United States Patent

[11] 3,560,783

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a corporation of Delaware
Division of Ser. No. 561,815, June 30, 1966, Patent No. 3,449,148, which is continuation-in-part of Ser. No. 459,582, May 28, 1965, now Patent No. 3,408,223

[54] **COLOR DISPLAY SYSTEM UTILIZING PHOSPHORS HAVING AN ELECTRON RETARDING SURFACE LAYER**
2 Claims, 5 Drawing Figs.

[52] **U.S. Cl.** **313/92,** 252/301.6
[51] **Int. Cl.** **H01j 29/20**
[50] **Field of Search** ..... 252/301.6 (S), 301.4; 117/33.5; 313/92, 108

[56] **References Cited**
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3,371,153	2/1968	Matzen	313/92
3,408,223	10/1968	Shortes	252/301.4X
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ABSTRACT: Zinc sulfide containing phosphors are formed having a surface layer that retards electron penetration. The surface layer consists essentially of either zinc oxide or zinc sulfide formed in situ on the phosphor particles by chemical reaction. These phosphors are utilized in color display systems.

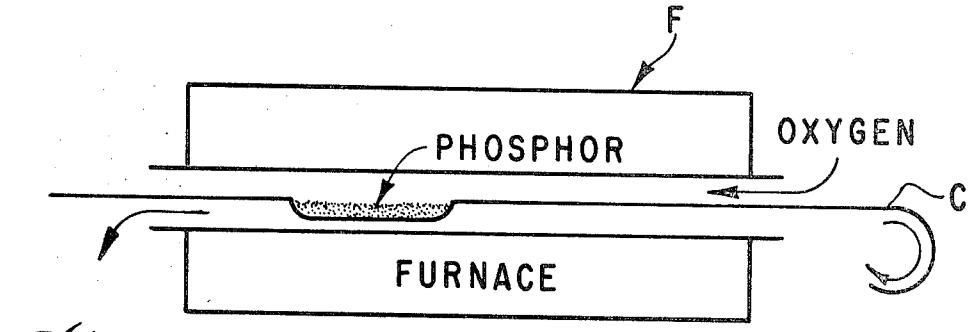


Fig. 1

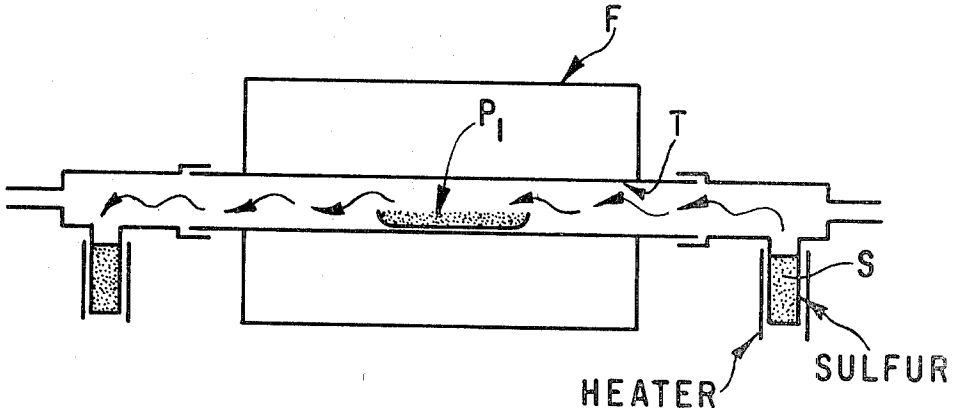


Fig. 2

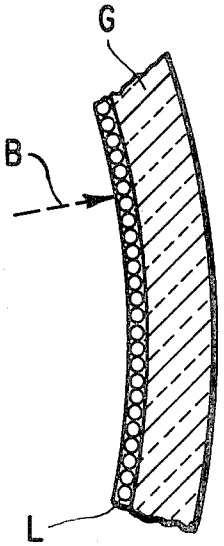


Fig. 5

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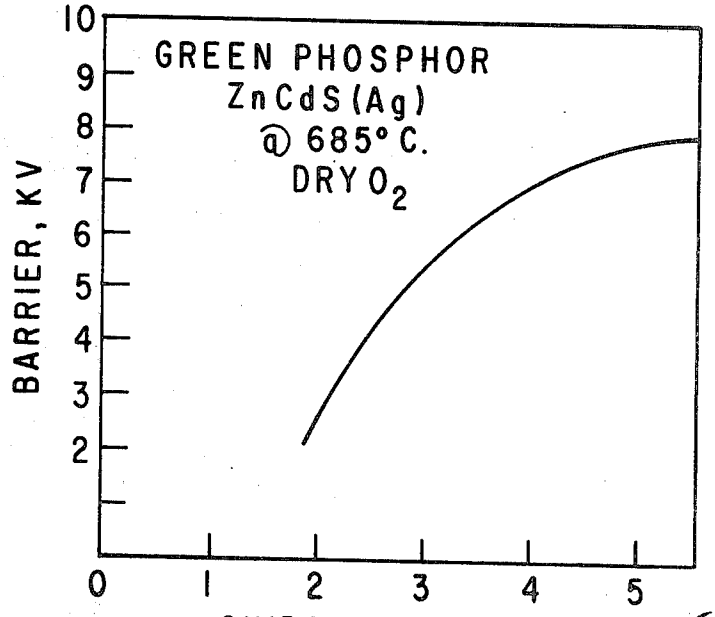

GREEN PHOSPHOR
ZnCdS(Ag)
@ 685° C.
DRY O_2
BARRIER, KV
10
9
8
7
6
5
4
3
2
0
1
2
3
4
5
OXIDATION TIME, HRS.

Fig. 3

