Feb. 20, 1951 B. S. ELLEFSON 2,542,122

LUMINESCENT MATERIAL AND METHOD OF MANUFACTURE

Filed Aug. 13, 1945 3 Sheets-Sheet 1

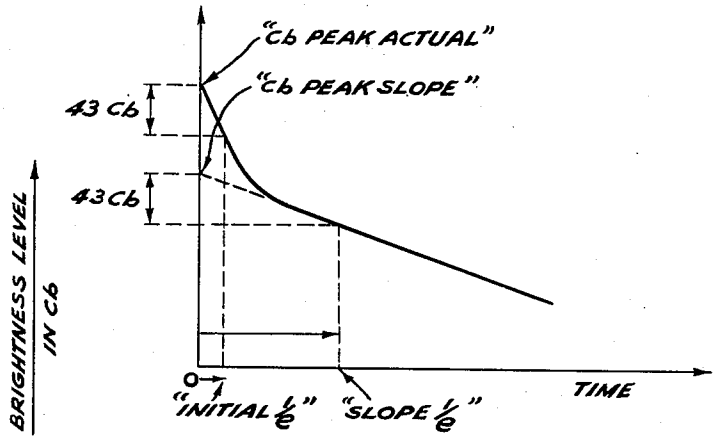


FIG. 1

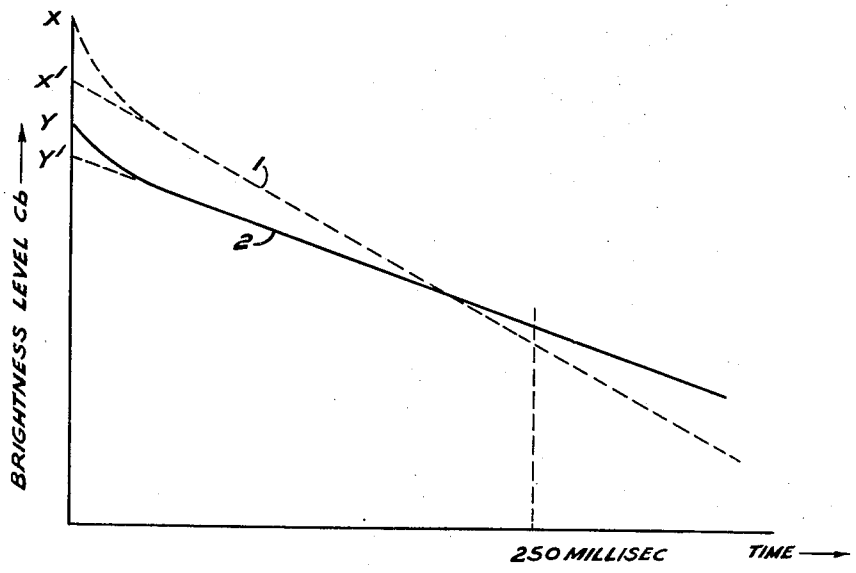


FIG. 2

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LUMINESCENT MATERIAL AND METHOD OF MANUFACTURE

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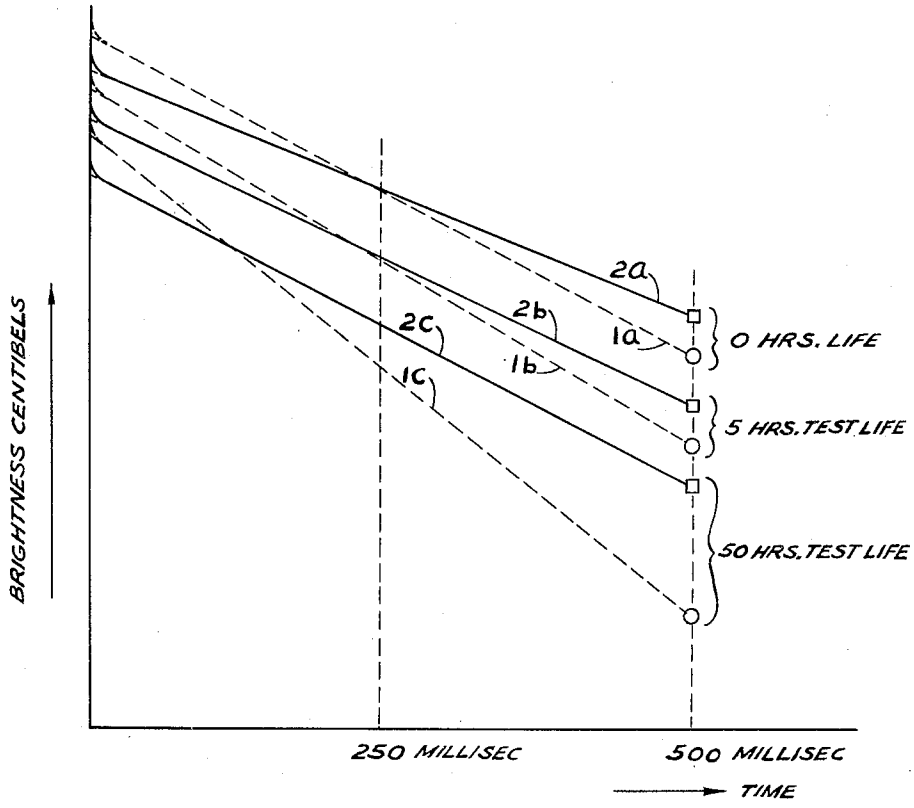


FIG. 3

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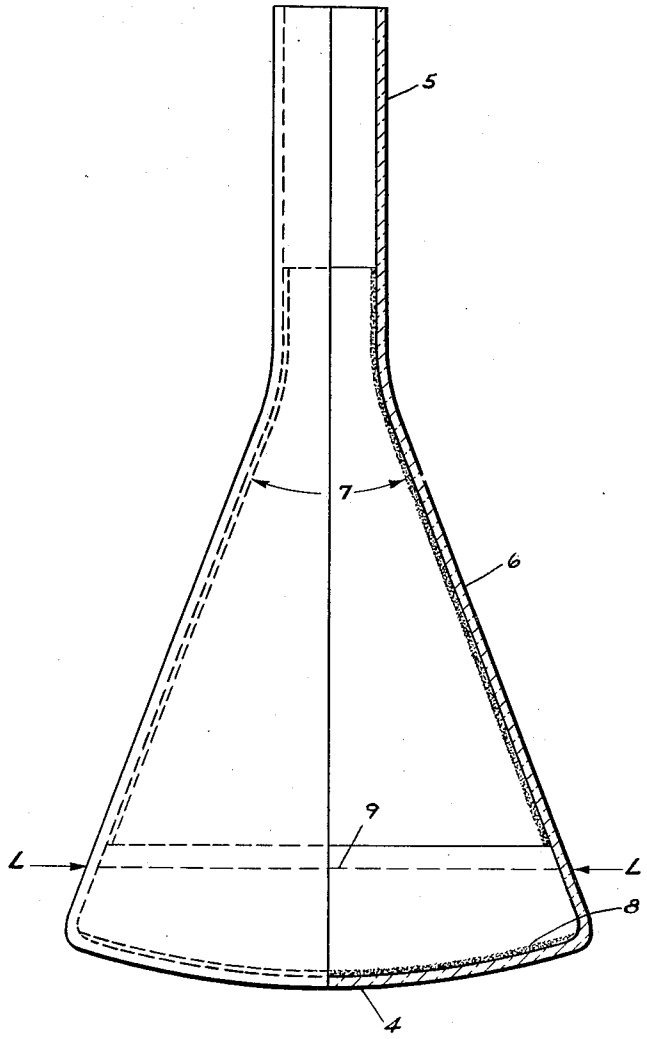


FIG. 4

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UNITED STATES PATENT OFFICE

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LUMINESCENT MATERIALS AND METHOD OF MANUFACTURE

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6 Claims. (Cl. 252—301.6)

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My invention relates to luminescent materials and more particularly to materials which have application in electronic devices which require a relatively long brightness-decay characteristic, such as cathode ray tubes and to a method of preparing the luminescent materials.

