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ELECTROLUMINESCENT DEVICE

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FIG. 1.

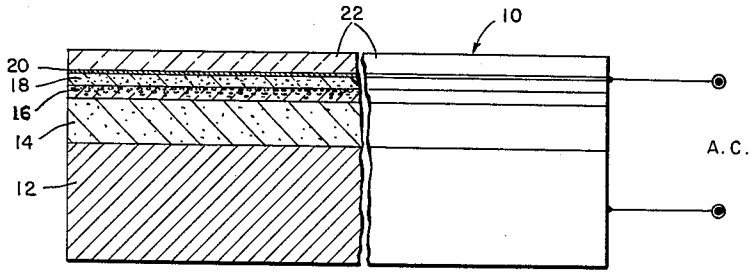
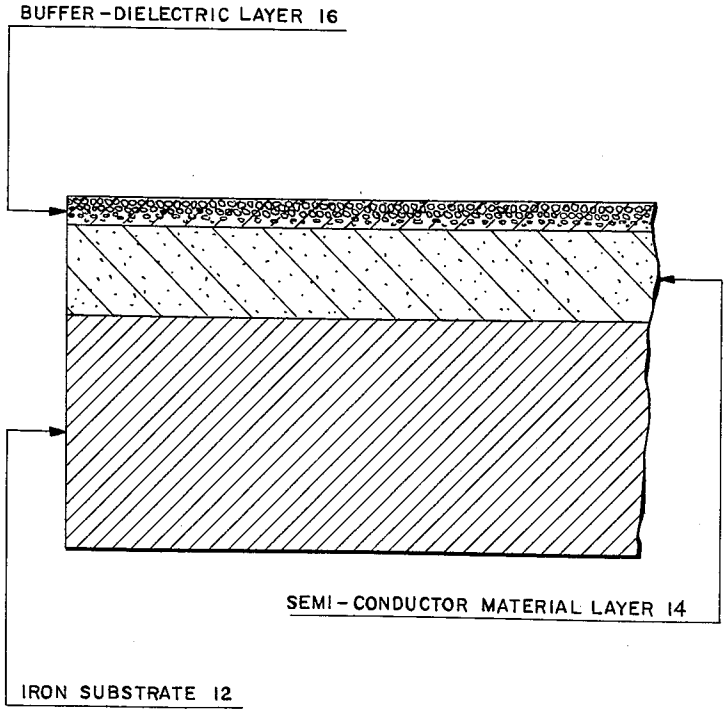


FIG. 2.



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ELECTROLUMINESCENT DEVICE

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This invention relates to electroluminescent devices and, more particularly, to an electroluminescent device which has improved performance characteristics.

The phenomenon of electroluminescence was first disclosed by G. Destriau, one of his earlier publications appearing in London, Edinburgh and Dublin Philosophical Magazine, Series 7, volume 38, No. 285, pages 700–737 (October 1947). Since this early publication, electroluminescent devices have been marketed commercially. In one construction for electroluminescent devices, the phosphor is embedded in a plastic dielectric material. In another construction for such devices, the phosphor is embedded in a glass or ceramic material in the form of a layer and the energizing electric field is applied across this layer to produce light. Electroluminescent devices which do not utilize plastic material between the spaced electrodes can be categorized as ceramic-type electroluminescent devices. The maintenance of light output for such ceramic-type devices is normally very good, but the level of illumination tends to be relatively low.

It is the general object of this invention to provide an electroluminescent device having improved brightness.

It is another object to provide a ceramic-type electroluminescent device which operates with a very large margin of safety so that a very high voltage is required to cause an electrical breakdown across the device electrodes.

It is a further object to provide a foundation-electrode and dielectric layer which can be used as a part of an improved electroluminescent device.

The aforesaid objects of the invention, and other objects which will become apparent as the description proceeds, are achieved by providing an electroluminescent device comprising a conducting substrate having carried thereover a layer of iron-titanate-including, semi-conductor material. Coated over the semi-conductor is a buffer-dielectric layer formed of tianate and glass. Over the buffer layer is carried a phosphor-dielectric layer and a light-transmitting electrode is carried over the phosphor-dielectric layer. The ratio of glass to titanate in the buffer layer is carefully controlled and this layer is applied in such manner that the layer surface which is adjacent the semi-conductor layer is rich in glass and the layer surface which is adjacent the phosphor-dielectric layer is substantially free of iron compound.