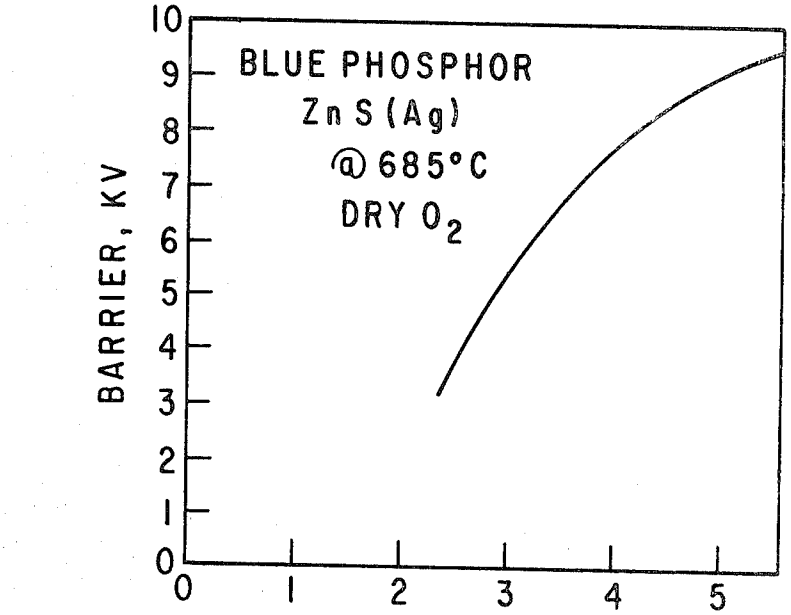

BLUE PHOSPHOR
Zn S (Ag)
@ 685°C
DRY O_2
BARRIER, KV
10
9
8
7
6
5
4
3
2
1
0
0
1
2
3
4
5
OXIDATION TIME, HRS.

Fig. 4

COLOR DISPLAY SYSTEM UTILIZING PHOSPHORS HAVING AN ELECTRON RETARDING SURFACE LAYER

This application is a division of application Ser. No. 561,815, filed June 30, 1966, now U.S. Pat. No. 3,449,148, which is a continuation-in-part of my copending U.S. Pat. application Ser. No. 459,582, filed May 28, 1965, now U.S. Pat. No. 3,408,223, for Phosphors for Color Display Systems.

This invention relates to phosphors for color display systems and more particularly to such phosphors which have increased electron energization thresholds and to methods for making such phosphors.

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 simple, economical and reliable methods of making such phosphors; the provision of such methods by which are formed on phosphor particles electron retarding surface barriers which are relatively independent of the size of the phosphor particles and the distribution of size thereof; and the provision of methods of the class described in which phosphor particles of different color light-emitting properties may be provided with closely controlled electron energization thresholds and which do not require exceptionally high voltage differentials for excitation thereof. Other objects and features will be in part apparent and in part pointed out hereinafter.

