Feb. 3, 1948. G. R. FONDA 2,435,436

CATHODE RAY TUBE SCREEN

Filed Dec. 18, 1943

Fig. 1.

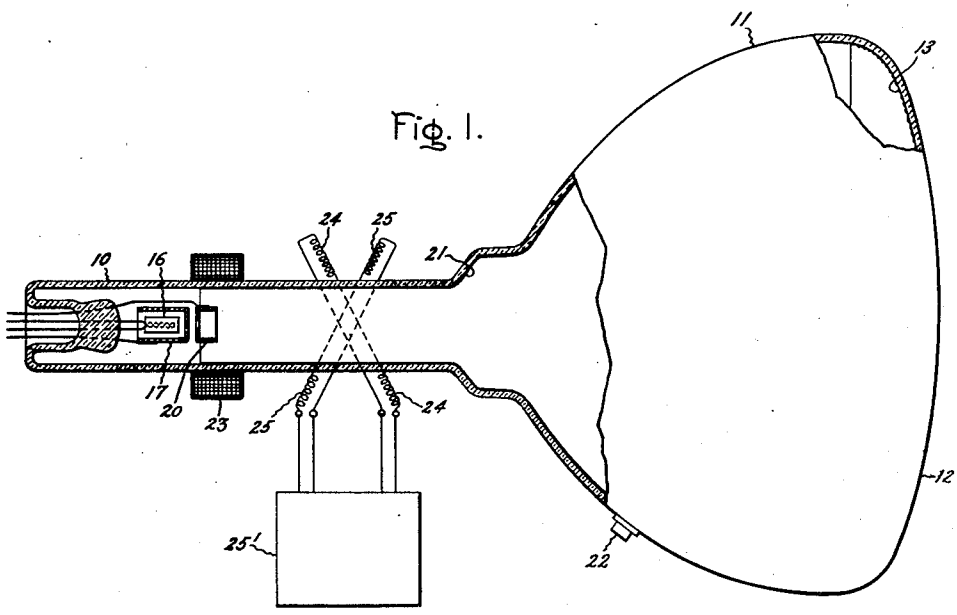


Fig. 2.

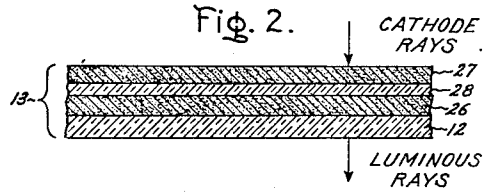
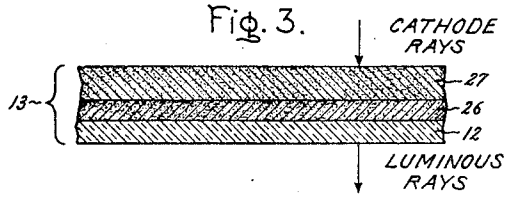


Fig. 3.



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CATHODE-RAY TUBE SCREEN

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Application Dec. 18, 1943, Serial No. 514,815

11 Claims. (Cl. 250—164)

1

The present application is a continuation-in-part of my prior application Serial No. 444,023, filed May 22, 1942, now abandoned.

The invention hereof relates to cathode ray tubes and more particularly to tubes adapted for use in indicating apparatus such as range-finding and direction-finding equipment.

One class of range- and direction-finding equipment functions by transmitting electromagnetic radiations and by determining the direction and time of return of such of these radiations as are reflected from the object whose location is to be ascertained. In equipment of this class, the cathode ray tube is a most useful tool for providing the required information concerning the reflected radiations. This result is obtained by causing the electron ray of the tube to produce on the tube screen a visible trace in a form which is determined directly by the radiations in question. However, in order to facilitate the interpretation of the information thus provided, and more especially in order to provide an indication of any change in the location of the object being considered, it is desirable that the trace produced on the tube screen persist for a longer time than is characteristic of conventional cathode ray tubes.

It is a primary object of the present invention to provide an improved form of cathode ray tube containing a duplex layer screen on which the luminous image will persist for a longer time and have greater brightness than obtainable from a conventional cathode ray screen consisting of any phosphor at present known.

