PATENTED APR 11 1972

3,655,978

SHEET 1 OF 2

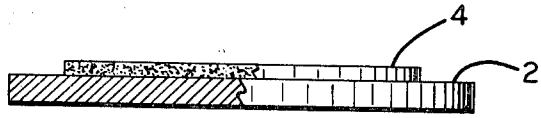


Fig. 1

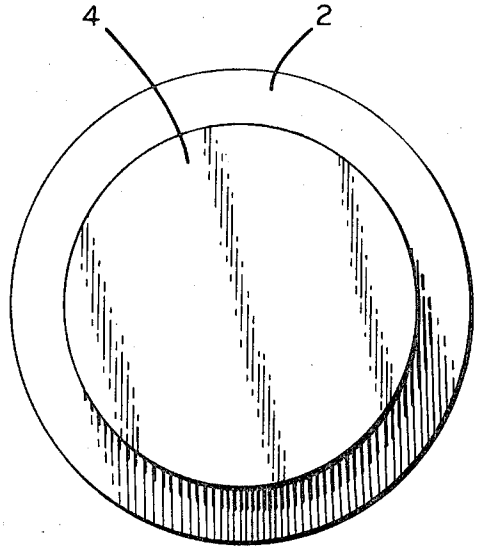


Fig. 2

INVENTORS.
SIXDENIEL FARIA &
DAVID J. HARRIGAN

BY Donald R. Castle

ATTORNEY

United States Patent

Faria et al.

[15] **3,655,978**

[45] **Apr. 11, 1972**

[54] ZINC CADMIUM SULFIDE CATHODOLUMINESCENT SCREEN

[72] Inventors: **Sixdeniel Faria; David J. Harrigan,** both of Towanda, Pa.

[73] Assignee: **Sylvania Electric Products Inc.**

[22] Filed: **Sept. 4, 1970**

[21] Appl. No.: **69,843**

[52] **U.S. Cl.** .....**250/80,** 250/71 R

[51] **Int. Cl.**.....**H01j 1/62**

[58] **Field of Search**.....250/80, 71 R; 117/33.5 C; 252/301.6 S

[56] **References Cited**

UNITED STATES PATENTS

3,197,636 7/1965 Wyatt et al. 250/80

2,623,858 12/1952 Kroger.....252/301.6 S

Primary Examiner—Morton J. Frome

Attorney—Norman J. O'Malley, Donald R. Castle and William H. McNeill

[57] **ABSTRACT**

An improved viewing screen for use in electron microscopes can be obtained when a phosphor consisting essentially of zinc sulfide and cadmium sulfide, in specific ratios, and a source of an activator material containing specified amounts of an aluminum source and specified amounts of either copper or silver is substrated on a rigid electrically conductive support.

