May 24, 1966 R. V. LEVETAN 3,253,173

ELECTROLUMINESCENT CELLS WITH PHOSPHOR-CONDUCTOR ADHESION AND MANUFACTURE THEREOF

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Fig. 1.

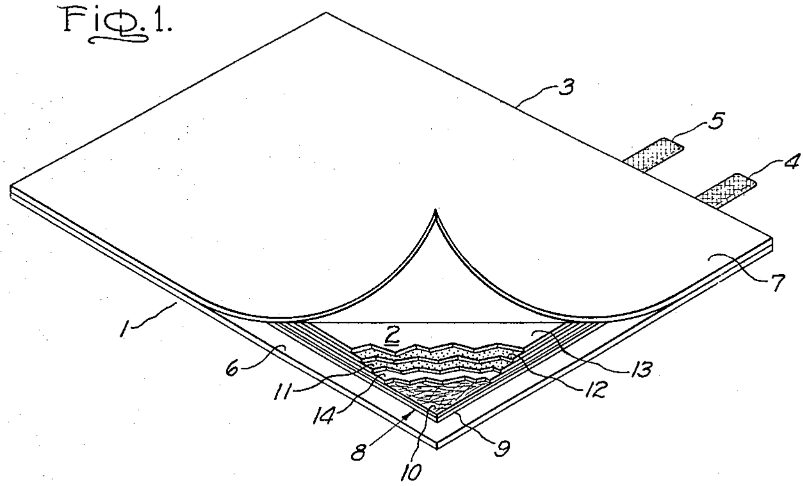
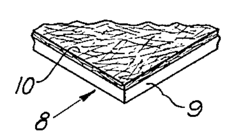


Fig. 2.



Inventor:
Robert V. Levetan
by James J. Laznan
His Attorney

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ELECTROLUMINESCENT CELLS WITH PHOSPHOR-CONDUCTOR ADHESION AND MANUFACTURE THEREOF

Robert V. Levetan, Twinsburg, Ohio, assignor to General Electric Company, a corporation of New York

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This invention relates in general to electroluminescent lamps or cells and to a novel method of making a flexible type electroluminescent cell.

An electroluminescent lamp or cell generally comprises a layer of phosphor, capable of generating light under the action of an electric field, sandwiched between the pair of conducting plates or films at least one of which is transparent or light-transmitting. One form of electroluminescent lamp now well known is of the flexible type described and claimed in U.S. Patent No. 2,774,004, Jaffe, assigned to the same assignee as the present invention and comprising a flexible laminated assembly of electrically active layers or elements each of which is of flexible character. The electrically active elements comprise an aluminum foil coated with an insulating layer of high dielectric constant material which in turn is overcoated with a layer of electroluminescent phosphor and finally overlaid with a transparent flexible conductive sheet such as a thin sheet of compacted glass fibers in the form of conducting glass cloth or paper. The aluminum foil and the conducting glass paper form the electrodes of the lamp to which an alternating potential is applied to cause the electroluminescent phosphor to generate light which is then emitted through the transparent conductive glass paper.

As stated above, one form of light-transmitting conductive sheet commonly employed in the production of such flexible type electroluminescent cells or lamps is comprised of electrically conductive glass paper around .002 inch thick, the glass fibers of which are coated with a thin light-transmitting film of electrically conductive material such as, for example, a metal or a metallic oxide, or an indium compound as described more fully in U.S. Patent No. 2,849,339, Jaffe, assigned to the assignee of this invention. Although the prior cell-making methods involving the use of such extremely thin conducting glass paper have resulted in the production of electroluminescent cells which have been entirely satisfactory in operating or lighting performance, the fragile or delicate nature of the thin glass paper severely handicaps the ease with which such electroluminescent cell assemblies can be produced. Specifically, the glass paper employed, due to its extremely delicate nature, crumbles or shatters easily, and therefore requires the utmost degree of care while cutting and while handling during cell assembly. Moreover, and perhaps most importantly, it should be noted that current techniques of producing such type flexible electroluminescent cells having an area of 26 square inches or greater, which techniques necessarily require the difficult step of cutting a sheet of glass paper to the appropriate dimensions, result in high production rejects or so-called shrinkage due apparently to the electrical shorting of the lamps caused by the contact of the conductive glass fibers with the underlying metallic base foil. An explanation of this phenomenon may be that during the subsequent pressure laminating operation, portions of the conducting glass paper are forced through the underlying phosphor and insulating layers to the extent that they contact the conductive metallic film, thus shorting the lamp. Whatever the cause of such shorting may be, it remains apparent that a new and improved method of producing electroluminescent cell assemblies which would obviate the problems attending the handling of extremely fragile

