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L. BURNS

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PHOTOCAPACITIVE ELECTROLUMINESCENT LIGHT AMPLIFIER

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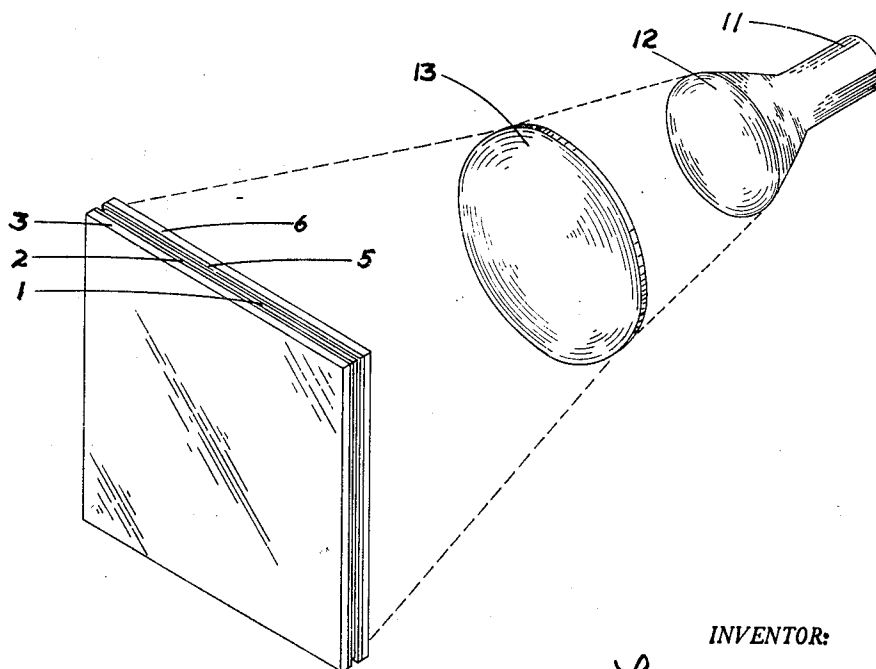
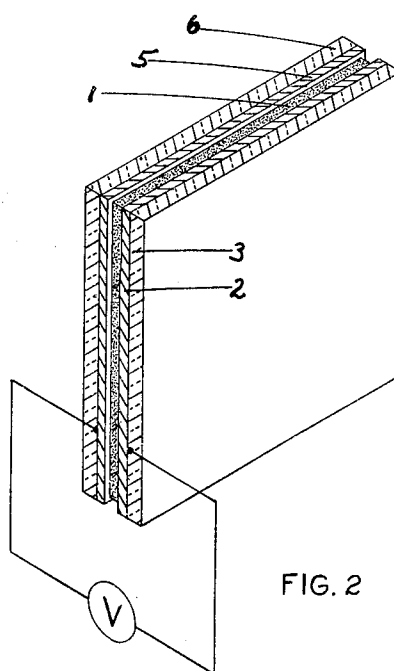
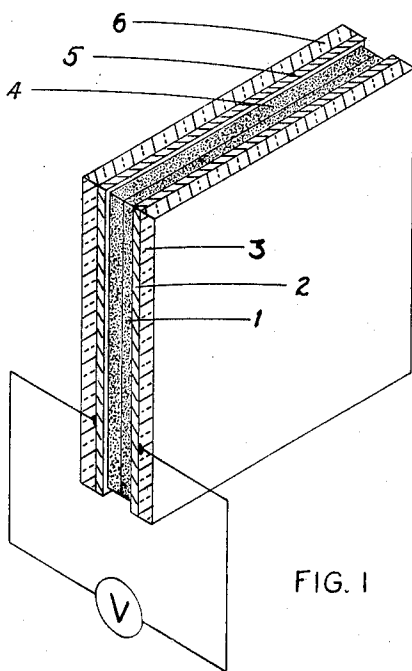


FIG. 3

INVENTOR:

Lanette Burns

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PHOTOCAPACITIVE ELECTROLUMINESCENT
LIGHT AMPLIFIER

Laurence Burns, Swampscott, Mass., assignor, by mesne
assignments, to Sylvania Electric Products Inc., Wil-
mington, Del., a corporation of Delaware

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12 Claims

This invention relates to electroluminescent devices, that is to devices in which light is produced by electrical action in a solid material. The latter is generally in the form of small crystals or particles, and is often called a phosphor.