Briefly, this invention is directed to increasing the electron energization threshold of phosphor particles by heating said particles to an elevated temperature and exposing them to an atmosphere of a material which reacts in vapor phase with the phosphor particle to effect an in situ surface chemical reaction on the phosphor particle surfaces to form a surface barrier layer. Preferably the phosphor particles are zinc sulfide containing phosphors, such as zinc sulfide-cadmium sulfide (silver activated), and the vapor phase reactant material is oxygen, the resulting surface barrier layer thereby formed being essentially zinc oxide. It is desirable in certain instances to further react the surface barrier layer with a second material in vapor phase, such as sulfur or hydrogen sulfide, again at an elevated temperature, to form in situ a sulfide-containing barrier layer. Also encompassed by this invention are viewing screens for color display systems which include particles of a first phosphor which emit light of a first color when excited by a beam of electrons having a velocity of at least a first predetermined value, and particles of a second phosphor having a surface layer which constitutes a partial barrier to electrons whereby the second phosphor particles have a higher electron energization threshold than that of said first phosphor particles. The surface layers of these second phosphor particles comprise a compound formed in situ on the particle surface by chemical reaction of the second phosphor particle material with a compound in vapor phase and these second phosphor particles therefore emit a second color light when excited by a beam of electrons having a velocity of at least a second predetermined value which is greater than said first value.

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 illustrates apparatus for carrying out a method of the present invention for increasing the electron energization threshold of phosphor particles;

FIG. 2 illustrates similar apparatus for carrying out a second optional step in the methods of this invention;

FIGS. 3 and 4 are graphical representations illustrating the increased electron energization threshold values of colored phosphor particles as effected by methods of this invention; and

FIG. 5 illustrates a portion of a viewing screen of a color display system employing phosphor particles having increased energization thresholds.

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

In recently developed 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, acccelerated 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 record 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 U.S. 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 particular 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 preceeding 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., as these terms will be subsequently used.

In the aforesaid application Ser. No. 459,582, 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, but the methods and viewing screen phosphors of this invention have significant advantages

over such physical deposition methods and the phosphors thus formed in that the present methods are much simpler to carry out and may be controlled more easily to provide barrier layers of more precise characteristics and properties. Thus the present invention is directed to improved methods for forming phosphors which are differently responsive to electrons of different velocities (and thus are particularly useful in the above-discussed color display systems), and also to novel viewing screens incorporating such phosphors.

Referring now more particularly to the drawings, a furnace F is diagrammatically illustrated in FIG. 1, together with a carrier C for moving a body of phosphor particles through the furnace. The phosphor particles are heated to an elevated temperature and exposed to an atmosphere of a material such as oxygen which reacts in vapor phase with the phosphor particles to effect an in situ surface chemical reaction on the phosphor particle surfaces to form a surface barrier layer. In accordance with this invention particles of about 16—20 microns in size of a blue light emitting sulfide type phosphor, ZnS (silver activated) (such as commercially available under the trade designation 01320 by Sylvania Electric Products, Inc.) are moved slowly through furnace F, being heated to a temperature of about 650° C. while passing oxygen through the furnace. An electron retarding unactivated barrier layer of zinc oxide is formed in situ on each of these particles. This zinc oxide layer of semiconductor nature has a thickness and electron retarding properties which are a readily controlled function of the time which these phosphor particles are exposed to the oxygen atmosphere. If desired, the oxygen can be bubbled through water, the use of wet oxygen increases the oxidation rate.

This method provides excellent phosphor particles which have an increased energy threshold, but where, for example, green light-emitting rather than blue fluorescing phosphor particles are to have their energy thresholds increased it is preferable to subject these phosphor particles to a further processing step. This is because the zinc oxide barrier layer, having a somewhat yellowish cast, absorbs emitted light of the green fluorescing phosphors, or otherwise decreases the efficiency of the phosphor. This subsequent step is illustrated in FIG. 2 where furnace F is diagrammatically shown to include an enclosed tunnel T for maintaining an atmosphere of a sulfur-containing material in vapor phase in intimate contact with particles P_1 of the phosphors having a barrier layer of zinc oxide formed thereon. In this example, elemental sulfur S is heated and the vapors thereof are permitted to course through the tunnel T to effect an in situ exchange reaction to convert the barrier layer to a zinc sulfide containing barrier layer. An elevated temperature in the order of about 650° C. is employed in this step. The resulting barrier layer is white and does not significantly affect the color character of blue fluorescing phosphors.

The conveniently controllable methods described above for increasing the electron energization thresholds are more specifically exemplified by the graphs of FIGS. 3 and 4. The increase in energization threshold of phosphors in kilovolts is plotted against hours of reaction time in the furnace F in an atmosphere of oxygen. In FIG. 3 a green light-emitting phosphor, ZnS-CdS (silver activated), such as that commercially available under the trade designation 01220 from Sylvania Electric Products, Inc., and having a median particle size of 16—20 microns, was moved through furnace F at 2.2 feet/minute while exposed to oxygen introduced at a flow rate of 6 liters/minute, the furnace temperature being maintained at 685° C. Samples were removed periodically, and all samples were individually further exposed to an atmosphere of hydrogen sulfide for 2 hours at a temperature of 750° C. The zinc oxide barrier layer formed in situ by the first step and converted to a zinc sulfide-containing barrier layer in the hydrogen sulfide treatment is shown to give an easily controlled increase in the energization threshold relative to the untreated material.