conductive glass paper, and which would, if possible, reduce or eliminate the production rejects in the case of larger size electroluminescent cells due to electrical shorting between the conducting glass paper and the underlying base foil, would indeed be highly desirable from the standpoint of simplicity and economy in manufacture.

The above-mentioned problems may be satisfactorily overcome by adopting the manufacturing procedure disclosed in copending U.S. application Serial No. 137,924 H. W. Longfellow, filed September 13, 1961, now Patent No. 3,226,272, and assigned to the same assignee as the present invention. According to the procedure therein disclosed, an electroluminescent cell is made by first prelaminating the electrically conductive glass paper to one face of a sheet of transparent thermoplastic material to form a light-transmitting electrically conductive plastic film material or prelaminate of tough and flexible character which may be handled and cut with ease without any liability of the glass paper component crumbling or shattering, and then laminating a sheet of such conductive plastic film material together with, or otherwise affixing thereto, the other component laminar elements of an electroluminescent cell assembly, comprising the phosphor and back electrode layers. With such a manufacturing procedure, however, it has been found that where the electroluminescent phosphor layer of the finished electroluminescent cell is applied to the glass paper face of the conductive plastic sheet or prelaminate by coating the said layer thereonto, there is a tendency for the phosphor layer, on drying, to separate from the conducting glass paper face of the conducting plastic sheet. The existence of such a separation between these layers in the finished electroluminescent cell would, of course, render the cell defective and adversely affect its operation and appearance.

It is an object of the present invention, therefore, to provide a novel form of, and a new and improved method of making an electroluminescent cell.

Another object of this invention is to provide a new and improved method of making an electroluminescent cell of the type having a conductive glass paper electrode onto which the phosphor layer of the cell is coated, which method substantially eliminates the possibility of the conductive glass paper and the phosphor layer of the cell subsequently becoming separated such as to adversely affect the lighting performance and appearance of the cell.

Briefly stated, in accordance with the invention, in the manufacture of an electroluminescent cell by the process of coating a layer of electroluminescent phosphor material onto electrically conductive glass paper which has been previously prelaminated to one side of a thermoplastic sheet, the glass paper face of the conductive plastic sheet or prelaminate, prior to the application of the phosphor coating thereto, is first coated with a thin layer of a suitable adhesion promotor such as an organic alkoxy titanate ester in order to thereby afford a firm bond of the phosphor coating to the glass paper face of the conductive plastic sheet such as prevents subsequent separation therebetween.

Further objects and advantages of my invention will appear from the following detailed description of a species thereof and from the accompanying drawing.

In the drawing, FIG. 1 is a pictorial view of a flexible electroluminescent cell made in accordance with the method of the present invention, the various constituent layers being delaminated or peeled open at one corner to show the internal construction thereof, and

FIG. 2 is a fragmentary perspective view on an enlarged scale of the electrically conductive plastic sheet or prelaminate element of the cell.

