Feb. 2, 1971 S. R. SHORTES 3,560,398

PHOSPHORS FOR COLOR DISPLAY SYSTEMS

Filed Dec. 2, 1966 2 Sheets-Sheet 1

FIG. 1.

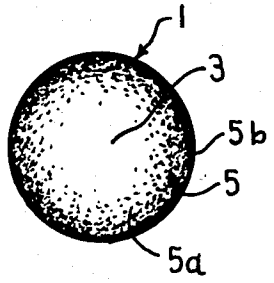


FIG. 2.

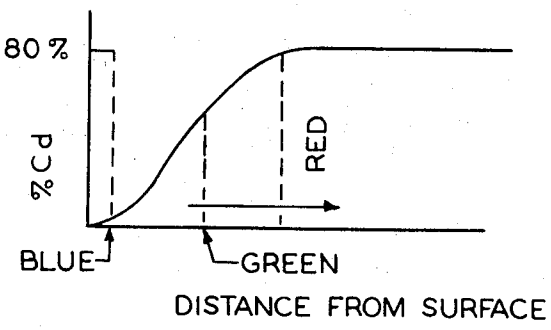


FIG. 3.

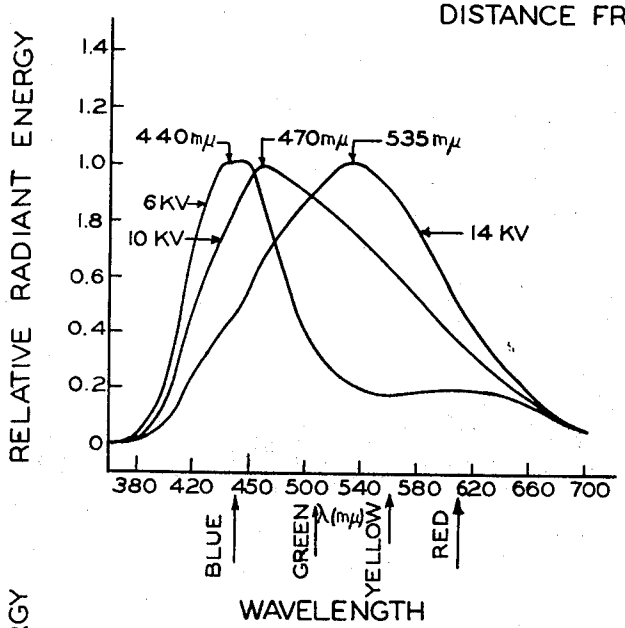


FIG. 4.

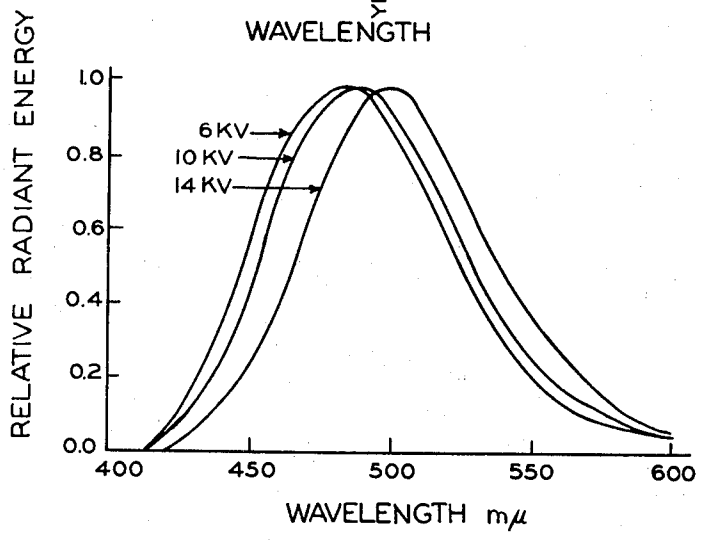


FIG. 5.

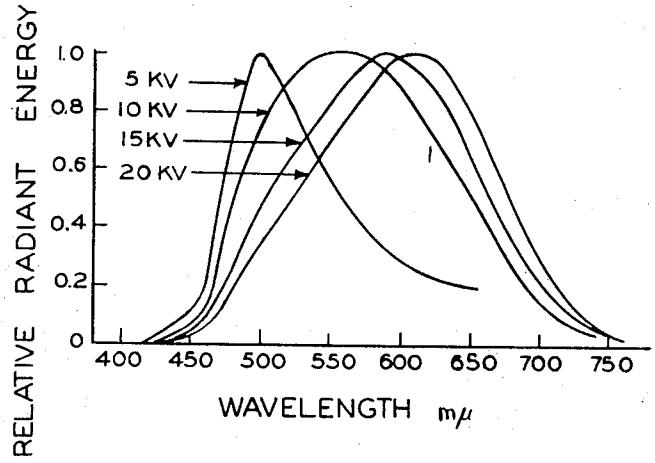


FIG. 6.

