Nov. 12, 1963 R. W. WOLLENTIN 3,110,837

ELECTROLUMINESCENT DEVICE AND METHOD

Filed April 4, 1961

FIG. 1.

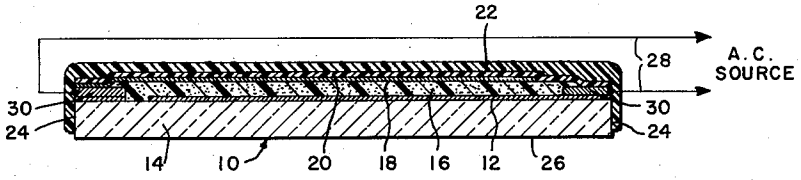
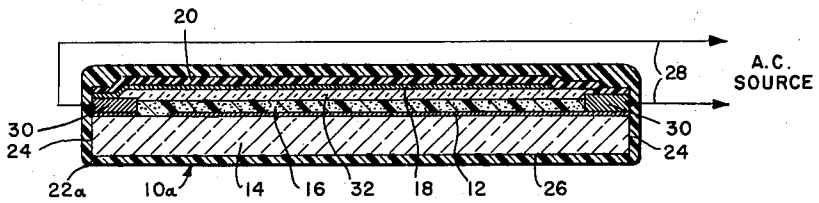



FIG. 2.



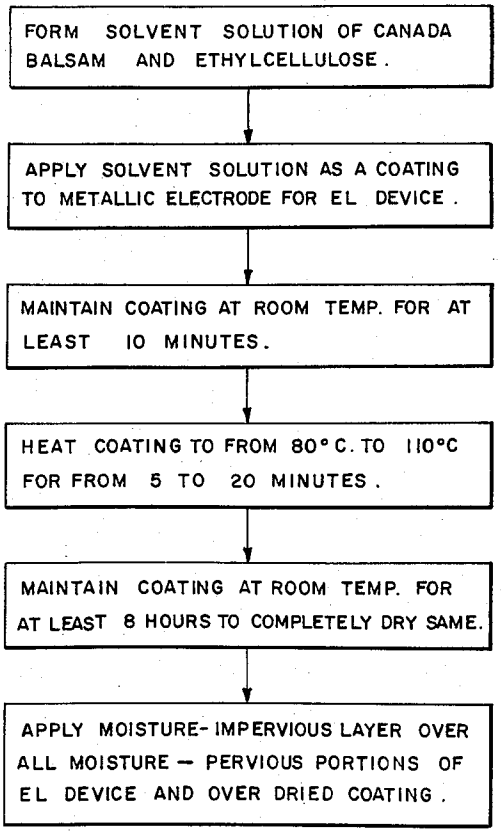




FIG. 3.

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United States Patent Office 3,110,837 Patented Nov. 12, 1963



# 3,110,837 ELECTROLUMINESCENT DEVICE AND METHOD

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Filed Apr. 4, 1961, Ser. No. 100,701
8 Claims. (Cl. 313—108)

This invention relates to electroluminescent devices and, more particularly, to an electroluminescent device which has improved operating characteristics and a method for making such an improved electroluminescent device.

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 time, considerable research and engineering effort has been expended on the phenomenon of electroluminescence and such devices have been marketed commercially. One of the main limitations to commercial utilization of electroluminescent devices is the inherent decrease in light output during operating life. The rate of light output decrease is known to be accelerated by the presence of moisture.

In order to prevent electroluminescent devices from being damaged by moisture, it has been suggested to encapsulate the moisture-pervious surface portions of such devices with a substantially moisture-impervious material. Such encapsulating moisture-impervious materials are normally fairly rigid, however, and if an incipient electrical breakdown occurs between the device electrodes, the resulting gases which are generated tend to cause the breakdown to become progressive in nature, thereby leading to the destruction of the electroluminescent layer. In addition, the encapsulating, substantially moisture-impervious materials are often not completely effective in preventing ingress of moisture with the result that under high-humidity conditions of operation, the useful operating life of such electroluminescent devices is severely limited.

It is the general object of the present invention to avoid and overcome the foregoing and other difficulties of and objections to prior-art practices by the provision of an electroluminescent device which has improved life when operated under conditions of high humidity.

It is another object to provide an electroluminescent device having good maintenance of initial brightness and which device has protection against progressive arcing between the device electrodes after an incipient arc has occurred therebetween.

