Feb. 19, 1963 W. A. THORNTON, JR 3,078,382

ELECTROLUMINESCENT DEVICE

Filed Sept. 21, 1960

FIG. 1.

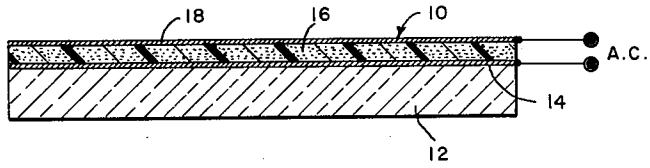


FIG. 2.

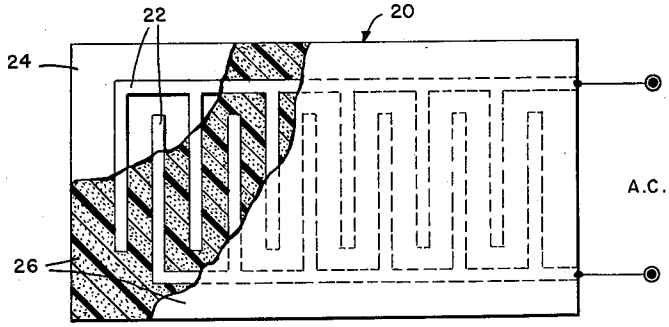
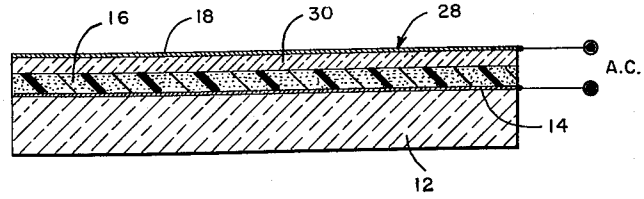


FIG. 3.



INVENTOR.
WILLIAM A. THORNTON, Jr.
BY
W. D. Palmer
ATTORNEY.

United States Patent Office

3,078,382
Patented Feb. 19, 1963

3,078,382

ELECTROLUMINESCENT DEVICE

William A. Thornton, Jr., Cranford, N.J., assignor to Westinghouse Electric Corporation, East Pittsburgh, Pa., a corporation of Pennsylvania

Filed Sept. 21, 1960, Ser. No. 57,563
6 Claims. (Cl. 313—108)

This invention relates to electroluminescent devices and, more particularly, to an electroluminescent device which displays 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. For best initial brightness, it is preferred to embed the finely divided electroluminescent phosphor in plastic dielectric material. During operation of such devices a blackening of the plastic has been observed. This blackening impairs the appearance of the devices when in an unenergized condition and also absorbs some of the light which is generated during operation. The degree of blackening varies somewhat, but appears to be present in all plastic-type electroluminescent devices which have been marketed commercially.

One application for which electroluminescence is particularly adapted is in conjunction with a digital display, such as described in U.S. Patent No. 2,922,993, dated January 26, 1960, to Sack. The preferred construction for this display device is shown in FIG. 1 of the aforementioned Sack patent. The blackening as described hereinbefore is particularly noticeable with such a digital display device, since the plastic-phosphor portions which are never energized remain quite white in appearance, while those plastic-phosphor portions which are energized tend to blacken during life. This blackening is particularly objectionable in that when the device is unenergized, a numerical indicia is visible in the form of a blackened "Figure 8."

It is the general object of this invention to avoid and overcome the foregoing and other difficulties of and objections to prior-art practices by the provision of an electroluminescent device having improved performance characteristics.

It is another object to provide an electroluminescent device having improved maintenance of initial light output.

It is a further object to provide an electroluminescent device in which blackening of the plastic portions adjacent the phosphor is greatly inhibited.

The aforesaid objects of the invention, and other objects which will become apparent as the description proceeds, are achieved by providing an electroluminescent device which comprises spaced electrodes. Included between the spaced electrodes is finely divided zinc-sulfide-type electroluminescent phosphor embedded in plastic dielectric material. In accordance with the present invention, additive ammonium halide is included in the plastic dielectric material in amount of from 0.01% to 2% by weight of the plastic dielectric material. This additive ammonium halide serves to inhibit blackening of the plastic during operation of the device, in order

to improve the appearance of the device as well as the maintenance of initial light output.

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 which incorporates additive ammonium halide in the dielectric, in accordance with the present invention;

FIG. 2 is a plan view, partly broken away, of an electroluminescent device incorporating additive ammonium halide in accordance with the present invention and wherein the device electrodes are formed as an interlacing, raster-type grid;

FIG. 3 is a sectional elevational view of an alternative device construction generally corresponding to FIG. 1, but wherein an additional layer of dielectric material is also included between the device electrodes.