9 Claims, 4 Drawing Figures

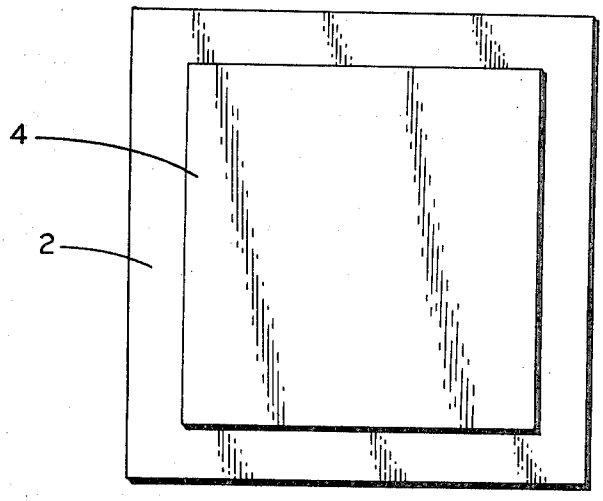


Fig. 3

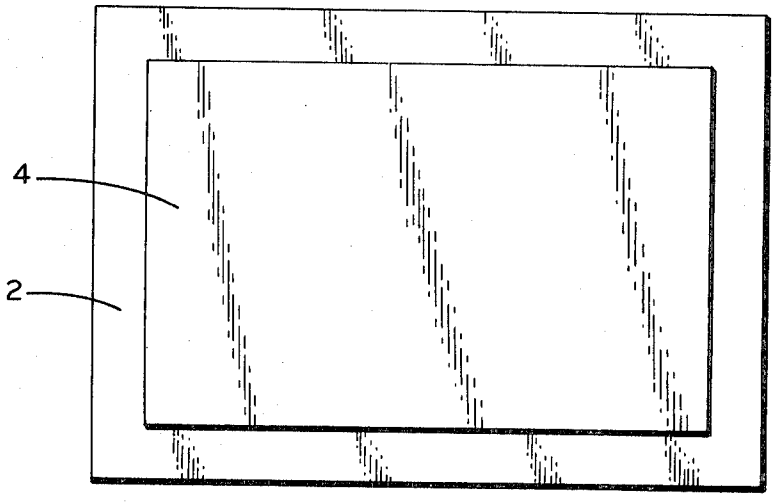


Fig. 4

INVENTORS.
SIXDENIEL FARIA &
DAVID J. HARRIGAN

BY Donald R. Castle

ATTORNEY

ZINC CADMIUM SULFIDE CATHODOLUMINESCENT SCREEN

CROSS REFERENCE TO RELATED APPLICATIONS

Co-pending U.S. Pat. Application Ser. No. 7,977 filed Feb. 2, 1970, and Ser. No. 8,041, filed Feb. 2, 1970 discloses processes for producing phosphors useful in the present invention. Co-pending U.S. Pat. Application Ser. No. 7,450 discloses zinc cadmium sulfide phosphors having silver and aluminum as activators which are useful in the present invention. All of the foregoing applications are assigned to the same assignee as the present invention.

BACKGROUND OF THE INVENTION

I. Field Of The Invention

This invention relates to phosphor screens and more specifically to fluorescent viewing screens used in electron microscopes or similar devices.

2. Prior Art

High voltage electron microscopes are now being used to examine cell structures of biological specimens, and to identify surface defects in metallurgical and solid state physics materials. Electronically and optically magnified specimens are imaged and focused on a fluorescent viewing screen which is generally perpendicular to the electron beam. Magnifications as high as 200,000 times can be achieved with the normal high voltage electron microscopes.

Theoretical limits of the resolving power of the electron microscope as viewed on the fluorescent viewing screen are in the order of a few Angstroms. This high resolution has been achieved by the high voltage used and the high stability of current passing through the lens arrangements, including efficient control through the objective and use of pointed filaments instead of hairpin cathodes.

Although the aforementioned electronic and optical refinements have been helpful in obtaining high resolutions, very little has been done to improve the properties of the viewing screen. As a result, problems still occur, especially at high magnification, when sample thickness and density reduce the penetrations of electrons to a low level, with resultant loss of image brightness when viewed on the fluorescent viewing screen.

The phosphor normally used in the fluorescent viewing screens is a green, silver-activated zinc cadmium sulfide. If crystals are favorably oriented; i.e., crystals exhibiting good transmission of electrons, they will allow enough electrons to pass through so that the crystals can generally be viewed with ample brightness and clarity of the image on the screen employing the aforementioned phosphor. Problems arise, however, if the crystal is not favorably oriented to the electron beam, or if the density and/or thickness is great. The electrons are then retarded with resultant loss of image brightness when viewed on the fluorescent viewing screen. Another problem is normally referred to as "beam damage." Some samples can suffer heat effects from the high energy electron beam necessary to produce enough viewing brightness using the aforementioned viewing screen.

It is believed, therefore, that a fluorescent viewing screen which offers greater brightness, with better viewing resolution and the ability to operate the electron microscope at a lower kilovolt setting to obtain equivalent brightness with no sacrifice in resolution or scanning speed, is an advancement in the art.

SUMMARY OF THE INVENTION

In accordance with one aspect of this invention, there is provided a viewing screen for use in electron microscopes. The viewing screen comprises a rigid support and a uniform layer of a cathodoluminescent phosphor adhered to the rigid electrically conductive support.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a side elevational view of one embodiment of the invention.

FIGS. 2, 3, and 4 are plan views of one embodiment of the invention.

DETAILED DESCRIPTION OF THE DRAWINGS AND THE PREFERRED EMBODIMENTS

For a better understanding of the preferred embodiments of the invention, together with other and further objects, advantages and capabilities thereof, reference is made to the following disclosure and appended claims in connection with the above-described drawings.