Light amplification can be obtained with such devices, that is, a small intensity of incident light can be used to control the emission of a higher intensity of light. For example, an image of low intensity can be focused on a screen, and a corresponding image of much higher intensity emitted from the screen.

Prior light amplifiers have used a layer of photoconductive material over an electroluminescent layer, thereby relying on the change in resistivity of the photoconductive layer, the latter acting as a resistance in series with the electroluminescent layer.

The electrostatic capacity of the photoconductive layer may in some cases be sufficient to by-pass the resistance of the photoconductive layer, especially at high frequencies, or with pulses of steep wave front.

However, by my invention, a photocapacitive layer, that is, a layer whose capacitance changes with incident light, is used in place of the photoresistive layer, with improved results. Such a photocapacitive layer can be produced by suspending or embedding phosphor particles, photoconductive particles, semiconductor particles of high activation energy, and the like in a dielectric material.

The variation in the capacity of the layer with irradiation, appears to be due to changes in dielectric constant of the particles in some cases, and in others to polarization effects produced by the release of electrons in the particle by the incident light. Both of the above effects can be present in the same material, and other effects can also be present, singly or in combination, to produce changes in capacitance with the intensity of the incident light.

If desired, a layer of particles whose capacity changes with the intensity of light falling thereon, can be placed directly over the electroluminescent layer, without being suspended in a solid dielectric medium. The electroluminescent particles also can be used without being suspended in a dielectric medium, that is in a layer containing only electroluminescent particles.

To improve the brightness and breakdown characteristics, a layer of a dielectric material of very high dielectric constant, such as barium titanate can be used between one of the electrodes and the other layers. Particles of such materials can also be suspended in the same part of the dielectric which suspends the electroluminescent particles, that is, in the electroluminescent layer.

Photocapacitive and photoconducting particles can also be used in the same part of the dielectric in which the phosphor is suspended, instead of in a separate part, although the latter is preferable. Particles of materials such as plain zinc sulfide, or zinc sulfide with an activator such as copper or manganese, can be used as the particles which change their dielectric constant, or which change the overall constant of the combination of themselves and the solid dielectric in which they are embedded. With copper activation, part of the change in capacitance can be due to the polarization of the electrons freed by the

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incident light, but if an activator such as manganese is used, the wavelength of the incident light can be kept above about 3800 angstrom units, if desired, in which case the manganese will be excited only to levels below the conduction band and hence cause a change in dielectric constant, without causing any electrons to be actually "freed" from their atoms, that is, raised to the conduction band, so there will be no photoconductivity in the particles.

The additional photocapacitive layer can be omitted, if desired, and the incident radiation used to free electrons directly in the phosphor particles themselves, these electrons being then accelerated by the field to energies sufficient for excitation or ionization of activator atoms in the phosphor, with consequent emission of light on the atom's return to normal. In that case, the electroluminescent particles, whether or not they are embedded in a solid dielectric, can be used without the additional photocapacitive layer, the electroluminescent particles themselves acting directly as light amplifiers. If ordinary electroluminescent particles are used for the purpose, the voltage across them should generally be reduced to too low a value for appreciable electroluminescence in the absence of incident radiation. However, the voltage may then be insufficient to accelerate the electrons to high enough energies, so it will be preferable to use a phosphor which in the dark does not have any appreciable quantity of free electrons or of electrons which can be easily freed by the field, and then let the free electrons be produced mainly by incident light.