Referring to the drawing, the electroluminescent cell or lamp **1** therein illustrated comprises an electrically active cell portion or assembly **2** made in accordance with the method of my invention and sealed within a substantially moisture-impervious outer encapsulating envelope **3**. The cell **1** is energized by applying a suitable potential such as an alternating voltage, for example, 120 volts 60 cycles A.C., to the copper terminals **4** and **5** projecting laterally from the edge of the outer envelope **3** composed of sheets **6** and **7** which may be made of suitable thermoplastic material which flows under heat and pressure. As shown, the two sheets **6** and **7** overreach the marginal edges of the electrically active cell portion **2** and are sealed together along their margins so as to completely enclose the cell portion **2**. The materials selected for the encapsulating envelope **3** are preferably tough and stable in addition to exhibiting light-transmitting qualities and high impermeability to moisture, and further they are preferably flexible in nature. Among the materials which may be satisfactorily employed for this purpose are polyethylene, polytetrafluoroethylene, polychlorotrifluoroethylene, polystyrene, methyl methacrylate, polyvinylidine chloride, polyvinyl chloride, polycarbonate materials such as, for example, the reaction products of diphenyl carbonate and bisphenol A, and polyethylene terephthalate. The materials preferably employed for such purpose, however, are either polychlorotrifluoroethylene film, known as Kel F, of approximately 0.005 inch thickness, or the resin-impregnated mica paper or micamat material described and claimed in copending U.S. application Serial No. 118,113, R. V. Levetan, filed June 19, 1961, and assigned to the same assignee as the present invention.

In accordance with the invention, the electrically active portion or assembly **2** of the electroluminescent cell **1** is comprised in part of a layer **8** of light-transmitting electrically conductive plastic sheet material consisting of a sheet **9** of thermoplastic film having a sheet **10** of electrically conductive micro-fiber glass paper such as described hereinbefore partially embedded in one face thereof but sufficiently exposed thereat to render the said face electrically conductive, the said conductive face serving as one of the electrodes of the cell **1**. The thermoplastic sheet **9** and the conductive glass paper **10** are preliminarily laminated together under pressure and heat to form a light-transmissive electrically conductive plastic sheet or prelaminate **8** as described and claimed in the aforementioned copending application Serial No. 137,924 of H. W. Longfellow. The prelaminating of the conductive glass paper **10** to the thermoplastic sheet **9** provides a conductive plastic sheet material of tough and flexible character which can be handled with ease and lends itself to cutting and bending without fracturing or breaking apart. This characteristic of the conductive plastic sheet material or prelaminate **8** is in marked contrast to that of the glass paper **10** by itself which, because of its exceedingly fragile or delicate character and its consequent susceptibility to breakage or fracturing, is very difficult to handle and cut without breaking.

In general, any thermoplastic material may be employed for the plastic layer **9** of the conductive plastic sheet material **8**. Included among the materials which have been found suitable for such purpose, however, are nylon, cellulose acetate, cellulose acetate butyrate, polyvinyl alcohol, polyvinylpyrrolidone, polyvinylchloride, polyvinylidine chloride, copolymers of polyvinylchloride and polyvinylidine chloride, polyvinylacetate, polystyrene and polymers of methyl methacrylate. In order to provide an electroluminescent cell which has a substantially improved resistance to water depreciation, it may be advantageous to select for the plastic layer **9** a thermoplastic material which exhibits hydrophilic properties, i.e., has an affinity for water. As disclosed in copending application Serial No. 80,613 of Devol et al., filed January 4, 1961, now U. S. Patent No. 3,148,299, and assigned to the same assignee as the present invention, polyamide condensation products such as nylon 6,6 or nylon 6 such as that known as "Caplene," have been found to be particularly effective as hydrophilic materials for the plastic layer **9**.

The pressure required to laminate together the contiguous layers of conducting glass paper **10** and plastic sheet material **9** to form the prelaminate **8** may be applied thereto in any suitable manner, as by compressing them between cooperating flat pressure plates or pressure rolls, or by means of a gas impervious conformable diaphragm in a hydrostatic press such as described in U.S. Patent 2,945,976, Fridrich et al., dated July 19, 1960, and assigned to the same assignee as the present invention. The electrically conductive plastic prelaminate material may be formed in large sheets or in continuous roll form, from which individual sheets **8** of proper size and shape may then be cut for assembly with the other component elements of the electrically active portion **2** of the electroluminescent cell **1**.