For a better understanding of the invention, reference should be had to the accompanying drawing wherein:

FIG. 1 is an elevational view, partly in section, of an electroluminescent device constructed in accordance with the present invention;

FIG. 2 is a fragmentary, sectional-elevational view of the foundation-electrode and overlaying dielectric layer portion of the device as shown in FIG. 1.

With specific reference to the form of the invention shown in the drawing the electroluminescent device **10** generally comprises a conducting substrate **12** over which is applied a semi-conductor material layer **14** which comprises an iron-titanate-containing material. A layer **16** comprising a mixture of barium titanate and glass is carried over the layer **14** and a phosphor-dielectric layer **18** is carried over the barium titanate-glass layer **16**. A light-transmitting electrode layer **20** is carried over the

phosphor-dielectric layer **18**. Preferably a protective, light-transmitting layer **22** which comprises a cover coat is carried over the electrode layer **20**.

As a specific example, the conducting substrate is formed of conventional enameling iron of 22 gauge thickness. The semi-conductor material layer **14** is formed of a titania-precipitating glass having the following percentage by weight composition: Na_2O, 10.5%; K_2O, 3.5%; B_2O_3, 14.0%; SiO_2, 45%; TiO_2, 20.0%; P_2O_5, 2.0%; and F_2, 5.0%. Any titania-precipitating glass which can be enameled can be substituted for the foregoing specific example and such glasses are very well known.

The buffer-dielectric layer **16** comprises from 80% to 95% by weight of finely divided barium titanate and from 20% to 5% by weight of glass which is fused about the barium titanate to form a substantially continuous layer. The surface of the layer **16** which is adjacent the semi-conductor material layer **14** is rich in glass and the surface of the layer **16** which is proximate the phosphor-dielectric layer **18** is substantially free of iron compound. As a specific example, the layer **16** has a thickness of approximately 1 mil and comprises 90% by weight of finely divided barium titanate and 10% by weight of glass. The percent by weight composition of the glass which is used in forming the layer **16** is as follows: ZnO, 15.4%; BaO, 31.7%; B_2O_3, 19.1%; SiO_2, 4.0%; K_2O, 7.7%; Na_2O, 3.8%; Li_2O, 1.3%; Al_2O_3, 3.9%; TiO_2, 11.2%; Sb_2O_3, 1.9%. Any glass which has a relatively low softening temperature can be substituted for this foregoing example. The average particle diameter of the finely divided barium titanate is about two microns and this is subject to considerable variation.

The phosphor in the layer **18** is preferably embedded in a light-transmitting glass dielectric material. Any suitable electroluminescent phosphor can be used and as an example, zinc sulfide phosphor which is activated by copper and coactivated by chlorine has been found to be very suitable. The phosphor is finely divided and as an example, has an average particle diameter of about ten microns. This particle diameter is subject to considerable variation. As a specific example, the glass in which the phosphor is embedded has the following formulation, as expressed in percent by weight: SiO_2, 10.1%; B_2O_3, 21.5%; TiO_2, 4.9%; ZnO, 29.2%; BaO, 16.3%; CaO, 4.5%; MgO, 1.8%; K_2O, 8.3%; Na_2O, 3.4%. Seven parts by weight of glass are used per four parts by weight of phosphor. The weight ratios of phosphor to glass are not critical and the glass content has been varied from ten parts by weight to 2.5 parts by weight per four parts by weight of phosphor. Even this indicated range can be extended.

The light-transmitting, electrically conducting layer **20** is preferably formed of tin oxide which is deposited in accordance with conventional practices. Other known materials such as indium oxide can be substituted for the tin oxide electrode. The exterior layer **22**, which is carried over the electrode layer **20**, provides electrical insulation and protection against atmospheric moisture. The layer **22** can be forced of any suitable enameling glass or it can be replaced by a suitable light-transmitting plastic material, such as epoxy resin. The layer **22** can be omitted if desired.