While the present invention can be used in conjunction with any type of electroluminescent device, such as the digital display device described in the aforementioned patent to Sack, the present invention also has utility with respect to electroluminescent devices which are intended to serve as light sources or lamps and the invention has been so illustrated and will be so described.

With specific reference to the form of the invention illustrated in the drawings, in FIG. 1 is shown an electroluminescent device 10 which generally comprises a glass foundation 12 having carried thereon a first electrode 14 which is formed of a thin layer of light-transmitting, electrically conducting tin oxide. Coated over the electrode 14 is a layer 16 comprising finely divided electroluminescent phosphor embedded in plastic dielectric and coated thereover is a second electrode 18, which is formed of vacuum-metallized aluminum or copper iodide, for example. The phosphor-dielectric layer 16 also includes the additive ammonium halide, as explained hereinafter. An alternating electric potential is adapted to be applied across the electrodes 14 and 18 in order to energize the electroluminescent device to light emission.

The tin oxide electrode layer 14 can be formed of other suitable light-transmitting, electrically conducting material, such as indium or titanium oxides or copper iodide, for example. In this specific example, the phosphor is mixed with equal parts by weight of a light-transmitting dielectric, such as polyvinyl-chloride and the thickness of the layer 16 is approximately two mils. The thickness of the layer 16 is not critical and can be varied considerably. The relative proportions of phosphor and dielectric can also be varied.

The electroluminescent phosphor which is incorporated in any of the device embodiments described herein is a zinc-sulfide-type electroluminescent phosphor. As a specific example for preparing such a phosphor, 1000 grams of zinc sulfide are mixed with 30 grams of sulphur, 12.8 grams of copper acetate, and 4.5 grams of ammonium chloride. This mixture is fired in a partially closed container in a nitrogen atmosphere at a temperature of about 950° C. for about 100 minutes. Thereafter the phosphor is slightly crushed, 30 grams of sulphur are added and it is refired in a similar manner. After final firing, the phosphor is lightly crushed to reduce it to finely divided status and it is then washed in a solution which is a good solvent for cuprous sulfide, but which is

not a good solvent for zinc sulfide. An example of such a washing solution is a one-normal solution of sodium cyanide, made alkaline by the addition of a small amount of sodium hydroxide. The dried phosphor has an average particle diameter of ten to twelve microns. The particle diameter is not critical and can be varied. To date, such zinc sulfide electroluminescent phosphors are the best known for electroluminescence. Other activators can be used to supplement the copper, examples being manganese or lead. In addition, the zinc sulfide can be replaced in part by cadmium sulfide, or mercury sulfide, or mixtures thereof, as described in copending application S.N. 807,730, filed April 20, 1959, and owned by the present assignee. All of the foregoing phosphors are generally classed as zinc-sulfide-type electroluminescent phosphors and devices constructed in accordance with the present invention can incorporate any of such electroluminescent phosphors.

The dielectric in which the finely divided phosphor is embedded comprises any suitable light-transmitting plastic which is solid at room temperatures and which has a reasonably high dielectric constant. Examples of suitable plastic dielectric materials are polyvinyl chloride, polyvinyl acetate, copolymers of the two foregoing plastics, polystyrene, polyethylene or polyvinyl butyral. Such plastic materials are well known for use as dielectrics in electroluminescent devices.

The device embodiment 20, as shown in FIG. 2, is fabricated generally as disclosed in FIG. 3 of U.S. Patent No. 2,684,450, dated July 20, 1954. Briefly, this device embodiment comprises interlacing, raster-type electrodes 22 which are formed on an insulating foundation 24. The mixed finely divided phosphor and plastic dielectric material 26, together with the additive ammonium halide of the present invention, are positioned between the interlacing electrodes 22.

The device embodiment 28, as shown in FIG. 3, corresponds to the embodiment 10, as shown in FIG. 1, except that an additional layer 30 of high-dielectric material, such as barium titanate or titania is also included between the lamp electrodes 14 and 18. This enables the energizing electric potential applied across the device electrodes to be increased. Because of the high dielectric constant of the layer 30, an increased electric field can be applied across the phosphor-dielectric layer 16 to increase the brightness. All of the foregoing electroluminescent device constructions essentially comprise spaced electrodes which include therebetween finely divided, zinc-sulfide-type electroluminescent phosphor embedded in plastic dielectric, with a specified amount of additive ammonium halide.