It is a further object to provide a method for making an improved electroluminescent device which has good maintenance of light output when operated in moist atmospheres and which device is protected against progressive arcing between electrodes.

The aforesaid objects of the invention, and other objects which will become apparent as the description proceeds, are achieved by providing an electroluminescent device wherein a prime coat layer consisting essentially of a mixture of from 80% to 50% by weight of Canada balsam and from 20% to 50% by weight of ethylcellulose having an ethoxyl content of from 47.5% to 49.0% is provided over one of the device electrodes. Over this so-called prime coat and over all moisture-pervious operative portions of the electroluminescent device is placed a layer of substantially moisture-impervious material, such as a layer of epoxy resin. The improved prime coat provides better protection against the deleterious effects of moisture and, in addition, tends to quench or suppress



incipient arcs which may occur between the device electrodes, in order to prevent such incipient arcs from becoming progressive in nature and destroying the device.

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

FIG. 1 is a sectional elevational view of an electroluminescent device wherein the phosphor material is embedded in plastic dielectric and wherein the uppermost electrode is covered with the so-called prime coat of the present invention, with this prime coat and all moisture-pervious surface portions of the device being encased by a layer of substantially moisture-impervious material;

FIG. 2 is a sectional elevational view of an alternative construction for a device embodiment generally as shown in FIG. 1, wherein an additional layer of material having high electrical puncture strength is also included between the device electrodes;

FIG. 3 is a flow chart setting forth the steps of the present method.

With specific reference to the form of the invention illustrated in the drawings, the numeral **10** in FIG. 1 indicates generally an electroluminescent device comprising a first electrode **12** formed on a glass foundation **14**. A layer **16** comprising electroluminescent phosphor embedded in light-transmitting dielectric material is positioned over the electrode **12** and a second conducting electrode layer **18** is positioned over the phosphor-dielectric layer **16**. The spaced electrodes **12** and **18** and phosphor-dielectric layer **16** form the operative portion of the device **10**. Over the second or uppermost electrode **18** and exterior to the operative portion of the device **10** is carried a prime coat **20** which is formulated in accordance with the present invention, as will be considered in greater detail hereinafter. This prime coat has a thickness of at least 5 mils and preferably has a thickness of from 7 to 10 mils. Over the prime coat **20** and also over all moisture-pervious portions of the device **10** is carried an additional layer **22** of substantially moisture-impervious material which extends down onto the sides **24** of the foundation **14**. Light which is generated by the device **10** is emitted from the viewing face **26** of the glass foundation **14**. Energization of the device **10** is effected through lead conductors **28** sealed through the moisture-impervious layer **22**. These lead conductors are electrically connected to conventional bus bars **30**, which in turn complete electrical contact to the device electrodes **12** and **18**.

The glass foundation **14** can be fabricated of any conventional light-transmitting glass material and as an example, the foundation **14** has a thickness of one-eighth inch. The first electrode **12** can be formed of a very thin coating of electrically conducting and light-transmitting tin oxide, and such electrode coatings are well known. Other similar coatings such as indium oxide can be substituted therefor. The layer **16** comprising the phosphor-dielectric can be formed of any electroluminescent phosphor embedded in light-transmitting dielectric material, with plastic dielectric being preferred for best brightness. As an example, the electroluminescent phosphor is formed of finely divided zinc sulfide which is activated by copper and coactivated by chlorine. Such phosphor is well known and other known electroluminescent phosphors are summarized in Destriau and Ivey article in "Proceedings of the I.R.E.," Volume 43, No. 12, pages 1911–1940 (December 1955). For best initial brightness, the dielectric material in which the phosphor is embedded is preferably plastic and, as one example, a suitable plastic dielectric is polyvinyl chloride acetate. Other known plastic dielectric material can be substituted therefor. The relative proportions of phosphor and dielectric which comprise the layer **16** are not critical and by way of ex-

ample, two parts by weight of phosphor per one part by weight of dielectric are used in the layer **16**. The thickness of the layer **16** is two mils and this thickness can be varied.

The second electrode **18** is formed of vacuum-metallized material, preferably aluminum, although other metals such as silver can be used. The thickness of the electrode **18** is not critical and as an example is 1500 A.U. The second electrode **18** need not be vacuum metallized and can be fabricated of a preformed sheet of aluminum or other metal, if desired. A vacuum-metallized electrode layer contains a plurality of voids which will permit ingress of liquid. This in turn can damage the device. The prime coat **20** of the present invention is particularly adapted for use with such a vacuum-metallized electrode layer, inasmuch as this prime coat prevents liquid from penetrating into such voids in the electrode layer.