For the latter result, the phosphor can be an ordinary cathode ray phosphor of say zinc sulfide activated by 0.001% copper by weight, although the brightness may then be low. Higher brightness can be obtained by using a large amount of copper activator, but without adding the additional material necessary for ordinary electroluminescence, such as the lead in a cubical ZnS:Cu phosphor having about 0.0002 to 0.002 gram-atoms of copper per mole of zinc sulfide, or the oxygen in the hydrogen sulfide firing atmosphere of the ZnS:Cu:Al phosphor.

A coactivator such as chlorine or aluminum should generally be present in the above phosphors to give good luminescence and to reduce the number of possible low-energy donor atoms present. Chlorine can be used, or aluminum or other trivalent metals, as is known in the art of coactivation, in amounts which in the fired phosphor can be about equal to the amount of activator present.

Such light-amplifying crystals can be excited by ultraviolet light or by infra-red, but will not generally be excitable by the same wavelengths which they emit. The device using a photocapacitive layer, however, can be excited by any light to which the photocapacitive layer will respond. When the light usable for excitation is the same as that of emission, the emitted light will feed back onto the photocapacitive layer and keep the latter excited and the device luminous even after the exciting radiation is cut off, thus producing a locking effect. The latter will not occur when the spectral excitation region of the photocapacitor is in a different range than the spectral emission region of the phosphor.

Where the feedback is not desired, and the spectral region to which the photocapacitive layer responds overlaps the region in which the electroluminescent layer emits, an opaque or reflective layer can be used between the photocapacitive and electroluminescent layers.

Other advantages, features and objects of the invention will be apparent from the following specification, taken in connection with the accompanying drawing in which:

FIG. 1 is a schematic representative of one embodiment of my device;

FIG. 2 is a representation of another embodiment of my device; and

FIG. 3 is a schematic diagram of apparatus in which an image is amplified.

In FIGURE 1, the electroluminescent layer 1 is applied over an electrically-conductive transparent coating 2 on a piece 3 of glass or other light-transmitting medium, and the photocapacitive layer 4, which can be a layer of photocapacitive or photoconductive particles suspended in a dielectric, is applied over the other side of the electroluminescent layer 1. A transparent electrically conductive layer 5 is over and in contact with the photocapacitive layer 4, said electrically-conductive layer being on the surface of the plate 6 of glass or other light-transmitting material.

The electroluminescent layer 1 can be of phosphor particles embedded in dielectric material, as shown in co-pending application, Ser. No. 180,783 filed Aug. 22, 1950 by Elmer F. Payne, issued on June 10, 1958 as U.S. Patent 2,838,715, or in application Ser. No. 365,617 filed July 2, 1953, by Richard M. Rulon, now abandoned and replaced by a continuation application which issued on Sept. 10, 1963 as U.S. Patent 3,103,607 or in some other convenient manner. The conducting layer can be, for example, of stannous chloride or the like applied on glass or other material as shown in said Rulon application, or in other manners known in the art.

The phosphors can be of copper-activated zinc sulfide, as shown in said Payne application, or in co-pending applications Ser. No. 230,711, filed June 8, 1951, and Ser. No. 230,713, filed June 8, 1951, respectively by Keith H. Butler and by Keith H. Butler and Horace H. Homer, issued, respectively, as U.S. Patent 2,772,242 on Nov. 27, 1956, and U.S. Patent 2,728,730 on Dec. 27, 1955 or can be any other suitable electroluminescent materials.

The photocapacitive layer 4 can be composed of particles of zinc sulfide, cadmium sulfide or selenium for example, suspended in a dielectric material such as a light-transmitting ceramic frit in the same manner as shown for electroluminescent particles in the applications of Payne and Rulon shown above. The same ceramics can be used, and the proportions of the photoconductive or photocapacitive particles can be the same as for the electroluminescent layer, the particles occupying about one-fifth of the volume of the layer, for example. The particles, like the electroluminescent particles, can be of 10 to 20 microns in size, although other particle sizes can be used.

In FIG. 2, the separate photocapacitive layer is omitted, and the photoconducting particles suspended in the same layer which contains the electroluminescent particles. In this case, the proportions of electroluminescent particles and photosensitive particles, expressed as volume of the total layer can each be somewhat less than the proportions in which they would occur when used in separate layers. The volume occupied by each set of particles can be about three-fourths of the proportion when the particles are used in separate layers, for example.