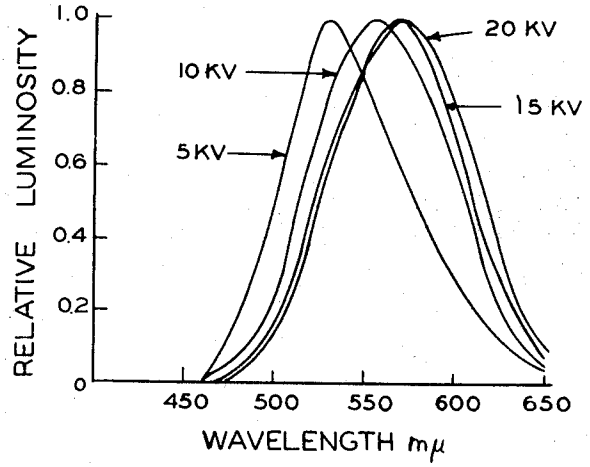
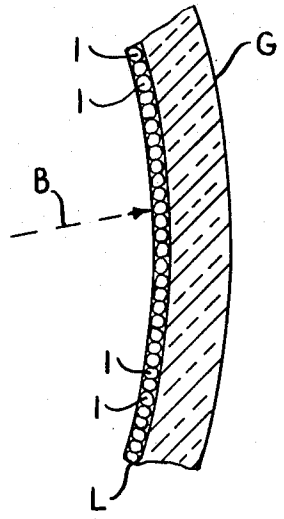


FIG. 7.



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PHOSPHORS FOR COLOR DISPLAY SYSTEMS

Samuel R. Shortes, Dallas, Tex., assignor to Texas Instruments Incorporated, Dallas, Tex., a corporation of Delaware

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U.S. Cl. 252—301.6 9 Claims

ABSTRACT OF THE DISCLOSURE

Disclosed are phosphor particles which emit light of different hues when energized by electrons of different energy levels, each particle being a compound phosphor material such as zinc cadmium sulfide (silver activated), having a core portion in which the constituents exist in a first ratio and having a surrounding outer surface portion in which the constituents exist in a second ratio different from the first, the constituent ratio varying gradually from the inner core portion ratio to the outer core portion ratio.

This inevntion relates to phosphors for color display systems, and more particularly to phosphor particles each of which will emit light of different hues when energized by an electron beam at different energy levels, and to methods for forming such phosphor particles.

Among the several objects of this invention may be noted the provision of phosphors for use in making viewing screens for color display systems in which image colors are controlled by varying the energy level or velocity of an electron beam; the provision of color display systems utilizing particles of a single phosphor which will selectively emit light of two or more different hues when energized by electrons at two or more different energy levels; the provision of phosphor particles each of which will emit light of different hues when energized by electrons having different energy levels; and the provision of simple, economical and reliable methods of making such phosphors. Other objetcs and features will be in part apparent and in part pointed out hereinafter.

Briefly, this invention is directed to phosphor particles which will emit light of different hues when energized by electrons of different energy levels. Each of the particles is an integral body having a core portion and a surrounding outer surface portion. The core portion comprises a composition of at least three different elements in a predetermined ratio, while the outer portion comprises a composition in which the ratio of the elements varies gradually from the predetermined ratio to a substantially different one. An example of a useful phosphor is zinc sulfide-cadmium sulfide (silver activated) in which the core composition of the particles is constituted by compounds of at least two different metals (zinc sulfide and cadmium sulfide) in a predetermined ratio, and the outer portion of integral phosphor particles has a ratio of zinc sulfide to cadmium sulfide which gradually increases from a minimum ratio at the core portion to a maximum at the surface of the outer portion. Also encompassed by this invention are color display system viewing screens composed of such phosphor particles and methods of forming such particles. These methods involve treating phosphor particles which emit light of one hue when energized by electrons at different energy levels to form phosphor particles which emit light of different hues when energized by electrons at different energy levels. In accordance with these methods the untreated particles are heated to a temperature at least equal to the lowest temperature at which one of said metals vaporizes, and the heating is carried out in an atmosphere which is inert relative to the elements and their compounds.

The invention accordingly comprises the products and methods hereinafter described, the scope of the invention being indicated in the following claims.