The invention depends in part upon the observation that certain phosphorescent materials which exhibit a very rapid decay of phosphorescence upon direct excitation by electrons have a much longer decay period when excited by light of appropriate wave length, preferably ultraviolet or visible light at the short wave length end of the spectrum (e. g. blue or blue-green light). With this fact in view, the present invention provides a composite or stratified screen having a first component which is adapted to generate light of wave length lying within the excitation range of the second component when struck by an electron beam and a second component which develops upon excitation by light emitted by the first components, a visible phosphorescence which has longer persistence than could be obtained by direct cathode ray excitation as in a single layer screen. The components referred to are provided in a desired relationship by superimposing a layer of the material emitting

2

the exciting light over a previously formed layer of the material from which the visible radiations are to be produced. The arrangement is such that the first mentioned material is directly exposed to the cathode ray beam while the other material is so disposed that it may be viewed by an observer. In order that the viewed component may not present the confusing composite picture of a rapidly fading trace resulting from direct excitation by the electrons superimposed on a persistent trace, resulting from light excitation, it is desirable that the electrons of the cathode ray beam be prevented from reaching and exciting this component. Accordingly, in one embodiment of the invention the active screen layers are separated by a layer of an electron-absorbing material which intercepts the preponderance of electrons which pass through the exciting-light generating layer but which permits the passage of the exciting light rays. In a second case, the exciting-light generating layer is itself made sufficiently impervious to electrons to prevent electrons from reaching the viewed layer.

The features of the invention desired to be protected herein are pointed out in the appended claims. The invention itself, together with further objects and advantages thereof, may best be understood by reference to the following description taken in connection with the drawings in which Fig. 1 is a sectional view of a cathode ray tube suitably embodying the invention and Figs. 2 and 3 are enlarged fragmentary views illustrating alternative modes of applying the invention.

Referring particularly to Fig. 1 there is shown schematically a cathode ray tube comprising an elongated glass envelope which has a relatively slender stem portion 10 and an enlarged bulbous portion 11. The latter portion is provided with a window 12 through which an observer may view a luminescent screen applied to the inner surface of the window as indicated at 13. The nature of the screen will be explained in detail at a later point.

At the end of the envelope remote from the screen 13 there is provided an arrangement for generating a cathode ray beam (i. e. a concentrated stream of electrons). The means employed for this purpose may comprise any conventional type of electron gun and in the present instance is illustrated diagrammatically as comprising an electrically heated cathode 16 which is enclosed within a control or focusing cylinder 17. Adjacent the extremity of the cylinder 17 there is provided an apertured electrode or grid 20

which is adapted to be maintained at a positive potential with reference to the cylinder and which has the function of initially accelerating the electrons developed by the cathode 16 toward the screen 13. Final acceleration of the electrons is provided by a high voltage anode consisting of a layer of colloidally suspended graphite, or other appropriate conductive material, deposited on the inner lateral wall surface of the tube envelope as indicated at 21. A terminal connection for this conductive layer is provided by a lead-in conductor arrangement shown at 22.

Outside the discharge envelope and between the electrode 20 and the screen 13 there is provided a magnetic focusing coil 23. In addition, there are two sets of deflecting coils respectively indicated at 24 and 25. These are adapted to produce mutually perpendicular deflections of the beam in such fashion as to cause it to move over the surface of the screen 13. The nature of the deflection which is thus obtained is controlled by connecting the terminals of the coils 24 and 25 to a suitable controlling apparatus which is represented by a rectangular block 25' and which for present purposes may be assumed to comprise the elements of a range- and direction-finding equipment. Depending upon the nature of the potentials impressed upon the deflecting coils 24 and 25 by the equipment 25', the cathode ray beam may be caused to develop varying traces upon the luminescent screen 13, which traces may be interpreted by an informed observer in terms of the factors desired to be ascertained by the use of the equipment.

The duplex fluorescent screen 13, as shown in the enlarged cross-sectional view thereof, Figs. 2 and 3, comprises separate and distinct layers 26 and 27 of two different phosphors. In the case of the embodiment shown by Fig. 2, the phosphor layers are separated by an intermediate layer 28 of a material impervious, or substantially impervious, to electrons. The two phosphorescent materials as well as the intermediate layer are so selected that when the phosphor of the inner layer 27 is excited by the cathode ray beam, as indicated by arrows, it will emit light rays capable of penetrating layer 28 and exciting the phosphor comprising the outer or viewed layer 26 to produce luminous light rays as indicated by arrows. The phosphor 26, when consisting of copper-activated zinc-cadmium sulfide, emits a visible yellow-to-orange luminescence which persists for an appreciable time after excitation, that is, for a period of about 5 to 15 seconds. If for any reason a period of shorter persistence should be desired, this phosphor may be modified by the introduction of more cadmium to be luminescent for less that 5 seconds. Other phosphors may be similarly employed.