Actually, the particles used in the layer 1 of FIG. 2 can all be of one kind if desired. They can for example, be of ordinarily non-luminescent zinc sulfide phosphors, activated by copper or manganese, or both. Such phosphors can be prepared as in the Butler, and Butler and Homer applications previously mentioned, except that the lead is omitted. The phosphor will then be substantially non-electroluminescent in the absence of light, but will become electroluminescent when irradiated by ultra-violet light, especially by light in the near ultraviolet range of 3000 to 4000 angstroms, or even up to 5000 angstroms, if a manganese activator be used.

A copper-activated zinc sulfide phosphor containing up to about 0.1% copper, or even more, by weight of zinc sulfide and a similar amount of aluminum or other trivalent metal, and prepared in an atmosphere of hydrogen sulfide, can also be used.

The above phosphors are given merely by way of example and not by way of limitation.

If desired, the phosphor layer 1 can be applied as a mosaic of separate regions, each just large enough in cross-sectional area to constitute a "dot" in the production of an image obtained by grouping of such dots at varying intensities of illumination from dot to dot. The photocapacitive layer can also be applied as a mosaic, in a similar manner, whether or not the layer 1 is so applied. The coatings can be applied through a screen such as a piece of cardboard or metal perforated with dots, to achieve such a result. For a 25-inch screen with 250 "dots" per side of 25 inches, the mosaic particles or areas would be spaced about 0.1 inch between centers, and would be preferably round or square. The dots should be about 0.06 to 0.09 inch in diameter, to keep them separated from each other.

In FIG. 3, a small cathode ray tube 11 has an image produced on its screen 12 which is enlarged by the lens 13, focussed onto one side of the photocapacitive layer 4. An electroluminescent layer 1 is in contact with the other side of the photocapacitive layer 4. Transparent conductive layers 2, 5, are in contact with the outside surfaces of layers 4 and 1, and are backed up by the glass supporting plate 3, 6. A source of voltage V, is connected to the conductive layers 2, 5.

In operation, an image is produced on the screen 12 of cathode ray tube 11 in the usual manner, for example, a moving picture as produced when the tube 11 is the picture tube of a television set. The image is enlarged by the lens 13 and focussed onto the photocapacitive layer 4, where it will appear in less bright form due to the increase in its area. The light falling on the photocapacitive layer 4 will reduce the impedance of that layer, however, and that will increase the voltage across the electroluminescent layer, thereby causing the latter to emit light. This light can be much greater in intensity than the light received on the photocapacitive layer 4.

It will generally be desirable to make the impedance of the photocapacitive layer 4 high enough so that the light emitted by the electroluminescent layer will be negligible when no light falls on the photocapacitive layer, despite the presence of a voltage across the whole device in series. In many cases, it will be desirable to make the photocapacitive layer 4 of a material which will respond to ultraviolet radiation and be relatively insensitive to visible light, so that it will not be affected by the general illumination in the room. However, visible light or even infra-red can be used, with proper choice of the materials in photocapacitive layer 4, of which many are known in the art.

The photocapacitive layer 4 can be applied to the electroluminescent layer 1 by spraying, evaporating, settling, painting, or the like, through a screen if desired, for example, through a sheet of paper or of metal having holes therein, the holes being close together, for example, the perimeters of the holes being spaced apart a distance equal to about one-fourth of the radius.

To increase the sensitivity to light of the photocapacitive or photoconductive particles, or of the phosphor particles, especially when the latter are used alone without the other particles, a portion of the surface of each particle, or of some of the particles, can be covered by a conductive layer, for example, a film of metal. The film can be applied to a layer of particles, and the layer then broken down into its separate particles, and preferably milled somewhat. The layer can be quite thin, for example, thin enough to transmit light, and need not in many cases be much thicker than a micron, and can even be less. The metal used is preferably such that a high contact potential between the metal and the phosphor particle exists in order to insure a high field in the neighborhood of the junction. The high field may only be present when light is incident on the phosphor, if there are no free electrons present in the absence of irradiation.