In the accompanying drawings, in which several of possible embodiments of the invention are illustrated,

FIG. 1 is a schematic representation on a greatly enlarged scale of a phosphor particles of the present invention;

FIG. 2 is a graphical representation interrelating certain significant physical and chemical characteristics of the phosphor particles;

FIGS. 3–5 are graphs illustrating light output of the phosphor particles as a function of wavelength or hue at various electron energy levels;

FIG. 6 is a graph illustrating the luminosity characteristics of an originally red-light emitting phosphor which has been treated by the method of the present invention; and

FIG. 7 illustrates a portion of a viewing screen of a color display system employing phosphor particles of this invention.

Corresponding reference characters indicate corresponding parts throughout the several views of the drawings.

In recently devolped color display systems, electron viewing screens are employed which include phosphor particles of different color light-emitting characteristics and which are respectively differently responsive to electrons of differing energies or velocities. In such systems, the viewing screen includes a first phosphor (e.g., one which emits light of relatively long wavelengths such as red) which is energized to emit light when struck by electrons having at least a first predetermined velocity or beam energy level, for example, accelerated by a kinescope accelerating voltage of perhaps 10 kv., this being the operating voltage for the red phosphor, although the phosphor turns on or begins to emit light at much lower voltages. The viewing screen also includes particles of a second phosphor, e.g., one which emits a substantial level of a second color light of shorter wavelengths, and preferably complementary in color to that of the first phosphor (such as a cyan colored light), when energized by electrons having at least a second and higher predetermined velocity, e.g., 15 kv., this being the operating voltage for the second phosphor. That is, while the second phosphor begins to emit light at a lower voltage, perhaps at 10 kv., a substantially higher voltage is used to achieve the required light level. If a beam of electrons of the lower velocity, 10 kv., is current modulated in accordance with the red record represented by the red color information signal derived in the receiver of any conventional color television receiver (such as those operating in accordance with the NTSC, SECAM or PAL systems), a red color image corresponding to the red records is presented on the viewing screen of the kinescope. At electron velocities of 10 kv., the second or cyan light-emitting phosphor will not be significantly energized to emit light, although it may be just turning on. By current modulating a beam of electrons having a beam energy of 15 kv. with the green record represented by the receiver's green color information signal, both the first and second phosphors will be concurrently energized to produce a white or substantially achromatic light. Thus red and white images are produced on the viewing screen either continuously or alternately, by two electron beams moving in registry in a raster scanning pattern across the viewing screen. These images combine to form a composite image which subjectively appears to include a full range of hues including those which are not actually present in a colorimetric sense. Such a two-color system of presenting full color images is known in the art and provides images of pleasing appearance in which the hues appear

more saturated than would be expected. Such a system is described in further detail in the copending and coassigned application Ser. No. 452,299, filed Apr. 30, 1965, now Pat. No. 3,371,153.

To obtain an even more desirable color display, a viewing screen is employed which also includes particles of a third phosphor having a higher beam energy threshold, e.g., one which emits a substantial level of light of a third color (e.g., blue) when energized by electrons having a higher velocity, e.g., 20 kv. As above, the third phosphor may begin to turn on at a lower voltage, perhaps at 15 kv., but much higher voltages are needed for an operating light level. A beam of such an energy level, modulated in accordance with the blue record represented by the blue color information signal of the television receiver, will energize all three phosphors and produce a third image of cooler achromatic light, and provide a composite image of particularly pleasing color. A more detailed description of such systems may be found in the copending and coassigned application Ser. No. 450,705, filed Apr. 26, 1965, now abandoned.

It will be noted in the preceding example that the second phosphor may be considered to have a "barrier" of 10 kv., while the third phosphor has a barrier of 15 kv.

In copending application Ser. No. 459,582, filed May 28, 1965, now Pat. No. 3,408,223 the methods more particularly described individually coating the particles by physical deposition of a vapor phase material on the surfaces of the phosphor particles. This provides an effective electron retarding barrier layer. In copending application Ser. No. 561,815, filed June 30, 1966, an improved method was disclosed for forming phosphors which are differently responsive to electrons of different energy levels or velocities, and thus are particularly useful in the above discussed color display systems. However, in each of these applications particles of different phosphors were utilized to emit light of different hues when the respective types of phosphor particles were energized by electrons at different energy levels. In accordance with the present invention only one type of phosphor particle is employed to emit light of at least two different hues when energized by electrons at at least two different energy levels.