In general, by the term "long persistence" as used herein, I mean a persistence of luminescence long enough to be usefully interpreted by an observer, the luminescence ordinarily lasting for a period of several seconds rather than a period less than one second.

I have found that zinc-cadmium sulfide and zinc sulfide, when respectively employed in preparing layers 26 and 27, represent one combination of phosphors which meets the above requirements. The zinc sulfide, which is preferably activated by the presence of a small amount, for example about 0.01 per cent, of silver, emits rays in the blue and near ultraviolet region when excited by the cathode ray beam. For convenience the emitted rays will be referred to as blue light

and the phosphor as a blue phosphor. The zinc-cadmium sulfide for convenience will be referred to as the yellow phosphor. When excited by the "blue light," as stated, it emits a visible yellow luminescence of long persistence. A continuous falling-off of the brightness of luminescence occurs so that the persistence of luminescence is not sharply defined. The length of the period of useful brightness, however, can be readily observed.

Zinc sulfide phosphor activated with silver occurs in two crystalline forms, namely, (1) one form of this phosphor comprises crystals of hexagonal structure, and (2) another form of the phosphor comprises crystals of cubic structure. Either form of blue phosphor may be used for the purposes of my present invention, but the zinc sulfide phosphor comprising cubic crystals is preferred. Its more rapid responsiveness to cathode ray excitation (also expressed as faster rate of pick-up) as compared with the phosphor having hexagonal structure, renders it superior. A faster rate of pick-up results in more copious fluorescent emission of blue light after a brief excitation by a received impulse. A greater blue light emission, in turn, results in greater yellow light emission from the zinc-cadmium phosphor, that is, the resulting signal is brighter.

The blue phosphor, which consists of zinc sulfide activated with silver, may be prepared as follows:

A batch may be prepared consisting of 1000 grams of zinc sulfide, 0.129 gram of silver phosphate and 20 grams of sodium chloride. The ingredients are thoroughly mixed while dry and then transferred to crucibles consisting of fused quartz or other suitable refractory material. The ingredients then are subjected to a firing treatment in an atmosphere of nitrogen. Most suitably, an electric furnace is employed, the material being fired at about 950° C. for about two hours to produce the cubically crystalline form. The hexagonal form of the blue phosphor results when a mixture such as above-described is heated above 1040° C., as for instance at 1200° C., for about 20 minutes. After firing, the phosphor mix is broken up and washed free of chloride with distilled water, before being applied on a support such as the glass plate 12 of Figs. 2 and 3.

The zinc-cadmium sulfide composition found to be most useful for this purpose comprises from 10 to 30 per cent (preferably about 13 to 15 per cent) cadmium sulfide, and from 0.002 to 0.015 per cent (preferably about 0.008 per cent) of a copper activator. An increase in the cadmium sulfide content of any particular zinc-cadmium sulfide phosphor shifts the color of the emitted light to longer wave lengths and also extends the excitation range to longer wave lengths, thereby increasing the sensitivity of the phosphor to excitation by "blue light." However, the duration of phosphorescence becomes less with increasing cadmium content so that the maximum allowable content is determined by the length of time desired for the luminescence to persist.

The yellow phosphor, which consists of zinc-cadmium sulfide activated with copper, may be prepared as follows. A batch may be employed consisting of 870 grams of zinc sulfide, 130 grams cadmium sulfide and 0.19 gram of copper phosphate (or 0.313 gram copper sulfate) and 20 grams of sodium chloride. Such a mixture is fired at elevated temperature in an atmosphere

of nitrogen. Preferably, the firing is carried out in two lots, one being fired at 1000° C. for two hours and the second lot being fired at 1100° C. for two hours. This is done to produce materials of different grain size so that they may be more readily compacted.

Both the blue phosphor in either form and the yellow phosphor after firing preferably are silicized, that is, the phosphor particles are coated with a thin layer of silica. For this purpose the phosphor powder is treated with a dilute solution of ethyl silicate in alcohol, as by stirring the phosphor powder in such solution and then decanting the liquid. To the residual powder a dilute aqueous ammonia solution is added and heat is applied. Thereafter the phosphor is washed and dried. The silicizing reduces adherence of the phosphor powder particles, that is, the powder acquires greater "fluidity."