In fabricating the device **10**, the enameling iron substrate **12** is placed in a substantially horizontal orientation and a frit of the titania-precipitating glass is sprayed thereover. The glass frit is very finely divided and to facilitate deposition, 100 parts by weight of the finely divided glass frit are mixed with 2 parts by weight clay, 0.24 part by weight magnesium carbonate, 0.24 part by weight sodium aluminate, 0.17 part by weight bentonite,

0.17 part by weight potassium carbonate, and 13.1 parts by weight barium titanate. These finely divided materials are mixed with 50 parts by weight of water to form a slurry which is sprayed onto the substrate **12**. In the preferred construction, the layer **14** has a thickness of about 10 mils and in order to make a layer of this thickness, it is preferred to form the layer **14** in two steps. In forming the layer **14**, the foregoing coating composition is sprayed onto the enameling iron substrate **12** to a thickness of slightly greater than 4 mils. The substrate is then heated to a temperature of 800° C. for approximately five minutes. The second layer is then sprayed over the first layer to a thickness of slightly greater than 6 mils and the foregoing firing repeated. During the indicated firings, which fuse the glass frit into a continuous layer, iron from the substrate **12** reacts with titania which is precipitated from the glass comprising the layer **14** to form an iron-titanate complex. This iron-titanate complex provides the layer **14** with the properties of a semi-conductor. In actual measurements, the electrical resistance, as measured through a three-quarter square inch portion of the layer **14**, was approximately 10,000 ohms. The layer **14** should have a thickness at least equal to that of the buffer layer **16** and preferably, the layer **14** has a thickness about ten times that of the buffer layer **16**.

In forming the buffer layer **16**, ninety parts by weight of the finely divided barium titanate are mixed with ten parts by weight of the finely divided glass and applied over the layer **14** to a thickness of about one mil by means of a conventional silk screen deposition process. As an example, a 225 mesh screen is used. The applied glass-barium titanate powder is then fired at a temperature of 620° C. for a period of five minutes. During this firing, the glass apparently settles or is attracted toward the bottom of the layer **16**, leaving a small residual portion of the glass dispersed throughout the remainder of the layer **16** to fuse the particles of barium titanate together. If the glass is present in amount of more than 20% by weight of the layer **16**, the dielectric constant of this layer will be excessively lowered, thereby decreasing the total brightness for the device. If less than 5% by weight of glass is used in forming the layer **16**, the finely divided barium titanate particles will not be adequately bonded together. The electrical resistance of the foregoing buffer or barrier layer **16**, as measured through a three-quarter square inch portion, was in the order of one megohm. The semi-conductor layer **14** thus has a very low electrical resistance as compared to the buffer layer **16**. The foregoing foundation-electrode and buffer layer is shown in Fig. 2.

In the next manufacturing step, the phosphor-dielectric layer **18** is applied over the buffer layer **16**. This phosphor-dielectric layer is preferably applied as a powder mixture, using a silk screen with a 163 mesh. Alternatively, conventional spraying can be used to deposit the phosphor-dielectric powder. This powder is deposited to a thickness of approximately 1 mil. The deposited powdered glass frit and phosphor are then fired at a temperature of approximately 670° C. for approximately five minutes. This will form a substantially continuous layer of phosphor and dielectric. To complete the fabrication of the device, the overlaying electrode layer **20** is applied in accordance with conventional practices, as in the cover coat or protective layer **22**.

The foregoing specific device operates with a relatively high brightness when excited with a potential of 120 volts, 60 cycles. If the device has a total area of approximately 3.5 square inches, the power consumption is in the order of 0.025 watt, the power factor is about 0.25 and the brightness is in the order of 1.2 to 1.5 ft. lamberts.