Referring now more particularly to the drawings, a phosphor particle **1** of the present invention is represented in a cross section view. The particle, which typically may range in size from about 8 or less microns to 18 or more microns in diameter, is constituted by an integral body of at least three different elements, e.g., compounds of at least two different metals, for example, a zinc-cadmium sulfide with an activator, such as silver. The particle has a core portion **3** in which the ratio of the compounds is a predetermined or preselected one, e.g., cadmium sulfide (80%) and zinc sulfide (20%) (silver activated). Surrounding core portion **3** is an outer portion **5** in which the ratio of the compounds varies gradually from the 80%–20% ratio to a different ratio in which the cadmium percentage is substantially reduced relative to that of the zinc. The increasing zinc percentage is represented in the integral phosphor particle **1** by the increasing concentration of dark particles as the outside surface is approached.

The physical and chemical nature of a typical phosphor particle **1** of this invention is represented graphically in FIG. 2 in which the varying concentration of cadmium sulfide and zinc sulfide is plotted versus the distance from the particle surface. This illustrates that in the core portion **3** the cadmium-zinc sulfide percentage is 80%–20% and when this portion of the particle is activated or energized by electrons of sufficient energy level the particle will emit light of a first hue, viz., red. In an inner zone **5***a* of portion **5** the relative concentration of cadmium is gradually reduced from 80% to another ratio, e.g., about 50% cadmium, and activation of this portion of the particle **1** by electrons at an appropriate energy level will cause emission of light of a second hue, viz., green. In an outer zone **5***b* of the outer portion **5** the cadmium concentration still further diminishes to approximately zero at the particle surface and, when energized by electrons at a relatively low energy level, light of a bluish hue is emitted.

In accordance with the methods of this invention, such novel phosphor particles are formed by treating phosphor particles, which emit light of one hue (e.g., red) when energized by electrons at different energy levels, to effect an out-diffusion of one of the elements at a temperature which is at least equal to the lowest temperature at which that one element will vaporize. It has been found that with cadmium sulfide-zinc sulfide (silver activated) phosphor particles such a temperature is about 350° C., although higher temperatures are usually preferred. As one specific example of such methods, red-light emitting phosphor particles, cadmium sulfide (80%)–zinc sulfide (20%) (silver activated), such as that commercially available under the trade designation #1100 from Sylvania Electric Products, Inc., and having a median particle size of about 16–20 microns, were heated for two hours in an atmosphere of dry hydrogen at a temperature of 700° C. in apparatus such as illustrated in FIG. 1 of my copending application Ser. No. 561,815, filed June 30, 1966, and described therein. During this heating it was observed that cadmium in an essentially elemental state was given off or removed from the particles and it would condense in relatively cooler areas of the apparatus. Sulfur was also removed from the particles. Although the mechanism is not precisely understood, it would appear that a dissociation of cadmium sulfide takes place, or in any event the cadmium vaporizes at temperatures of at least about 350° C. and diffuses outwardly from the particle, effecting a gradually diminished cadmium concentration in the outer portions of the particles.

These treated phosphor particles were applied in a thin layer L to a glass face plate G (FIG. 7) of a cathode ray tube to form a viewing screen of a color display system which may be scanned by a narrow electron beam B which is controlled to generate electrons at a different energy levels or velocities. The relative radiant energy of light emitted by the thus treated particles **1** is plotted in FIG. 3 versus the wavelength or hue of light emitted at three different electron energy levels, 6 kv., 10 kv., and 14 kv. It is to be noted that, with an electron beam having an energy level of about 6 kv., a bluish hue light was emitted while at a second increased electron beam energy level (10 kv.) a greenish hue light was emitted. At a third and higher beam energy level of 14 kv., a yellowish hue light approaching red was emitted. Thus the emission peak of the phosphor particles **1** is shifted to higher wavelengths as the accelerating voltage for the electron beam is increased.

Using green light-emitting phosphor particles, cadmium sulfide (52%)–zinc sulfide (48%) (silver activated), such as that commercially available under the trade designation #1220 from Sylvania Electric Products, Inc., the preceding example was repeated, heating these particles at a temperature of 650° C. for 30 minutes in wet hydrogen (hydrogen bubbled through water). The resulting emission characteristics of these treated particles are illustrated in FIG. 4, in this instance the curves being corrected or compensated for the response curve of the human eye. As green rather than red light-emitting particles were treated, and the time and temperature parameters were reduced relative to the previous example, the shift in wavelength was not as great as previously obtained with the same increase in accelerating voltages. In each of these examples it will be noted that a very low percentage of cadmium sulfide exists on the outer surface portion zones of the particles, the bluish hue of the light emitted indicating that this zone is preponderantly zinc sulfide (silver activated).