The so-called prime coat **20** of the present invention is formed of a mixture of from 80% to 50% by weight of Canada balsam and from 20% to 50% by weight of ethylcellulose having an ethoxyl content of from 47.5% to 49.0%. The substantially moisture-impervious layer **22** is preferably formed of a material which at least principally comprises epoxy resin. Such epoxy resins represent a class of condensation polymers, are well known, and are available from a number of different manufacturers. A catalyst is normally used to promote polymerization of the resin. On polymerization the molecular chain lengthens and considerable cross-linking occurs between individual molecular chains. There are numerous suitable catalysts which can be used in forming the epoxy resin layer **22** and the preferred catalyst is a mixture of 50% by weight diethylene triamine and 50% by weight acrylonitrile. Many other suitable catalysts for these epoxy resins are known and for a further discussion of such resins, see "Epoxy Resins" by Lee and Neville, published by McGraw-Hill (1957). Other materials can be added to the epoxy resins in forming the layer **22** to modify the characteristics of this layer. As an example, from 20 to 45% by weight of a polyamide can be added to the epoxy resins to increase their flexibility. This inhibits any tendency for stress failure of the layer **22**.

In fabricating the device **10**, the phosphor-dielectric layer **16** is first applied to the light-transmitting electrode **12** by conventional practices and the second electrode **18** vacuum metallized onto the layer **16**. As shown in the flow chart of FIG. 3, before applying the prime coat **20** to the exposed surface of the second electrode **18**, Canada balsam and the indicated ethylcellulose are mixed together with a siutable solvent to a viscosity which will facilitate spraying. The preferred relative proportions by weight of Canada balsam to ethylcellulose are 60–40 and this preferred ratio will be considered in detail. As a specific example 150 grams of Canada balsam and 50 cc. of turpentine are mixed with 100 grams of ethylcellulose having an ethoxyl content of from 47.5% to 49.0%, known in the art as "N-type" ethylcellulose. To the mixed Canada balsam and ethylcellulose are added 400 cc. of toluene and 200 cc. of n-butyl acetate. The resulting mixture is diluted with toluene in the proportion of one part by volume of toluene to four parts by volume of the mix for spray application. The solvent solution is then applied as a coating to the exposed surface of the second conducting layer **18** in such amount that the solids component of the applied solution will dry to a total thickness of at least 5 mils and preferably from 7 to 10 mils. It is preferred to form the prime coat by applying successive layers, allowing for a short drying period between each applied layer. As an example, in forming an eight-mil-thick prime coat **20**, this coating can be sprayed on as four successive layers, one on top of the other, each having a thickness of two mils. Thereafter the applied solvent-containing layer is maintained at room temperature for a period of at least ten minutes, and preferably for about fifteen minutes, in order to permit an appreciable



portion of the solvent therein to volatilize. Most of the remaining solvent is then volatilized from the applied coating by heating the coating at a temperature of from 80° C. to 110° C. for a period of from five minutes to twenty minutes, with the higher the heating temperature, the shorter the heating time. Preferably the coating **20** is heated to a temperature of about 100° C. for a period of from seven to ten minutes. Thereafter the applied coating **20** is maintained at room temperature for an additional period of at least 8 hours, in order to permit any residual solvent therein to volatilize therefrom.

The initial solvent coating drying period of at least ten minutes at room temperature has been found necessary to permit an appreciable portion of the solvent in the applied coating to volatilize at a relatively slow rate. If the coating were immediately heated after application in order to volatilize solvent, there would be some tendency to develop a "skin" over the applied coating. The follow-up heating period, as indicated, serves to drive nearly all remaining solvent from the applied coating, It has been found that any residual solvent remaining in the applied coating will damage the performance of the electroluminscent device. The last prolonged holding period at room temperature, as indicated hereinbefore, serves to permit any residual solvent to volatilize from the applied coating before the device is encapsulated, in order to insure that the performance of the device is not impaired by any entrapped residual solvent.