The presence of the buffer layer **16** is extremely important. If this layer **16** is dispensed with and the phosphor-dielectric layer **18** is placed directly on the semi-conductor material layer **14**, the operation of the device will be extremely poor. Similar devices so constructed have a reasonably good surface brightness, but operate with a power consumption varying from 0.5 to 2 watts and with a power factor approaching unity. Apparently these poor performance characteristics are due to the iron reacting with the glass in which the phosphor is embedded, and also perhaps with the phosphor, to increase the electrical conductivity of the overall device and thereby impair performance. Devices similarly constructed but without the buffer layer **16** displayed a total electrical resistance between the electrodes **12** and **20** of approximately 10,000 to 30,000 ohms. Such devices which include the buffer layer, however, display a total resistance between the electrodes varying from 10^8 to 10^{10} ohms. The buffer layer **16** thus functions to prevent any migration of iron, during the firing processes, from the semi-conductor material layer **14** to the phosphor-dielectric layer **18**. This is attributable to the fact that barium titanate is quite inert with respect to reacting with iron. In addition, while the surface of the buffer layer **16** which is adjacent the semi-conductor material layer **14** is quite rich in glass, the other surface of the buffer layer **16** which is adjacent the phosphor-dielectric layer contains only a very small amount of glass. Accordingly, the upper surface of the buffer layer **16** which is adjacent the phosphor-dielectric layer **18** is substantially free of any iron compound which can contaminate the phosphor-dielectric layer.

Another requirement for the buffer layer **16** is that it should have an extremely high dielectric constant, in order that the capacitive reactance of this layer is very small. If glass per se is used to replace the barium titanate in forming the buffer layer, the performance of the device is impaired, since a considerable potential drop will appear across this glass layer due to increased impedance, in addition to the tendency of the usual glass to react with iron.

Each layer **14**, **16** and **18**, of the foregoing device **10** can be expressed as a parallel-connected capacitance and resistance, with each parallel-connected capacitance and resistance being connected in series. With respect to the semi-conductor material layer **14**, the capacitive reactance of this layer is quite high as compared to its relatively low electrical resistance. The power factor of this semi-conductor layer **14** thus approaches unity and because of the relatively low electrical resistance of the layer **14**, there is very little power consumed in this layer. The electrical characteristics of the layer **14** are such as to place substantially all applied potential across the layers **16** and **18**. The semi-conductor material layer **14** also imparts very high electrical breakdown characteristics to the device **10**, since the layer **14** places in series with the phosphor-dielectric layer **18** what amounts to an infinite number of resistances. When incipient electrical breakdown starts to occur across any portion of the layer **18**, the additional current which is drawn immediately quenches such breakdown by virtue of the potential drop generated across the semi-conductor layer **14**. Thus the electrical breakdown characteristics of the device **10** are greatly improved by the high electrical-breakdown characteristics of the semi-conductor material layer **14**.

The equivalent circuit for the buffer layer **16** can also be expressed as a parallel-connected capacitance and resistance, as indicated hereinbefore. Because of the extremely high dielectric constant of barium titanate, and the predominance of this material, the capacitive reactance across the layer **16** is extremely small and substantially all of the potential which is applied across the layers **16** and **18** appears across the phosphor-dielectric layer **18**. Since the phosphor-dielectric layer **18** is extremely thin, a relatively intense electric field is applied to excite the phosphor.

In the usual plastic-type electroluminescent device intended to operate with 120 volts excitation, wherein the phosphor is embedded in a plastic material such as poly-

vinyl chloride, it is desirable to make the phosphor-plastic dielectric layer approximately 2 mils thick, in order to insure adequate protection against electrical breakdown across the device electrodes. Such a device will operate with a surface brightness of approximately 0.7 to 0.8 ft. lambert and electrical breakdown will normally be encountered at a potential of approximately 300 volts. In the present device, the spacing between the electrodes is approximately 12 mils. Because the semi-conductor material layer **14** serves to provide breakdown protection and consumes but very little power due to its low electrical resistance, the device operates, when excited with 120 volts 60 cycles, with a surface brightness of 1.2 to 1.5 ft. lamberts, as indicated hereinbefore. In addition, the potential required to cause electrical breakdown between the device electrodes is in the order of about 900 volts.

Plastic-type electroluminescent devices have been fabricated with an additional layer of high-dielectric material in order to provide improved electrical breakdown characteristics, while maintaining the surface brightness at a relatively high value. Such plastic-type devices normally have relatively poor maintenance of light output, however, and as a general rule, the maintenance of light output of plastic-type electroluminescent devices will not be as good as that which is obtained with ceramic-type electroluminescent devices. The present electroluminescent cell construction can be operated at a high level of brightness and with a large margin of safety against electrical breakdown. In addition, because of the ceramic-type construction, the maintenance of light output for the device is very good.