As an electron-impervious layer **28** I may use a film of an alkali silicate, such as sodium or potassium silicate. These substances have been found to act as barriers for the electrons of the cathode ray without materially interfering with the passage of the blue and near ultraviolet rays.

One method of applying these dual coatings which has been found to work exceptionally well involves the use of an alkali silicate, preferably a soluble potassium silicate, both as a binder for the respective phosphors and as an electron-impervious layer. A very thin film of a dilute water solution of the silicate, for example a 7 per cent solution, is sprayed in the form of a very fine spray on to the clean inner face of the window in an amount sufficient to wet the glass. The "yellow" zinc-cadmium sulfide phosphor is immediately dusted on to the wet film and the above steps repeated if necessary to obtain a yellow phosphor layer of the desired thickness. Good results are obtained when the layer **26** of yellow phosphor has sufficient thickness to comprise twelve milligrams of phosphor per square centimeter of phosphor area.

To provide an electron-shielding layer an additional coating or coatings or the same binder may be sprayed on top of the yellow phosphor coating and the tube is then baked, for example at 200° C. for 20 minutes, to set the binder.

After the tube has cooled, a "blue" zinc sulfide layer is applied over the electron-impervious layer employing the same procedure and binder used in forming the yellow phosphor layer. If desired, the final layer of zinc sulfide may be sprayed with a very small amount of the finely atomized binder to make sure that the zinc sulfide layer will adhere firmly and not come loose in the tube during use thereof. If this final coating is used, only a very small amount of silicate should be applied as otherwise this coating may prevent an appreciable percentage of the electrons from reaching the zinc sulfide phosphor. My invention, of course, is not restricted to any particular method of applying the phosphor coatings. The thickness of the layer **27** of blue phosphor of Fig. 2 in which the barrier layer **28** is present may be less than the thickness of the blue phosphor in Fig. 3 in which the electron-impervious layer is absent. Finally, the tube is again baked at 200 to 350° C., preferably with a filling of nitrogen for a time sufficient to set the silicate and to degas the carbon deposit **21**.

In the form shown in Fig. 3, the screen consists of a layer of zinc-cadmium sulfide applied directly to the window **12** but, instead of using a layer of sodium silicate to protect the zinc cadmium sulfide from the electrons, the bonded zinc sulfide layer is made sufficiently thick and dense to prevent appreciable penetration of the electrons therethrough. Good results are obtained when the thickness of the layer **27**, Fig. 3, contains eight milligrams per square centimeter of surface.

Although my invention has been described with particular reference to the preferred duplex screen comprising separate layers of silver-activated zinc sulfide and copper-activated zinc-cadmium sulfide, it is to be understood that it is not limited thereto. Acceptable, though less striking, results may be obtained, for example, by substituting a layer of copper-activated zinc sulfide phosphor which emits a green light for the copper-activated zinc cadmium sulfide "yellow phosphor" layer. Likewise, calcium tungstate which emits blue rays when excited by electron impingement, or lead-activated calcium silicate which emits rays principally in or near the ultraviolet region upon electron impingement thereon, may be employed in place of the silver-activated zinc sulfide "blue phosphor."

In actual operation a screen of the type I have described gives a clear visible trace which is a result of radiations received by the equipment **25'** (Fig. 1) over a short period of time. By proper interpretation of the rate and direction of growth and decay of this visible trace, the rate of change in location of the object causing the radiations, as well as the direction in which the object is moving, and even other information concerning it, may be quickly determined.

What I claim as new and desire to secure by Letters Patent of the United States is:

1. For use in a cathode ray tube having means for producing and deflecting an electron beam, a screen comprising a layer of silver-activated zinc sulfide phosphor exposed to the electron beam, a layer of copper-activated zinc cadmium sulfide phosphor exposed to the radiations emitted by the zinc sulfide layer on excitation thereof and a layer of alkali silicate between said phosphor layers protecting the zinc cadmium sulfide layer from electron impingment.

2. For use in a cathode ray tube having means for producing and deflecting an electron beam, a screen comprising a layer of silver-activated zinc sulfide adapted to be exposed to the electron beam, a layer of copper-activated zinc cadmium sulfide exposed to the radiations emitted by the zinc sulfide layer on excitation thereof and an intervening electron-shielding layer of an alkali silicate.