Referring now to the invention with greater particularity, it has been found that a viewing screen for use in electron microscopes and similar devices, which comprises a rigid electrically conductive support and a substantially uniform layer of a cathodoluminescent phosphor adhered to the support, wherein the phosphor consists essentially of zinc sulfide and cadmium sulfide in specific ratios, and a co-activator of specified amounts of aluminum and as an activator specified amounts of either copper or silver, has greater brightness, better viewing resolution, and the ability to operate an electron microscope or similar device at lower kilovolt settings with no reduction in resolution or scanning speed.

Blue or green-emitting phosphors can be used, depending on the activators used and weight ratios of zinc and cadmium sulfides. When the silver-activated aluminum co-activator blue-emitting phosphors are desired, the weight ratio of zinc sulfide to cadmium sulfide can vary from about 90:10 to about 97:3, although a weight ratio of from about 92:8 to about 95:5 is preferred. In the green-emitting phosphors, the ratio of zinc to cadmium will vary depending upon the activator material. When the activator is copper and the co-activator aluminum, essentially the same ratios are used as for the blue-emitting phosphor described above, although it is preferred to have Zn:Cd of from about 95:5 to about 90:10. When the activator is silver and the co-activator aluminum, the ratio of Zn:Cd can vary from about 55:45 to about 65:35, although ratios of from about 57:43 to about 63:37 are desired. The amount of each activator and co-activator is calculated on the basis of the total weight of the source of host material. On the foregoing basis, from about 0.005 percent to about 0.030 percent of an activator selected from the group of copper and silver are used and from about 0.01 percent to about 0.06 percent of aluminum is used as a co-activator.

Although various methods can be used to achieve adherence of the phosphor to the support, depending upon the type of support, one of the preferred methods is to form a suspension of the phosphor in a suitable transparent solution castable film material and thereafter form a layer of the phosphor and the film materials. Such film materials are well known in the art and are discussed in detail in Vol. 9. ENCYCLOPEDIA OF CHEMICAL TECHNOLOGY, Kirk-Othmer Interscience Publishers, New York, N. Y.

The phosphor is dispersed in the film material, preferably a plasticized cellulose derivative such as cellulose acetate, cellulose propinate, cellulose acetate propinate, cellulose acetate butyrate, ethyl cellulose, nitrocellulose and the like or other film materials such as polyvinyl polyvinvyl chloride, acrylonitride, polyvinyl butyral, polymethyl methacrylate, butyl acetate, and the like and applied to a rigid support by methods well known in the art, such as settling, spraying, blading, slurrying and silk screening. A substantially uniform phosphor layer is obtained which is generally from about 0.5 mils to about 10.0 mils thick. Layers greater than about 10 mils can be obtained, but they are generally avoided because of excessive flaking and cracking. Likewise, layers below about 0.5 mils can be obtained, but they are generally avoided to insure flatness of the flatness and evenness of the screen surface.

FIG. 1 is a side elevational view of the viewing screen. The phosphor layer 4 can be adhered on any rigid non-metallic electrically conducting support 2 such as conducting glass, conducting mylar, or metallic electrically conducting supports such as copper, aluminum, stainless steel and the like. Especially preferred, however, are stainless steel and aluminum.

FIGS. 2, 3 and 4 illustrate but three geometric shapes in which the screen can be made. Generally, any geometric shape can be employed; the shape being limited only by the machinability or cutability of the support and the needs of the user. The phosphor 4 can be applied to the entire area of the support 2 or to a section of the support. In practice it has been found to be advantageous to leave a border or section of the support 2 phosphor free to facilitate handling.

To more fully illustrate the present invention, the following detailed examples are given. All parts, percentages, and proportions are by weight unless otherwise given.

EXAMPLE 1

About 10 parts $(Zn_{90}Cd_{10})S$:Cu,Al phosphor is added to about 10 parts of a lacquer composition (97.5 percent n-butylacetate — 2.5 percent nitrocellulose) in a receptacle containing about 10 parts glass beads (5 mm) and is blended by roll milling for about 10 to about 15 minutes. The well dispersed phosphor-lacquer composition is poured through a 60 mesh stainless steel screen into a reservoir containing an adjustable steel blade at one end. The reservoir is drawn over a round stainless steel plate at a uniform speed to yield a phosphor screen measuring about 5 mils thick.