The partially fabricated device is then either dipped into an unpolymerized epoxy resin-catalyst mixture or such epoxy resin mix is flowed thereover to cover the applied layer **20** and moisture-permeable surface portions of the device **10**. In the case of the preferred indicated catalyst, resin polymerization is accomplished by heating the resin-coated device to a temperature of 50° C. for thirty minutes. In the device embodiment **10**, as shown in FIG. 1, the epoxy resin layer **22** covers the back portion of the device including the prime coat **20** and extends down onto the sides of the device so as to form a substantially moisture-impervious seal with the sides **24** of the glass foundation **14**. As an example, the epoxy resin layer **22** has a thickness of 45 mils. This thickness is not critical and is subject to considerable variation.

In FIG. 2 is shown a further device embodiment **10*a*** which generally corresponds to the embodiment **10**, as shown in FIG. 1, except that an additional layer **32** of material having a very high electrical breakdown resistance is also included between the device electrodes **12** and **18**. Such an additional layer can be formed of barium titanate or titania for example, as disclosed in British Patent No. 765,076, published October 22, 1954. The device embodiment **10*a***, as shown in FIG. 2 is also modified somewhat in that the layer **22*a***, which comprises light-transmitting epoxy resin, encapsulates the entire device. Such a construction lends itself to a dip process for applying the epoxy resin layer **22*a***.

In controlled tests, electroluminescent devices incorporating the improved prime coat of this invention were operated at a temperature of 50° C. and at a relative humidity of approximately 98%. The control electroluminescent devices were otherwise similar but incorporated, as a so-called prime coat, an equivalent layer of Canada balsam which was not modified by the addition of the specified ethylcellulose. The devices incorporating the improved prime coat of the present invention operated for approximately twice as long as the control devices before the first indication of deleterious moisture penetration. Also, under normal ambient operating conditions, the devices incorporating the present improved prime coat operated for approximately twice as long as the control devices before the light output dropped to one-half of its initial value. In addition, when incipient arcs did occur, both the control devices and the present devices acted to quench the arcs and prevent them from becoming progressive.

Devices incorporating a prime coating formed of Can-

ada balsam, without the addition of ethylcellulose in accordance with the present invention, are limited in operating temperature because of the low melting point of Canada balsam, which is about 80° C. In addition, the Canada balsam is a relatively expensive material to purchase. A mixture of 60% by weight Canada balsam and 40% by weight ethylcellulose has a melting point of about 105° C. so that the temperature range under which the device can be operated is appreciably increased when the present improved prime coat is used.

If less than 20% by weight of the specified ethylcellulose is utilized, the melting point for the prime coat layer **20** will be decreased to about 90° C. or less. From a commercial standpoint, this is barely acceptable. If more than 50% by weight of the specified ethylcellulose is utilized, the melting point of the prime coat layer **20** increases further, but the coating layer is overly hard and brittle. As a result, there is lack of adherence of the prime coat layer to the operative portion of the device. In addition, because of the increased melting point and brittleness, the arc-suppressant qualities of such a coating layer are impaired, apparently because the coating layer does not melt rapidly enough to enable the gases generated on incipient breakdown to be dissipated in sufficiently rapid fashion to quench such an incipient arc. If the coating layer **20** is less than 5 mils in thickness, the performance of the device is somewhat marginal from the standpoint of protecting the device from progressive arcing and possible contamination by the overlying layer of substantially moisture-impervious material. As indicated hereinbefore, the preferred thickness for the layer **20** is from 7 to 10 mils. There appears to be no technical limitation to how thick the layer **20** can be, except as limited by the considerations of cost of materials and cost of manufacture.

Other materials can be utilized to replace the epoxy resin in forming the moisture-impervious layer **22**. As an example, the layer **22** can be formed of glass which is adhered to the prime coat layer **20** by means of a very thin layer of epoxy resin.

As a possible alternative embodiment, the plastic dielectric material which is used as an embedding medium for the phosphor can be replaced by a glass or ceramic dielectric, such a construction being well known. In accordance with the present invention, the prime coat still would be placed over the uppermost electrode and the entire device encapsulated with the substantially moisture-impervious material, in order to inhibit any ingress of moisture to the operative portions of such a ceramic-type device.

It will be recognized that the objects of the invention have been achieved by providing an electroluminescent device which operates very well under conditions of high humidity as well as in a normal environment. In addition, this device is not subject to progressive arcing between the electrodes. There has also been provided a method for fabricating such an improved device.