In addition to the electrically conductive plastic sheet or prelaminate **8**, the electrically active portion **2** of the electroluminescent cell **1** is comprised of a layer **11** of an electroluminescent phosphor coated onto the conductive glass fiber side **10** of the conductive plastic sheet or prelaminate **8**, a thin layer **12** of an insulating material coated over the phosphor layer **11**, and a layer **13** of electrically conductive material laid over the insulating layer **12** and serving as the other electrode of the electroluminescent cell. The electroluminescent phosphor layer **11** consists of any known electroluminescent phosphor such as, for example, zinc sulfide-zinc oxide with suitable activators such as copper, manganese, lead or silver, dispersed in an organic polymeric matrix. Examples of suitable organic polymeric matrices are cellulose nitrate, polyacrylates, methacrylates, polyvinyl chloride, cellulose acetate, alkyd resins, epoxy cements, and polymers of triallyl cyanurate, to which may be added modifying substances or plasticizers such as camphor, dioctyl phthalate, tricresyl phosphate and similar materials. A preferred organic polymeric matrix forming a dense tough film of high dielectric constant and good mechanical and thermal stability and consisting of cyanoethyl cellulose with suitable plasticizers such as cyanoethyl phthalate is described and claimed in U.S. Patent 2,951,865, Jaffe et al., assigned to the same assignee as the present invention. The phosphor dispersed in the suspending medium such as the abovementioned cyanoethyl cellulose solution, may be applied to the conductive glass fiber surface **10** of the conductive plastic sheet **8** in any suitable manner, for instance, as by spraying or through the use of a doctor blade, to form the phosphor layer **11**. The phosphor coating is then dried as by means of a bank of heat lamps.

It has been found that where the phosphor layer **11** is coated directly onto the conductive glass fiber side **10** of the conductive plastic sheet **8**, there is a tendency for the phosphor layer **11** to separate from the conductive glass fiber surface **10** of the conductive plastic sheet **8** in the finished electroluminescent cell. Such a separation between these elements would, of course, render the electroluminescent cell defective and adversely affect its appearance and its operation or lighting performance. In accordance with the invention, therefore, the conductive glass fiber side **10** of the conductive plastic sheet **8** is suitably treated, prior to the application thereto of the phosphor coating **11**, in order to thereby prevent the occurrence of any such separation between the phosphor layer **11** and the conductive glass fiber side **10** of the conductive plastic sheet **8**. For such purpose, a coating **14** of a suitable bonding substance of the type commonly referred to as an adhesion promoter material is applied to the conductive glass fiber surface **10** of the conductive plastic sheet **8** to serve as a bonding interlayer between the conductive glass fiber surface **10** and the phosphor layer **11**. Adhesion promoter materials which have been found suitable for use for the bonding interlayer **14** are certain organic alkoxy titanate esters such as, for example, tetra-butyl titanate or poly-dibutyl titanate, or a mixture of tetra-isopropyl titanate and tetra-stearyl titanate, preferably that commercially known at Tyzor AP, made by E. I. du Pont de Nemours & Company of Wilmington, Delaware, and comprising approximately four parts, by weight, of tetra-isopropyl titanate and one part, by weight, of tetra-stearyl titanate. The adhesion promoter material or layer **14** may be applied onto the plastic sheet **8** in the form of a solution to form a film which is then dried and baked on the plastic sheet **8**. According to a specific example, a 4 to 5% solution of Tyzor AP adhesion promoter in a suitable hydrocarbon solvent, such as toluene or normal heptane, may be coated onto the conductive glass fiber surface **10** of the plastic sheet **8** to form a wet film thereon around 4 mils thick which is then either air dried and baked for a period of around 10 minutes at approximately 110° C., or else simply air dried under heat lamps or similar heating means, to thereby form the bonding interlayer **14**.