The oxygen flow referred to above may be entirely O_2, or diluted O_2 may be used to control oxidation at elevated temperatures. To this end, the O_2 would be diluted with helium, nitrogen or argon. Also, as previously mentioned, either dry O_2, or wet O_2, bubbled through water, may be used.

The FIG. 4 graph similarly illustrates the increase in the energization threshold as a function of oxidation time for a blue light-emitting phosphor, as identified previously. In this instance, the oxidation temperature was maintained at 685° C. and the phosphor particles were moved at 2.2 feet/minute.

While temperatures of 685° C., etc., are mentioned above, it will be understood that the oxidation and sulfiding reactions can be carried out at temperatures of about as low as 400° C., although the higher temperatures are preferable.

Also, in accordance with this invention viewing screens for color display systems are advantageously made with such treated phosphor particles. For example, green or cyan light-emitting phosphor particles with such in situ formed barrier layers may be applied randomly mixed together with red light-emitting phosphor particles in a thin layer L (approximately one particle thick) to form a viewing screen on a glass face plate G, as illustrated in FIG. 5. The phosphor particles are quite closely packed so as to be directly subjected sequentially in small domains to a narrow electron scanning beam B. As each domain includes some of the red light-emitting phosphors and some of the cyan phosphors with an increased electron energization threshold, only the red phosphors will emit light when struck by electrons of a relatively low velocity, while both the red and the cyan light-emitting phosphors will be simultaneously energized by higher energy electrons and thus emit a white or substantially achromatic light.

Random mixtures of two or three types of phosphor particles of different energy threshold barriers may be economically applied to the interior of face plate G by flushing on the glass a thin liquid slurry of a homogeneous or random mixture of the differently responsive phosphor particles suspended in a suitable vehicle, followed by pouring off any excess and evaporation to form a thin dry layer of phosphor particles.

It will be noted that the particles of phosphor having the lowest energy threshold may or may not have a surface barrier layer and that, if desired, the differently responsive phosphor particles may be applied to the face plate in sequentially deposited thin layers, each layer being constituted by one type phosphor.

Ordinarily a continuous conducting film, of evaporated aluminum for example, would be added over the layer of phosphor particles. To this film an accelerating voltage is applied in the operation of the kinescope.

It will be understood that other types of phosphors and atmospheres in addition to those specifically described above are also equivalent for the purposes of this invention. Similarly, the voltage energization levers and increased electron energization thresholds are also exemplary and may be varied widely in accordance with this invention.

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

As various changes could be made in the above methods and products 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.

I claim:

1. In a color display system for producing colored images: a viewing screen comprising particles of a first phosphor which emit light of a first color when excited by a beam of electrons having a velocity of at least a first predetermined value, a particles of a second phosphor selected from the group consisting of zinc sulfide and since sulfide-cadmium sulfide, said second phosphor having a surface layer consisting essentially of zinc oxide which constitutes a partial barrier to electrons whereby the second phosphor particles have a higher electron energization threshold than that of said first phosphor particles, said

surface layer formed in situ on the particle surface by chemical reaction of the second phosphor particles with oxygen in the vapor phase, said second phosphor particles emitting a second color light when excited by a beam of electrons having a velocity of at least a second predetermined value which is greater than said first value, and means for generating a beam of electrons to excite said phosphor particles.

2. In a color display system for producing colored images: a viewing screen comprising particles of a first phosphor which emit light of a first color when excited by a beam of electrons having a velocity of at least a first predetermined value, and particles of a second phosphor selected from the group consisting of zinc sulfide and zinc sulfide-cadmium sulfide, said

second phosphor having a surface layer consisting essentially of zinc sulfide which constitutes a partial barrier to electrons whereby the second phosphor particles have a higher electron energization threshold than that of said first phosphor particles, said surface layer formed in situ on the particle surface by chemical reaction of said second phosphor particles having a zinc oxide layer with sulfur in the vapor phase, said second phosphor particles emitting a second color light when least a second predetermined value which is greater than said first value, and means for generating a beam of electrons to excite said phosphor particles.