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

I claim:

1. An electroluminescent device comprising, a light-transmitting first electrically conducting layer carried on a light-transmitting foundation, a second electrically conducting layer spaced from said first conducting layer, a layer comprising electroluminescent phosphor included between said first and said second conducting layers, said first and said second conducting layers and said layer comprising electroluminescent phosphor defining the operative portion of said device, a prime coat having a thickness of at least 5 mils carried on said second conducting layer and external to the operative portion of said device, said prime coat consisting essentially of a mixture of from 80% to 50% by weight of Canada balsam and from 20% to 50% by weight of ethylcellulose having an ethoxyl content of from 47.5% to 49.0% and a substantially moisture-impervious layer over said prime coat and encapsulating all moisture-pervious operative portions of said device.



2. An electroluminescent device as specified in claim 1, wherein said substantially moisture-impervious layer at least principally comprises epoxy resin.

3. An electroluminescent device as specified in claim 1, wherein said second conducting layer contains a plurality of voids which will permit ingress of liquid.

4. An electroluminescent device comprising, a light-transmitting first electrically conducting layer carried on a light-transmitting foundation, a second electrically conducting layer spaced from said first conducting layer, a layer comprising electroluminescent phosphor included between said first and said second conducting layers, said first and said second conducting layers and said layer comprising electroluminescent phosphor defining the operative portion of said device, a prime coat having a thickness of from 7 to 10 mils carried on said second conducting layer and external to the operative portion of said device, said prime coat consisting essentially of a mixture of about 60% by weight of Canada balsam and about 40% by weight of ethylcellulose having an ethoxyl content of from 47.5% to 49.0% and a substantially moisture-impervious layer over said prime coat and encapsulating all moisture-pervious operative portions of said device.

5. The method of protecting from damage by moisture an electroluminescent device comprising a light-transmitting first electrically conducting layer carried on a light-transmitting foundation, a second electrically conducting layer spaced from said first conducting layer, and a layer comprising electroluminescent phosphor included between said first and said second conducting layers, which method comprises: forming a solvent solution having dissolved solids consisting essentially of from 80% to 50% by weight Canada balsam and from 20% to 50% by weight ethylcellulose having an ethoxyl content of from 47.5% to 49.0%; applying said solvent solution as a coating to the exposed surface of said second conducting layer in such total thickness that the solids components of such applied solvent coating will dry to a thickness of at least 5 mils; maintaining said applied solvent coating at room temperature for a period of at least ten minutes to permit an appreciable portion of solvent therein to volatilize therefrom; further volatilizing solvent from the applied coating by heating same at a temperature of from 80° C. to 110° C. for a period of from five minutes to twenty minutes, with the higher the heating temperature the shorter the heating time; maintaining said applied coating at room temperature for an additional period of at least eight hours to permit any residual solvent therein to volatilize therefrom; and thereafter applying a substantially moisture-impervious layer over said applied Canada balsam-ethylcellulose coating as well as over all moisture-pervious portions of said device.

6. The method as specified in claim 5, wherein said solvent solution is initially applied as a plurality of successive coatings to the exposed surface of said second conducting layer, with the total thickness of such applied coatings being such that the solids components thereof will dry to a thickness of at least 5 mils.

7. The method as specified in claim 5, wherein said solvent solution is applied as a coating to the exposed surface of said second conducting layer in such total thickness that the solids components of such applied solvent coating will dry to a thickness of from 7 mils to 10 mils.

8. The method of protecting from damage by moisture an electroluminescent device comprising a light-transmitting first electrically conducting layer carried on a light-transmitting foundation, a second electrically conducting layer spaced from said first conducting layer, and a layer comprising electroluminescent phosphor including be-

tween said first and said second conducting layers, which method comprises: forming a solvent solution having dissolved solids consisting essentially of from 80% to 50% by weight Canada balsam and from 20% to 50% by weight ethylcellulose; applying said solvent solution as a coating to the exposed surface of said second conducting layer in such total thickness that the solids components of such applied solvent coating will dry to a thickness of from 7 to 10 mils; maintaining said applied solvent coating at room temperature for a period of about fifteen minutes to permit an appreciable portion of solvent therein to volatilize therefrom; further volatilizing solvent from the applied coating by heating same at a temperature of about 100° C. for a period of from seven minutes to ten minutes; maintaining said applied coating at room temperature for an additional period of at least eight hours to permit any residual solvent therein to volatilize therefrom; and thereafter applying a substantially moisture-impervious layer at least principally comprising epoxy resin over said applied Canada balsam-ethylcellulose coating as well as over all moisture-pervious portions of said device.



No references cited.