After the application of the adhesion promoter layer **14** to the conductive plastic film material or prelaminate **8**, the phosphor layer **11** as described previously is then applied over the layer **14** and the dried phosphor layer then overcoated with a thin insulating layer **12**. The insulating layer **12** is preferably comprised of a material having a high dielectric constant, such as barium titanate for instance, dispersed in an organic polymeric matrix such as that employed for the phosphor layer **11** as described hereinbefore. The insulating layer **12** is applied over the phosphor layer **11** in any suitable manner, as by spraying or through the use of a doctor blade, after which the entire assembly is again dried as in the manner employed for the phosphor layer **11**.

Following the drying of the insulating layer **12**, the second or back electrode layer **13** is then applied over the said insulating layer to thereby complete the fabrication of the electrically active portion **2** of the electroluminescent cell **1**. This electrode **13** may be comprised of some form of conductive paint or paste, or a similar conductive material, which may be brushed, sprayed, rolled or silk screened onto the insulating layer **12** either in the form of a continuous imperforate layer thereon or in the form of various patterns, designs or indicia. Alternatively, a layer of a suitable metal such as aluminum may be applied over the insulating layer **12** by evaporation under high vacuum according to techniques well known in the art, or metal foil such as aluminum foil may be either laminated to the insulating layer **12** or cemented thereto by conductive cement.

The electrically active cell portion **2** as thus fabricated in accordance with the invention is then preferably enclosed within the outer envelope **3** to complete the manufacture of the electroluminescent cell or lamp **1**. The encapsulation of the electrically active cell portion **2** may be conveniently performed in the manner disclosed in the aforementioned U.S. Patent 2,945,976, Fridrich et al., i.e., by stacking and laminating the cell portion **2** between two sheets **6** and **7** of thermoplastic material overreaching the marginal edges of the cell portion **2**, with the projecting copper terminals **4**, **5**, which may comprise flat braids or ribbons of copper or a similar electrically conductive material, positioned between the sheets **6** and **7** so as to be in electrical contact, respectively, with the back electrode layer **13** and the conductive glass fiber surface **10** of the prelaminate **8**. To enable the electrical contact of the terminal **5** with the conductive glass fiber surface **10**, a portion of the said surface **10** such as a narrow strip thereof along one edge, may be left uncoated or uncovered with the phosphor and insulating coatings **11**, **12** and the back electrode layer **13**, so as to be exposed along the said edge. Also, to avoid the possibility of the back electrode layer **13** contacting the conductive glass fiber surface **10** of the prelaminate **8** and thus forming an electrical short therebetween, the marginal edges of the back electrode layer **13** may be terminated a short distance back from the marginal edges of the insulating layer **12**. The stacked assembly comprised of the cell portion **2**, terminals **4**, **5**, and plastic sheets **6**, **7**, is then laminated together by placing it in a hydrostatic laminating press, between the press platens thereof which are separated by a conformable diaphragm suitably of aluminum foil. Compressed fluid or air is admitted into the press chamber, over the diaphragm therein, to exert hydrostatic pressure on the stacked cell components, vacuum is applied under the diaphragm to remove any trapped gases or moisture, and heat is supplied by suitable means to the stacked assembly in order to cause the plastic sheets **6**, **7** to seal together at their margins so as to encapsulate the electrically active cell portion **2**. During the laminating process, the conductors **4** and **5** become embedded in the plastic sheets **6**, **7** and are at the same time pressed into intimate contact with the back electrode layer **13** and the conductive glass fiber surface **10** of the prelaminate **8**.

The encapsulation of the electrically active cell portion **2** in an outer moisture-resistant envelope **3** may also be accomplished in the manner disclosed and claimed in my copending U.S. application Serial No. 118,112, filed June 19, 1961, and assigned to the same assignee as the present invention, wherein the cell portion **2** is laminated between sheets **6**, **7** of epoxy resin impregnated micamat or mica paper sheets.