3. For use in a cathode ray tube having means for producing and deflecting an electron beam, a screen comprising a layer of silver-activated zinc sulfide exposed to the electron beam and of such thickness that it effectively intercepts substantially all electrons impinging upon it, and a layer of copper-activated zinc-cadmium sulfide exposed only to the radiations emitted by the zinc sulfide layer on electron excitation thereof.

4. A cathode ray screen comprising a foundation of transparent material, a phosphor comprising copper-activated zinc-cadmium sulfide thereon and a second phosphor superimposed thereon for generating ultraviolet and short wave radiations when excited by electron impingement, said latter phosphor having a sufficient thickness to effectively shield said underlying phosphor from electrons impinging on said second phosphor.

5. A cathode ray tube screen comprising a layer of a silver-activated crystalline zinc sulfide of

cubic form and emitting blue light in response to electronic excitation and a layer of a second phosphor which is shielded from electron impingement and which is adapted to produce visible luminescence of long persistence.

6. A cathode ray tube fluorescent screen consisting of the combination of a transparent support, a coating thereon of copper-activated zinc-cadmium sulfide, a second coating thereon of the cubically crystalline variety of silver-activated zinc sulfide superimposed on said first layer, said second coating having sufficient thickness to effectively shield the first coating from cathode rays impinging on the second coating.

7. A cathode ray long persistence fluorescent screen consisting of the combination of a transparent support, a first coating thereon of copper-activated zinc-cadmium sulfide phosphor containing about 10 to 30 per cent cadmium sulfide, and a second coating of phosphor superimposed on said first coating, said second phosphor coating being capable of emitting ultraviolet and blue light when excited by electron impingement, said second coating having sufficient thickness to shield said underlying first coating from electron impingement.

8. A cathode ray tube comprising the combination of an envelope providing a window, means in said envelope for generating a beam of electrons directed upon said window, a luminescent screen applied upon the interior surface of said window, said screen comprising a foundation layer of copper-activated zinc-cadmium phosphor containing about 13 to 15 per cent cadmium sulfide and a second layer of silver-activated zinc sulfide phosphor superimposed on said foundation layer being exposed to said beam of electrons and having sufficient thickness to effectively shield said underlying foundation phosphor layer from said electron beam.

9. A luminescent device comprising an envelope having a transparent window constructed to be viewed from the exterior thereof, a source of cathode rays within said envelope, a luminescent screen applied on said window and comprising at least two layers of unlike inorganic phosphors, one of such layers being superimposed on the other, the phosphor layer which is exposed to cathode rays consisting of silver-activated zinc sulfide, the underlying phosphor adjoining said window consisting of copper-activated zinc-cadmium sulfide which in response to short wave light radiation emitted by the overlying zinc sulfide phosphor emits radiation of longer phosphorescent persistence than is attainable by direct cathode ray excitation of said zinc-cadmium phosphor.

10. A luminescent device comprising an envelope having a transparent window constructed to be viewed from the exterior thereof, a source of cathode rays within said envelope, and a luminescent screen on the interior surface of said window facing said source and comprising at least two layers of unlike inorganic phosphors, one of such layers being superimposed on the other, the phosphor layer nearest said source which is exposed to cathode rays consisting of silver-activated zinc sulfide, and being of sufficient thickness to be substantially opaque to cathode rays impinging thereon, the underlying phosphor adjoining said window consisting of copper-activated zinc-cadmium sulfide which in response to short wave light radiation emitted by the zinc sulfide phosphor emits radiation of longer phosphorescent persistence than is attainable by direct cathode ray excitation of said zinc-cadmium phosphor.

11. A luminescent device comprising an envelope having a transparent window constructed to be viewed from the exterior thereof, a source of cathode rays within said envelope a luminescent screen on said window and comprising at least two layers of unlike inorganic phosphors, one of such layers being superimposed on the other, the phosphor layer which is exposed to cathode rays consisting of silver-activated zinc sulfide and being of sufficient thickness to be substantially opaque to cathode rays impinging thereon, the underlying phosphor adjoining said window consisting of copper-activated zinc-cadmium sulfide which in response to short wave light radiation emitted by the zinc sulfide phosphor emits radiation of longer phosphorescent persistence than is attainable by direct cathode ray excitation of said zinc-cadmium phosphor and means for substantially excluding from observation light emitted by said zinc sulfide phosphor.

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