The foregoing specific example is subject to considerable modification. For example, the electroluminescent phosphor layer can be replaced by a continuous thin film of electroluminescent phosphor which is formed directly onto a light-transmitting electrode. Such a construction is disclosed in copending application S.N. 837,988, filed September 3, 1959 and owned by the present assignee. As another possible embodiment, the semi-conductor material layer **14** can be made much thinner, if desired. This will decrease somewhat the potential which is required to cause breakdown between the electrodes of the device. For some applications, however, a large degree of breakdown protection is not essential. The additional buffer-dielectric layer **16** can be made thicker if desired, in order to insure that no possible iron migrates through the layer **16** to contaminate the phosphor-dielectric layer **18**. As a general rule, in order to provide an adequate barrier against migration of iron to the phosphor layer **18**, the thickness of the layer **16** should be at least about as great as the thickness of the phosphor layer **18**. It should be understood that while the foregoing specific device is intended to be operated with an excitation potential of 120 volts, the device can be operated with a greatly increased excitation potential, in order to increase the brightness.

Finely divided barium titanate is preferred for use in the buffer layer **16**. Equal amounts of other finely divided materials which have a very high dielectric constant can be substituted therefor. Examples of other suitable materials are strontium titanate, any solid solution of barium titanate and strontium titanate or a physical mixture of barium titanate and strontium titanate in any proportions. Any of these other indicated materials can be substituted for the barium titanate in the foregoing specific example.

It will be recognized that the objects of the invention have been achieved by providing an electroluminescent device having improved brightness and performance. Such a device can be operated with both high brightness and a very large margin of safety with respect to preventing any tendencies for electrical breakdown across the device electrodes. There has also been provided a foundation-electrode and dielectric layer for an electroluminescent device.

While a best embodiment has been illustrated and described in detail, it is to be particularly understood that the invention is not limited thereto or thereby.

We claim:

1. A foundation-electrode carrying thereon a dielectric material layer for use as a component part of an electroluminescent device, said foundation-electrode and dielectric material layer comprising: a conducting substrate; a semi-conductor layer comprising an iron-titanate-containing material carried on said conducting substrate; and a mixed glass and titanate layer carried over said semi-conductor layer; said semi-conductor layer having a very low electrical resistance compared to the electrical resistance of said glass-titanate layer; said semi-conductor layer also having a thickness at least equal to the thickness of said glass-titanate layer; said glass-titanate layer comprising from 80% to 95% by weight of at least one finely divided material of the group consisting of barium titanate, strontium titanate and barium-strontium titanate, with from 20% to 5% by weight of glass fused about the particles of the material of said group; the surface of said glass-titanate layer adjacent to said semi-conductor layer being rich in glass and the opposite surface of said glass-titanate layer being substantially free of iron compound.

2. A foundation-electrode carrying thereon a dielectric material layer for use as a component part of an electroluminescent device, said foundation-electrode and dielectric material layer comprising, a conducting substrate, a semi-conductor layer comprising an iron-titanate-containing material carried on said conducting substrate, and a mixed glass and titanate layer carried over said semi-conductor layer, said semi-conductor layer having a very low electrical resistance compared to the electrical resistance of said glass-titanate layer, said semi-conductor layer also having a thickness at least equal to the thickness of said glass-titanate layer, said glass-titanate layer comprising from 80% to 95% by weight of barium titanate particles and from 20% to 5% by weight of glass fused about the barium titanate particles, the surface of said glass-titanate layer adjacent to said semi-conductor layer being rich in glass and the opposite surface of said glass-titanate layer being substantially free of iron compound.