By the provision, in accordance with the invention, of the intermediate bonding layer **14** of suitable adhesion promoting material between the phosphor layer **11** and the conductive glass fiber surface **10** of the prelaminate **8**, good adhesion of the phosphor layer to the glass fiber surface **10** is assured in the finished electroluminescent cell **1** so that subsequent separation therebetween is prevented. As a result, a useful, bright and attractive appearing electroluminescent cell is produced.

What I claim as new and desire to secure by Letters Patent of the United States is:

1. An electroluminescent cell comprising a transparent thermoplastic sheet having a sheet of electrically conductive glass paper partially embedded in one face thereof, a layer of an adhesion promoter material coated on the said glass paper face of said thermoplastic sheet, a layer of phosphor coated on the said adhesion promoter layer, and a layer of electrically conductive material on said phosphor layer.

2. An electroluminescent cell as specified in claim 1 wherein the said adhesion promoter material comprises an organic alkoxy titanate ester.

3. An electroluminescent cell as specified in claim 1 wherein the said adhesion promoter material comprises an organic alkoxy titanate ester of the group consisting of tetra-butyl titanate, poly-dibutyl titanate, and mixtures of tetra-isopropyl titanate and tetra-stearyl titanate.

4. An elecroluminescent cell as specified in claim 1 wherein the said adhesion promoter material comprises a mixture of approximately 4 parts, by weight, of tetra-isopropyl titanate and one part, by weight, of tetra-stearyl titanate.

5. A method of making an electroluminescent cell comprising the steps of first laminating a flexible and structurally weak electrically conductive lamina to one face of a flexible thermoplastic sheet, under pressure and heat, to form an electrically conductive plastic prelaminate, coating the said face of said prelaminate with a layer of an adhesion promoter material, overcoating the said layer of adhesion promoter material with a layer of electroluminescent phosphor, and then applying an electrically conductive layer over the said phosphor layer.

6. A method of making an electroluminescent cell comprising the steps of first laminating a sheet of electrically conductive glass paper to one face of a flexible thermoplastic sheet, under pressure and heat, to form an electrically conductive flexible plastic sheet having conductive glass fibers partly embedded in the said one face thereof, coating the said face of the conductive plastic sheet with

a layer of an adhesion promoter material, overcoating the said layer of adhesion promoter material with a layer of electroluminescent phosphor, and then applying an electrically conductive layer over the said phosphor layer.

7. A method of making an electroluminescent cell comprising the steps of first laminating a sheet of electrically conductive glass paper to one face of a flexible thermoplastic sheet, under pressure and heat, to form an electrically conductive flexible plastic sheet having conductive glass fibers partly embedded in the said one face thereof, coating the said face of the conductive plastic sheet with a layer of adhesion promoter material, coating the said layer of adhesion promoter material with a layer of electroluminescent phosphor, overcoating the said layer of electroluminescent phosphor with an insulating layer of high-dielectric constant material, and then applying an electrically conductive layer over the said insulating layer.

8. A method of making an electroluminescent cell comprising the steps of first laminating a sheet of electrically conductive glass paper to one face of a flexible thermoplastic sheet, under pressure and heat, to form an

electrically conductive flexible plastic sheet having conductive glass fibers partly embedded in the said one face thereof, coating the said face of the conductive plastic sheet with an adhesion promoter layer of organic alkoxy titanate ester material, overcoating the said adhesion promoter layer with a layer of electroluminescent phosphor, and then applying an electrically conductive layer over the said phosphor layer.

9. A method of making an electroluminescent cell as specified in claim 8 wherein the said adhesion promoter layer comprises a mixture of tetra-isopropyl titanate and tetra-stearyl titanate.

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GEORGE N. WESTBY, *Primary Examiner.*

BENNETT G. MILLER, *Examiner.*

C. R. CAMPBELL, *Assistant Examiner.*