If the deposited metal is of a photoemissive type, for example caesium, free electrons may be emitted from the

metal into the phosphor or other particles under the influence of incident light, thus providing another kind of source of photoelectrons for light amplification.

The cubical ZnS:Cu phosphor and the ZnS:Cu, Al phosphor, the latter fired in hydrogen sulfide, previously mentioned, appear to be phosphors of a type having only shallow traps, and phosphors having only shallow traps, or nearly free from traps, can be effective for use when the phosphor crystals themselves do the amplification, whether or not the phosphor is immersed in a solid dielectric material. However, if phosphors having deep traps are used, such as air-fired ZnS:Cu, then the electrons for acceleration can be freed by infra-red radiation and amplification is thus available for infra-red excitation. The trap depth in this case should be deep enough so that the trapped electrons are not readily freed by the field.

The presence of some traps of a depth from which electrons can be freed by the field, especially at or near its maximum value under alternating current excitation, can be helpful in insuring the presence of electrons released at sufficient fields for acceleration to energies high enough for excitation of activator atoms. The electrons released from other traps can fall into these and then be released by the field.

When the voltage applied to the amplifier is alternating, its frequency should preferably be greater than the frequency of variation of the phosphor particles in the cathode ray screen 12, from which the image is focused on my light amplifying device. There may be higher frequencies present in the electron beam exciting the cathode ray screen 12, but these will not ordinarily appear on the image incident on my device, because they will be smoothed out by the decay time of the phosphor in the cathode ray screen 12.

What I claim is:

1. An electroluminescent unit comprising an electroluminescent device and a photocapacitive device in series.

2. An electroluminescent device comprising an electroluminescent layer and a photocapacitive layer in series electrically.

3. An electroluminescent device comprising an electroluminescent layer with a photocapacitive layer thereover and in series electrically therewith.

4. An electroluminescent device comprising a transparent conductive electrode, a layer of electroluminescent phosphor thereon, a photocapacitive layer thereover, and another electrode over said photocapacitive layer.

5. An electroluminescent device comprising a transparent conductive electrode, a layer of electroluminescent phosphor thereon, a photocapacitive layer thereover, and a transparent conductive electrode over said photocapacitive layer.

6. An electroluminescent device comprising a transparent conductive electrode, a layer of electroluminescent phosphor embedded in a solid dielectric material, a photocapacitive layer thereover, and another electrode over said photocapacitive layer.

7. An electroluminescent device comprising a transparent conductive electrode, a layer of electroluminescent

phosphor thereover, a photocapacitive layer of photoconductive material embedded in a solid dielectric material over said electroluminescent layer, and another electrode over said photocapacitive layer.

8. An electroluminescent device comprising a dielectric material in which is suspended a phosphor which contains activator atoms and is non-electroluminescent at a predetermined voltage in the absence of incident radiation, means for irradiating said phosphor to produce free electrons therein, and means for applying said predetermined voltage to said dielectric material to accelerate said free electrons to energies sufficient to excite said activator atoms to light-emitting energy levels.

9. The combination of claim 8, in which the phosphor consists essentially of cubical zinc sulfide activated with between about 0.0002 and about 0.001 gram-atoms of copper per mole of zinc sulfide and an amount of chlorine between about 0.0002 and 0.001 gram atoms per mole of zinc sulfide.

10. The device of claim 3, a cathode ray tube having a screen on which an image can be produced, means for optically focusing said image on the photocapacitive layer of said device, and a source of voltage connected across the layers of said device in series.

11. An electroluminescent device comprising an electroluminescent layer in series with a photocapacitive layer, said latter layer comprising photoconductive particles embedded in a ceramic dielectric.

12. A coherent, photoconductive body comprising a homogeneous mixture of a photoconductive material and a glass enamel, and an electrical connection to said body.

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JAMES W. LAWRENCE, Primary Examiner

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250—71, 211, 217; 252—301.6, 501; 338—15