3. A foundation-electrode carrying thereon a dielectric material layer for use as a component part of an electroluminescent device, said foundation-electrode and dielectric material layer comprising, a conducting substrate, a semi-conductor layer comprising an iron-titanate-containing material carried on said conducting substrate, and a mixed glass and titanate layer carried over said semi-conductor layer, said semi-conductor layer having a very low electrical resistance compared to the electrical resistance of said glass-titanate layer, said semi-conductor layer also having a thickness of about ten times the thickness of said glass-titanate layer, said glass-titanate layer comprising about 90% by weight of barium titanate particles and about 10% by weight of glass fused about the barium titanate particles, the surface of said glass-titanate layer adjacent to said semi-conductor layer being rich in glass and the opposite surface of said glass-titanate layer being substantially free of iron compound.

4. An electroluminescent cell comprising: a conducting substrate; a semi-conductor layer comprising an iron-titanate-containing material carried on said conducting substrate; a titanate and mixed glass buffer layer carried on said semi-conductor layer; a layer comprising electroluminescent phosphor carried on said buffer layer; and a light-transmitting electrode layer carried on said layer comprising electroluminescent phosphor; said semi-conductor layer having a very low electrical resistance compared to the electrical resistance of said buffer layer; said semi-conductor layer also having a thickness at least equal to the thickness of said buffer layer; said buffer layer comprising from 80% to 95% by weight of at least one finely divided material of the group consisting of barium titanate, strontium titanate and barium-strontium titanate,

and with from 20% to 5% by weight of glass fused about the particles of the material of said group; the surface of said buffer layer adjacent to said semi-conductor layer being rich in glass and the surface of said buffer layer adjacent to said layer comprising electroluminescent phosphor being substantially free of iron compound.

5. An electroluminescent cell comprising, a conducting substrate, a semi-conductor layer comprising an iron-titanate-containing material carried on said conducting substrate, a titanate and mixed glass buffer layer carried on said semi-conductor layer, a layer comprising electroluminescent phosphor carried on said buffer layer, and a light-transmitting electrode layer carried on said layer comprising electroluminescent phosphor, said semi-conductor layer having a very low electrical resistance compared to the electrical resistance of said buffer layer, said semi-conductor layer also having a thickness at least equal to the thickness of said buffer layer, said buffer layer comprising from 80% to 95% by weight of barium titanate particles and with from 20% to 5% by weight of glass fused about the barium titanate particles, the surface of said buffer layer adjacent to said semi-conductor layer being rich in glass and the surface of said buffer layer adjacent to said layer comprising electroluminescent phosphor being substantially free of iron compound.

6. An electroluminescent cell comprising, a conducting substrate, a semi-conductor layer comprising an iron-titanate-containing material carried on said conducting substrate, a titanate and mixed glass buffer layer carried on said semi-conductor layer, a layer comprising electroluminescent phosphor carried on said buffer layer, and a light-transmitting electrode layer carried on said layer comprising electroluminescent phosphor, said semi-conductor layer having a very low electrical resistance compared to the electrical resistance of said buffer layer, said semi-conductor layer also having a thickness at least equal to the thickness of said buffer layer, said buffer layer comprising about 90% by weight of barium titanate particles and about 10% by weight of glass fused about the barium titanate particles, the surface of said buffer layer adjacent to said semi-conductor layer being rich in glass and the surface of said buffer layer adjacent to said layer comprising electroluminescent phosphor being substantially free of iron compound, and said buffer layer having a thickness at least about as great as the thickness of said layer comprising phosphor.

7. An electroluminescent cell comprising, a conducting substrate, a semi-conductor layer comprising an iron-titanate-containing material carried on said conducting substrate, a titanate and mixed glass buffer layer carried on said semi-conductor layer, a layer comprising electroluminescent phosphor carried on said buffer layer, and a light-transmitting electrode layer carried on said layer comprising electroluminescent phosphor, said semi-conductor layer having a very low electrical resistance compared to the electrical resistance of said buffer layer, said semi-conductor layer also having a thickness about ten times the thickness of said buffer layer, said buffer layer comprising about 90% by weight of barium titanate particles and about 10% by weight of glass fused about the barium titanate particles, the surface of said buffer layer adjacent to said semi-conductor layer being rich in glass and the surface of said buffer layer adjacent to said layer comprising electroluminescent phosphor being substantially free of iron compound, and said buffer layer having a thickness at least about as great as the thickness of said layer comprising phosphor.

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