In certain applications, such as cathode ray tubes, it is desirable to employ a luminescent material which has a relatively long brightness-decay characteristic, that is, that the luminescent brightness after excitation by electron bombardment decreases below the threshold of visibility during a period of time of the order of one-half to one second after a particular standard excitation.

The ideal decay characteristic of such luminescent material subsequent to excitation would be a constant brightness with an instantaneous cut-off of light emission after the desired period, say about one-half second. The actual decay of light emission after excitation is, however, continuous, usually beginning with a very high intensity at the instant of excitation followed by a sudden decrease in brightness within a short period after excitation. The closest approach to the above ideal decay characteristic is one having essentially an exponential decay characteristic. Log brightness vs. time= straight line. Other materials having a decay characteristic in which log of brightness follows decay law of

$$\frac{1}{t^n}$$

(bimolecular decay) decay more rapidly initially but more slowly in the later stages of decay

Materials which have been used in the past having an exponential decay function include, for example, several luminescent silicate materials, and those having a bimolecular characteristic include several luminescent sulphides. Such materials, however, although they have a satisfactory stability, have not been employed successfully where a relatively long decay brightness characteristic is required for an approach to the above ideal type. Materials including fluorides have also been suggested as having the desirable brightness decay characteristic, but such materials in the forms that have been suggested have been relatively unstable and also difficulties have been experienced in applying these materials as a screen.

It is, therefore, an object of my invention to provide a luminescent material which has a relatively high stability, as well as a relatively long brightness-decay characteristic.

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A further object of my invention is to reduce the initial flash and to decrease the variations of decay characteristics with operational life under electron bombardment.

A further object of my invention is to reduce the discoloration experienced during the processing and heat treatment of the tubes in which the material is deposited for use in the form of a luminescent screen.

A still further object of my invention is to provide a method of producing the material of smaller crystal size without destroying its luminescent efficiency or changing its decay characteristics.

A still further object of my invention is to provide an improved method of processing the materials which results in an improvement of the desired decay characteristic.

Further objects and advantages of my invention will become apparent from the following description referring to the accompanying drawing, and the features of novelty which characterize my invention will be pointed out with particularity in the claims annexed to and forming a part of this specification.

In the drawing, Figs. 1, 2, and 3 illustrate brightness-decay characteristics which will be employed in a description of my invention, and Fig. 4 is a diagrammatic representation of a cathode ray tube to which my improved fluorescent screen material may be employed.

Referring to Fig. 1, I have illustrated by a characteristic curve what is meant by a brightness-decay characteristic, and in the figure a logarithmic function of brightness is plotted on the ordinate axis and time on the abscissa axis.

The brightness of a luminescent source may be expressed in terms of centibels (abbrveiated cb). This logarithmic unit is convenient to use in analogy to the decibel widely known for the characterization of noise in acoustics.

The conversion from the usual brightness units, viz., foot lamberts and millilamberts to the centibel unit is given by the equation X (foot lamberts) $=2.10^{y(cb)/100}.10^{-6}(1)$. As a foot lambert is equal to 1.076 millilamberts, a foot lambert is roughly equal to a millilambert. The threshold of visibility of the human eye (not adapted to perfect darkness) has been found to be about 0.2 microlambert, or very nearly equal to 0.2 millifoot lambert. According to Equation 1, 0.2 millifoot lambert corresponds to about 200 cb.

It is convenient to draw the brightness decay characteristics of a luminescent material as a function of time in a diagram in which the cb is plotted vs. time in milliseconds. The curves of Figs. 1, 2, and 3 are plotted in this reference system. The abscissa axis is the time (t) and brightness in centibels is measured along the ordinate axis.

In this scale of brightness the decay curve consists substantially of two parts connected by a curved portion: A first steep, approximately straight line portion, immediately following excitation. The intersection of this line with the cb axis (i. e., for $t=0$) is called cb peak actual. This is indicated in Fig 1 by the legend "cb peak actual."