The screen made with $(Zn_{90}Cd_{10})S$:Cu,Al is placed in an electron microscope and compared with a standard fluorescent viewing screen made with (Zn,Cd)S:Ag. The results are tabulated in Table I.

TABLE I

Brightness Comparison

K. V. Setting	Standard Screen Light Output*	Screen From Example I
40	0.27	0.48
60	0.70	1.53
80	1.53	3.10
100	2.77	5.99

*Based on the measurable light emitted from a screen measuring 2 × 4 in. (520 mm.²), with the meter at a distance of 7 in. (18 cm.) from the center of the screen, in Foot-Lamberts.

Resolution (at 80 K. V.)

	Standard Screen	Screen From Example I
1000 A. Particle	Yes	Yes
100 A. Particle	Yes	Yes
20 A. Particle	No	Yes

The above data indicate that there is a substantial increase in brightness and resolution without any loss in scanning speed or residual florescence.

EXAMPLE 2

About 10 parts $(Zn_{55}Cd_{45})S$:Ag,Al phosphor is added to about 10 parts of a lacquer composition (90 percent amyl acetate — 10 percent ethyl cellulose) in a receptacle containing about 10 parts glass beads (5 mm) and is blended for about 10 minutes to about 15 minutes by roll-milling. The well-dispersed phosphor-lacquer composition is poured through a 60 mesh stainless steel screen into a reservoir containing an adjustable steel blade on one end. The reservoir is drawn over a rectangular aluminum plate at a uniform speed to yield a phosphor screen measuring about 2 mils thick.

The screen made with $(Zn_{55}Cd_{45})S$:Ag,Al is placed in an electron microscope and compared with a standard fluorescent viewing screen made (Zn,Cd)S:Ag. The results are tabulated in Table II.

TABLE II

Brightness Comparison

K. V. Setting	Standard Screen Light Output*	Screen From Example II
40	0.27	0.7
60	0.70	1.35
80	1.53	2.80
100	2.77	6.40

*Based on the measurable light emitted from a screen measuring 2 2 × 4 in. (520 mm²), with the meter at a distance of 7 in. (18 cm) from the center of the screen, in Foot-Lamberts.

Resolution (At 80 K. V.

	Standard Screen	II
1000 A. Particle	Yes	Yes
100 A. Particle	Yes	Yes
20 A. Particle	No	Yes

The above data indicate that there is a substantial increase in brightness and resolution without any substantial loss in scanning speed or residual fluorescence.

While there have been shown and described what are at present considered the preferred embodiments of the invention, it will be obvious to those skilled in the art that various changes and modifications may be made therein without departing from the scope of the invention as defined by the appended claims.

What is claimed is:

1. An electron microscope viewing screen comprising
   a. a rigid electrically conductive support having a flat smooth face and
   b. a substantially uniform layer of a cathodoluminescent phosphor having a thickness of from about 0.5 mils to about 10 mils and consisting essentially of a host of zinc cadmium sulfide, from about 0.005 percent to about 0.03 percent by weight of an activator selected from the group consisting of silver and copper and from about 0.01 percent to about 0.06 percent by weight of an aluminum coactivator, said phosphor layer adhered to said support and said phosphor exhibiting an emission spectra in the blue to green visible light when subjected to electron bombardment in said electron microscope.

2. A screen according to claim 1, wherein said cathodoluminescent phosphor is suspended in a transparent solution castable film material.

3. A screen according to claim 2, wherein said rigid support is metallic.

4. A screen according to claim 2, wherein said rigid support is non-metallic.

5. A screen according to claim 1, wherein said phosphor has a zinc to cadmium weight ratio of from about 90:10 to about 97:3.

6. A screen according to claim 5, wherein said activator is silver.

7. A screen according to claim 5, wherein said activator is copper.

8. A screen according to claim 1, wherein said phosphor has a zinc to cadmium weight ratio of from about 55:45 to about 65:35.

9. A screen according to claim 8, wherein said activator is silver.

* * * * *

PO-1050
(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,655,978 Dated April 11, 1972

Inventor(s) Sixdeniel Faria and David J. Harrigan

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Col. 2, line 64 - "polyvinyl" first instance should read "polyethylene,"

Col. 2, line 74 - "flatness" first instance should read "control"

Col. 4, line 15 - "22 x 4" should read "2 x 4"

Signed and sealed this 12th day of September 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents