an appropriate phosphor is originally luminescent (as in this application) or non-luminescent (as in our co-pending application) is operative.

In this invention a phosphor material which is normally luminescent (in the visible range) under a given ultra-violet radiation is reduced in the intensity of its luminescence upon being irradiated by high-frequency radiation having a wave length between 0.001 Å. and 500 Å., said reduction being proportional to the quantity of radiant energy reaching the phosphor material. Thus the invention constitutes a means of making negative radiographic images (shadowgraphs) or diffraction patterns of an opaque object.

An advantage of the invention is that a permanent record of the image or pattern is made without the employment of photographic means. The image or pattern, resulting from a permanent change in the nature of the phosphor material, is not susceptible to dissipation with time, temperature (except possibly at high levels), or to continued application of the ultra-violet radiation.

The phosphor material used in a preferred embodiment of this invention is a solid solution of salts of lead and manganese and at least one other salt wherein the Pb^{++}-Mn^{++} combination constitutes the "activator" ingredient. However, phosphors containing other "activators," for example, Sn^{++}, may be used. This phosphor material may be prepared by fusion together of the respective components and subsequent solidification, or by precipitation from a concentrated aqueous solution of said components. In the preparation of the lead-containing phosphors the precipitation method is preferred since volatilization may occur during fusion. The relative quantities are not critical, only a small amount of the "active" ion or ion combination being required to make a phosphor luminescent under ultra-violet radiation. The solid solution is ground mechanically (if prepared by fusion) to a particle size in the order of 200–300 mesh and applied to a suitable backing material to form a phosphor screen.

As an illustration of one way in which the process may be carried out the accompanying drawings are shown and the following procedure described:

A phosphor material is prepared by fusion or precipitation of a mixture of one part lead chloride, one part manganese chloride and fifty parts sodium chloride. The material is then ground and mounted on a suitable backing material. If it is now examined under ultra-violet radiation, for example 2537 Å., it will be seen that the material luminesces brightly emitting visible light. This particular radiation is desirable since it is conveniently produced (by "germicidal" lamps) and creates a strong luminescence in this phosphor.

The screen is then placed in the film position

1 in a radiographic assembly, Fig. 1, arranged for example, to X-ray a steel flange 2, and a high frequency radiation 3 such as from a tungsten target 4 operating at 30 kv. (0.5–1.0 Å.) is directed toward and through the flange. After exposure the phosphor screen is again examined, Fig. 2, under ultra-violet radiation 10 of wave length 2537 Å. and it is observed that the screen 11 has lost much of its luminescence and now is quite dark over the directly exposed areas. Furthermore, the loss of luminescence is proportional to the intensity of the X-irradiation reaching the screen. Of course, the practical value of such a technique lies in showing up differences in density in the X-rayed object, such as result from internal defects, rather than differences in thickness.

The above example is intended to be illustrative and not limitative of the invention except as to the extent defined in the herewith appended claims.

The invention described herein may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment of any royalties thereon or therefor.

What is claimed is:

1. The method of permanently reducing luminescent responsivity to a given ultra-violet radiation in a phosphor material originally responsive to said ultra-violet radiation, said material consisting essentially of a solid solution of one part each of a lead salt and a manganese salt and fifty parts of sodium chloride, comprising subjecting said ultra-violet responsive material to high-frequency radiation having a wave length within the range of 0.001 Å. to 500 Å.

2. In apparatus for the preparation of a permanent, negative with respect to luminescence, radiographic image or a diffraction pattern of an opaque object on a luminescent screen, the combination of a phosphor screen having an X-ray sensitive, fluorescent responsivity to a given ultra-violet radiation consisting essentially of one part each of a lead salt and a manganese salt and fifty parts of sodium chloride, ultra-violet radiation means providing said radiation, and high-frequency radiation means providing radiation having a wave length within the range of 0.001 Å. to 500 Å.

3. In apparatus for the preparation of a permanent, negative with respect to luminescence, radiographic image or a diffraction pattern of an opaque object on a luminescent screen, the combination of a solid solution of one part each of a lead salt and a manganese salt and fifty parts of sodium chloride mounted on a suitable backing material, ultra-violet radiation means providing a radiation having a wave length between 2400 Å. and 3000 Å., and high-frequency radiation means providing radiation having a wave length within the range of 0.001 Å. to 500 Å.

4. In the preparation of a permanent, negative with respect to luminescence, non-photographic, radiographic image of an opaque metal object upon a luminescent screen, the method comprising, placing in the film position in a radiographic assembly a phosphor screen luminescent under a given ultra-violet radiation comprised essentially of a lead salt and a manganese salt of about one part each and sodium chloride of about fifty parts, transmitting high-frequency radiation of a wave length within the range of 0.001 Å. to 500 Å. toward and through said metal object, thereby

permanently affecting said phosphor screen, and subsequently irradiating said permanently affected phosphor screen with said ultra-violet radiation to bring out, negatively, the image of said opaque object.

5. The method of detecting the permanent reduction in the luminescent responsivity of a phosphor material responsive to a given ultra-violet radiation brought about by exposure of said material to X-ray radiation, said material consisting essentially of one part each of a lead salt and a manganese salt and fifty parts of sodium chloride comprising subjecting said X-ray exposed material to said given ultra-violet radiation.

6. The method of evaluating the intensity of a high-frequency radiation of wave-length between 0.001 Å. and 500 Å. comprising, irradiating a quantity of phosphor material consisting essentially of one part each of a solid solution of a lead salt and a manganese salt and fifty parts of sodium chloride with an ultra-violet radiation having a wave-length from 2400 Å. to 3000 Å. to produce a given fluorescent response, irradiating a quantity of said phosphor material with said high-frequency radiation, and irradiating said irradiated quantity of phosphor material with said ultra-violet radiation to produce a different fluorescent response, the difference in the respective fluorescent responses being an evaluation of the intensity of the high-frequency radiation.

7. The method of preparing an image of a pattern of high-frequency radiation having a wave-length between 0.001 Å. and 500 Å., comprising, forming a permanent, invisible image of said pattern on an ultra-violet responsive, X-ray sensitive phosphor screen comprising essentially one part each of a solid solution of a lead salt and a manganese salt and fifty parts of sodium chloride mounted on a suitable backing material, by exposing said screen to said pattern, and forming a fluorescent, visible, negative image of said pattern by exposing said exposed phosphor screen to ultra-violet radiation having a wave-length between 2400 Å. and 3000 Å.

JAMES H. SCHULMAN.
LYLE W. EVANS.
ROBERT GINTHER.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,418,240	Curie et al.	May 30, 1922
2,213,138	Hayward	Aug. 27, 1940
2,247,112	Batchelor	June 24, 1941
2,360,326	Adrian et al.	Oct. 17, 1944

OTHER REFERENCES

"Luminescent and Tenebrescense as applied to Radar," by H. W. Leverenz, R. C. A. Review, vol. 8, No. 2, June 1946, Fig. 15.