The time constant of this section, i. e., time required for light to decrease by a value of

$$\frac{1}{e}$$

can be directly read in milliseconds as the abscissa of the point in which the continuation of the first steep line section intersects with a parallel to the time axis through the point on cb axis having the ordinate cb peak actual minus 43 cb. This time is called initial

$$\frac{1}{e}$$

It represents the period of time it would take to reduce the brightness of the flash to

$$\frac{1}{e}$$

of its value at excitation, as shown at the beginning of the time axis in Fig. 1.

The second part of the cb curve is again approximately a straight line of smaller steepness. This second straight line section begins after the short period of initial sudden decay and prevails for the relatively long portion of total decay time. The continuation of this line in the diagram intersects the cb axis in a point called cb peak slope, which is characteristic of each material. Finally, the

"slope $\frac{1}{e}$"

time constant is the abscissa of the point in which the second section of the cb vs. time curve intersects a parallel to the time axis through a point of the ordinate axis 43 cb below the cb peak slope. These points are indicated clearly in Fig. 1. This

"slope $\frac{1}{e}$"

time constant is the significant characteristic in comparing performance of materials.

As long as one is interested in the relative value of the time constant of different sections of the decay curve or of two decay curves representing different materials, it is only necessary to compare the curves in regard to their steepness. The steeper curve has the shorter time constant.

As I have already mentioned, various types of silicates have been employed and although they may be formed to produce a relatively stable screen, they have a relatively short time constant, while the fluorides which have been suggested as having a longer time constant have, in the form heretofore suggested, been relatively unstable.

I have found, however, that a relatively stable fluorescent material may be formed of the exponential type and having a relatively long time constant when the screen is formed of zinc magnesium fluoride, manganese activated. Thus, the addition of magnesium fluoride to a raw batch of zinc fluoride and manganese fluoride in certain preferred proportions and processed as will be described below results in luminescent materials which have the following characteristics as compared with the previously suggested luminescent zinc fluoride.

My improved materials are generally characterized by lower values of cb peak actual and of cb peak slope.

In Fig. 2, curve 1 represents (qualitatively) the decay characteristics of the known zinc fluoride material under standard conditions of excitation. Curve 2 represents the corresponding decay characteristics of my improved zinc magnesium fluoride having substantially equal proportions of zinc and magnesium fluoride and a relatively small percentage of manganese fluoride, that is, about 1.5%. Fig. 2 shows the higher values of cb peak actual (point X) and of cb peak (point X^1) of curve 1 as compared with the corresponding points Y and Y^1 of curve 2.

My improved materials are characterized by a higher value of initial

$$\frac{1}{e}$$

and of slope

$$\frac{1}{e}$$

time constant. As a result, the absolute value of their brightness, for example after 250 milliseconds following excitation, is higher. This results in a screen having lower flash and a higher level of brightness at time intervals of interest in connection with the observation of phenomena in which the repetition rate is of the order of two per second. The actual increase of

"slope $\frac{1}{e}$"

time constant obtained in my new material is about 20% to 25% above the value of that of the known zinc fluoride. Fig. 2 indicates the higher values of

"initial $\frac{1}{e}$"

and of

"slope $\frac{1}{e}$"

time constant of curve 2 as compared with curve 1, and the high brightness of the new material (curve 2) after about 250 milliseconds following excitation.

My improved materials undergo smaller changes in

"slope $\frac{1}{e}$"

time constant during a life up to 200,000 microcoulombs of bombardment by 4000 v. electrons (at a current density of 1.2 micro-amps./cm.^{2}). This compensates for the lower value of cb peak slope, thus still further reducing the undesirable flash and yet yielding a higher level of brightness after about 250 milliseconds following excitation.

Fig. 3 shows two sets of curves illustrating the variations of the decay curves with life. Curves

1a, 1b, and 1c were plotted from standard tests with a tube using a screen made of the known zinc fluoride; curves 2a, 2b, and 2c from similar tests with a tube made with a screen of my improved zinc magnesium fluoride material. As indicated in Fig. 3, the letter (a) refers to a test made at the beginning of the test life; letter (b) refers to a test made after about five hours of test life; and (c) refers to a test made at about 50 hours of test life. The life test is carried out with 4000 v. electrons at a current density of 1.2 micro-amps./cm.^{2}. It is estimated that one hour of test life corresponds to about 20 hours of operational life. Note the small change of the slope

$$\frac{1}{e}$$

of curves 2 with life, in contrast to the considerable change in slope of curves 1 in Fig. 3.