Red-light emitting phosphor particles were treated as described above in an atmosphere of dry hydrogen at 600° C. for four hours and the emissivity characteristics

of the resulting phosphor particles at four different beam energy levels are shown in FIG. 5. It will be noted that at low energy levels, such as 5 kv., the hue of the light emitted is in the blue-green region, while at higher electron electron energy levels, such as 20 kv., these integral treated particles emit light of a reddish hue. FIG. 6 illustrates the luminosity characteristics of originally red-light emitting phosphor particles after a similar treatment, the curves being corrected or compensated for the response of the human eye.

It will be understood that atmospheres, other than hydrogen and which are inert relative to the metals and their compounds which constitute the activated phosphor, may be used in accordance with this invention. For example, helium and argon may be employed as equivalents for hydrogen. Similarly phosphors comprising compositions of at least three elements, other than the zinc-cadmium sulfide particles, may be used in the practice of this invention, and equivalent activators other than silver may be employed. For example, a zinc sulfide-zinc selenium phosphor may be used and sulfur selectively removed in accordance with the present invention, the phosphor composition in this example being constituted by two nonmetals and one metal, but again the ratio of the elements would be graded from one value to another from the core portion to the outer particle surface. It will also be understood that the voltage energization levels are merely exemplary and may be varied widely.

Accordingly, the phosphor particles of the present invention, with their highly advantageous characteristics of emitting different colors or hues of light at different energy levels, are very useful in all types of color display systems. Thus only one type of phosphor particle need be used in fabricating the viewing screen of this invention and the hue of the light emitted is a function of the particular energy level of the electron beam, a relatively small change in this level producing a marked difference in the wavelength of the light produced.

In view of the above, it will be seen that several objects of the invention are achieved and other advantageous results attained.

As various changes could be made in the above products and methods without departing from the scope of the invention, it is intended that all matter contained in the above description or shown in the accompanying drawings shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. A phosphor particle which emits light when excited by an electron beam, comprising:

a compound of at least three elements including cadmium, zinc and sulphur, said particle having an inner core and an outer surrounding surface,

said at least three elements defining a first ratio predominately cadium sulfide at said inner core, a second ratio at said outer surface having less cadmium sulfide than said inner core, and a gradually varying ratio changing from said first to said second ratio between said inner core and said outer surface,

whereby the hue of the light emitted from said particle is dependent upon the energy level of said electron beam.

2. Phosphor particles as set forth in claim **1** wherein the particles each comprise silver activated zinc sulfide-cadmium sulfide.

3. Phosphor particles as set forth in claim **1** wherein

the outer surface portion has an inner zone adjacent the core portion and in which the ratio of said elements varies gradually from said predetermined ratio to a second ratio, said outer surface portion having an outer zone adjacent the particle surface and in which the ratio of said elements varies gradually from said second ratio to a third ratio, said particles emitting light of a first hue when energized by electrons of a first energy level and emitting light of a second hue when energized at a second energy level higher than the first level and emitting light of a third hue when energized by electrons at a third level higher than that of said second level.

4. Phosphor particles as set forth in claim **3** wherein the particles each comprise a silver activated zinc sulfide-cadmium sulfide phosphor which emits light of a bluish hue when energized by electrons at said first level and emits light of a greenish hue when energized by electrons at said second level and emits light of a reddish hue when energized by electrons at said third level.

5. In a color display system for producing colored images, a viewing screen comprising integral phosphor particles each of which emit light of different colors when energized by electrons of different energy levels, each of said particles comprising zinc cadmium sulfide having a core portion predominately cadium sulfide and a surrounding outer surface portion of zinc cadmium sulfide having less cadmium sulfide than said core portion

6. In a color display system as set forth in claim **5**, said phosphor being silver activated zinc sulfide-cadmium sulfide and the ratio of the zinc sulfide to cadmium sulfide in the outer portion graduallly increasing to a maximum value at the outer surface thereof.

7. A method of treating phosphor particles which emit light of one hue when energized by electrons at different energy levels to form phosphor particles which emit light of different hues when energized by electrons at different energy levels, said particles each comprising a composition of at least three different elements including cadmium; said method comprising placing said particles in an atmosphere which is inert relative to said elements and compounds comprising said elements, and heating said particles to a temperature at least equal to the lowest temperature at which cadmium vaporizes to produce a cadmium gradient within said particle, decreasingly from the center of said particle outwardly to the surface thereof.

8. A method as set forth in claim **7** in which the phosphor particles are silver activated zinc sulfide-cadmium sulfide and the temperature is at least 350° C.

9. A method as set forth in claim **8** in which the inert atmosphere is hydrogen and the temperature is at least about 600° C.

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TOBIAS E. LEVOW, Primary Examiner

R. D. EDMONDS, Assistant Examiner

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