My improved materials can stand higher baking temperatures during exhaust and processing of the tubes in which they are used, without the discoloration usually occurring in this case with the known manganese activated zinc fluoride processed at the same temperature.

In the preparation of zinc fluoride various methods may be used. The following four methods have been tried out:

1. Precipitation reaction in aqueous medium between purified zinc sulphate solution and ammonium fluoride solution.
2. Precipitation reaction in aqueous medium between purified zinc sulphate solution and hydrofluoric acid solution.
3. Precipitation reaction in aqueous medium between suspension of basic zinc carbonate and ammonium fluoride solution.
4. Precipitation reaction in aqueous medium between suspension of basic zinc carbonate and hydrofluoric acid solution.

The sulphuric acid forming during the reaction of method 2 leads to an incomplete precipitation. In the reaction with ammonium fluoride, complex hydrated double salts are formed which must be removed by washing.

The precipitation of the fluoride from an aqueous suspension of the basic carbonate by hydrofluoric acid is completed in a rather short period of time, and the solubility of the precipitate is so low that good yields are obtained.

This method is advantageously applied, therefore, in the precipitation of the zinc fluoride and of the magnesium fluoride to be used as initial materials in preparing the mixtures for my new luminescent powders. The precipitation may be carried out in two ways: The zinc fluoride and the magnesium fluoride can be precipitated from separate suspensions of the corresponding carbonates with hydrofluoric acid. The basic zinc and magnesium carbonates may be suspended in the same aqueous medium in the desired proportions, and their fluorides are precipitated from the suspension with hydrofluoric acid.

Various proportions of zinc carbonate and magnesium carbonate have been tried out. A preferred proportion is such that in the final product substantially equal weights of zinc fluoride and magnesium fluoride are obtained. The activator is introduced in the form of manganese fluoride in the desired proportions. It may be added to the dried zinc and manganese fluoride powders by mechanical mixing and homogenizing by pebble milling or by mortar and pestle. If desired, the three fluorides may also be co-precipitated from an aqueous suspension of the carbonates by reaction with hydrofluoric acid, as described above for the co-precipitation of zinc fluoride and magnesium fluoride.

A preferred proportion of the three fluorides is such that, after firing, a mass is obtained the composition of which is 49.25 weight per cent of zinc fluoride, 49.25 weight per cent of magnesium fluoride and 1.5 weight per cent of manganese fluoride. The ratio of ZnF_2 to MgF_2 may be varied. Specifically, the MgF_2 content of the ZnF_2-MgF_2 mixture has been chosen as 3%, 5%, 10%, and 25% in some of my experiments, in addition to the 50% ratio designated above as the preferred ratio. It will be understood that these mixtures include the small amount of activator, the remainder being ZnF_2.

It has been found that additions of magnesium below about 50% do not produce the desired increase in time constant as is obtained with the screen as illustrated by curve 2 in Fig. 2. Increasing the magnesium content above 50% lowers the light level to a value below that indicated by curve 2 in Fig. 2. Thus it is desirable to employ magnesium fluoride in an amount of about 50% or within the range of 40% to 60%.

The proportion of MnF_2 may be varied between 1% and 5% in the three component powders. Proportions of MnF_2 lower than 1% or higher than 5% lead to reduced luminescent efficiency. After precipitation, the fluoride powder mixture is properly dried at a temperature low enough to avoid hydrolysis decomposition of the fluorides. Preferably the dried precipitates are milled before firing. The firing schedule is so chosen that small crystal sizes are obtained, but the temperature must be high enough to insure the proper formation of crystals. It has been determined that a temperature of 725° to 750° C. produces the desired results. Firing time depends on crucible size and charge. A satisfactory firing time for the charge contained in a covered 50 milliliter platinum crucible is 30 minutes.

The agglomerate crystalline particles of the fired mass can be broken by rod milling in an acetone medium without decreasing their luminescent efficiency. Finally the dried milled powder is passed through a 325 stainless steel sieve. It may then be applied with or without auxiliary binder as a screen to a cathode ray tube bulb simply by settling from either a suspension in non-aqueous media such as acetone or methanol or from water or aqueous solutions. The preparation conditions to yield powders satisfactory for good screen adherence are not as critical in the case of zinc magnesium fluoride, because the addition of magnesium fluoride produces a material of smaller particle size. I have also found that when employing my improved zinc magnesium fluoride in producing a screen that it is possible to use an aqueous medium from which the screen may be settled. Thus I have found that when employing zinc magnesium fluoride rather than zinc fluoride that the time in which the material may be in contact with the aqueous medium is sufficiently long that a desirable screen may be formed without any significant loss in brightness or decay characteristic.

The settling of screens from the suspension is carried out in the usual manner. The suspension is filled into a cathode ray tube bulb 3, see Fig. 4. The bulb rests on its viewing window 4, the acetone suspension is filled in through neck 5 up to a convenient level (L—L) of the conical part 6 of the bulb. Screen 8 is formed on window 4 by settling from suspension 9. The cath-

ode ray tubes can then be processed with the normal sequence of operations. In the event that a graphite conductive coating is applied to a part of neck 5 and of conical part 6 of bulb 3 after the screening operation, a satisfactory baking schedule consists of a prebake of one-half hour at 350° C. with a flow of dried air through the coated bulb followed by an exhaust bake of one half hour at 330° C. If a conductive coating such as silver has been applied and processed previous to the screening operation in which a non-aqueous medium without auxiliary binder is used, then the step of prebaking the screen may be eliminated.

Although I have shown and described particular embodiments of my invention, I do not desire to be limited to the embodiments described, and I intend in the appended claims to cover all modifications which do not depart from the spirit and scope of my invention.

What I claim is:

1. A phosphor composition for use in a cathode ray screen consisting of a manganese-activated mixture of zinc fluoride and magnesium fluoride.

2. A luminescent powder containing approximately 40 to 60 weight percent of magnesium fluoride, 39 to 59% of zinc fluoride and 1 to 5 percent of manganese fluoride.

3. A luminescent powder containing approximately 49.25 weight per cent of zinc fluoride, 49.25 weight per cent of magnesium fluoride and 1.5 weight per cent of manganese fluoride.

4. The method of making a luminescent material which comprises the steps: co-precipitating zinc fluoride and magnesium fluoride from an aqueous suspension of the basic carbonates of zinc and magnesium, by adding a hydrofluoric acid solution; drying the precipitate at a temperature below the hydrolysis and oxidation decomposition of the fluorides; adding a small percentage of manganese fluoride; homogenizing the resulting mixture by milling; firing the homogenized mixture at a temperature of about 725° C.; rod milling the fired mass in acetone as a vehicle; drying the milled powder and passing it through a 325 mesh sieve.

5. The method of preparing luminescent powders which comprises the steps: co-precipitating zinc fluoride, magneisum fluoride and manganese fluoride from a suspension of the basic carbonates of zinc and magnesium and of manganese carbonate in an aqueous vehicle by a precipitation reaction with hydrofluoric acid, drying the precipitate at a temperature below the hydrolysis and oxidation decomposition of the fluorides; firing the resulting dry powder at a temperature of approximately 725° C.; rod milling the fired mass in a non-aqueous vehicle; drying the milled powder and sieving it through a 325 mesh stainless steel sieve.

6. The method of producing a small crystal size luminescent material of the fluoride type having a luminescent decay time constant at least 20% higher than manganese activated zinc fluoride, which comprises the steps: preparing a mechanical homogenized mixture of purified zinc fluoride, magnesium fluoride and manganese fluoride, said mixture containing approximately 49.25 weight per cent of zinc fluoride, 49.25 weight per cent of magnesium fluoride and 1.5 weight per cent of manganese fluoride; firing the mixture at 725° C.; rod milling the fired mass in acetone as a vehicle; drying the resulting milled powder at a temperature below the hydrolysis and oxidation decomposition of the fluorides; and selecting from the dried powder the particles passing through a 325 stainless steel sieve.

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