As a specific example for fabricating an electroluminescent device in accordance with the present invention, a phosphor-plastic-vehicle slurry is first prepared. This slurry comprises polyvinyl-chloride plastic dissolved in xylene and methyl isobutyl ketone solvent in such proportions that the viscosity of the resulting lacquer is from 16 to 22 seconds, as measured with a No. 3 Zahn Cup. Phosphor is suspended in this lacquer to form a slurry, with the suspended phosphor and dissolved polyvinyl chloride present in equal parts by weight. Also added to the slurry is from 0.01% by weight to 2% by weight of the dissolved plastic of an ammonium halide such as the iodide, bromide, chloride, fluoride, or any mixtures thereof. The preferred halide is ammonium iodide and the preferred amount of ammonium halide addition is about 0.3% by weight of the plastic dissolved in the lacquer. The formed slurry is sprayed or otherwise applied to the device foundation as a substantially even layer. When the solvent volatilizes, there remains a layer of plastic having embedded therein the finely divided, zinc-sulfide-type electroluminescent phosphor and also included in the plastic is the added ammonium iodide in the indicated additive amount. The fabrication of the electroluminescent device is then completed in accordance with conventional practices. The phosphor-plastic layer can also be applied by other methods such as dip coating, although spraying is preferred.

In testing the present invention, lamps were fabricated generally as disclosed in FIG. 1. A portion of these lamps served as controls and no additive ammonium halide was included in the plastic dielectric. The remainder of the lamps included 0.3% by weight of ammonium iodide in the plastic. Under identical test conditions, the control lamps blackened considerably after 160 hours of operation. The lamps which incorporated the iodide displayed substantially no blackening during this period of operation. With respect to the maintenance of initial light output, at the end of this indicated period of operation, the maintenance of initial light output for the lamps containing the additive iodide was 12% better than the controls.

Apparently the blackening does not occur on or in the phosphor crystals, but in the embedding plastic dielectric material proximate the phosphor particles. This blackening is attributed to the liberation of free zinc from the phosphor during operation. Apparently the free zinc reacts with the plastic to form a dark compound. By including the indicated amount of ammonium halide in the plastic, the free zinc, on liberation, reacts with the halide to form stable zinc halide. In order to realize any appreciable improvement, at least 0.01% by weight of additive ammonium halide should be included in the plastic dielectric. When more than 2% by weight of ammonium halide is included in the plastic dielectric, some yellowing of the plastic is apparent. It should be noted that with ammonium halides having a lower molecular weight than the iodide, a greater molecular concentration of halide can be tolerated in the plastic without encountering the yellowing effect.

It will be recognized that the objects of the invention have been achieved by providing a plastic-type electroluminescent device having improved performance characteristics in that blackening of the plastic portions adjacent the phosphor is greatly inhibited and the maintenance of initial light output is improved.

While a best example of the invention has 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, spaced electrodes, finely divided zinc-sulfide-type electroluminescent phosphor embedded in plastic dielectric material and included between said spaced electrodes, and additive ammonium halide included in said plastic dielectric material in amount of from 0.01% to 2% by weight of said plastic.

2. An electroluminescent device comprising, spaced electrodes, finely divided zinc-sulfide-type electroluminescent phosphor embedded in plastic dielectric material and included between said spaced electrodes, and additive ammonium halide included in said plastic dielectric material in amount of about 0.3% by weight of said plastic.

3. An electroluminescent device comprising, spaced electrodes, finely divided zinc-sulfide-type electroluminescent phosphor embedded in plastic dielectric material and included between said spaced electrodes, and additive ammonium iodide included in said plastic dielectric material in amount of from 0.01% to 2% by weight of said plastic.

4. An electroluminescent device comprising, spaced electrodes, finely divided zinc-sulfide-type electroluminescent phosphor embedded in plastic dielectric material and included between said spaced electrodes, and additive ammonium bromide included in said plastic dielectric material in amount of from 0.01% to 2% by weight of said plastic.

5. An electroluminescent device comprising, spaced

electrodes, finely divided zinc-sulfide-type electroluminescent phosphor embedded in plastic dielectric material and included between said spaced electrodes, and additive ammonium chloride included in said plastic dielectric material in amount of from 0.01% to 2% by weight of said plastic.

6. An electroluminescent device comprising, spaced electrodes, finely divided zinc-sulfide-type electroluminescent phosphor embedded in plastic dielectric material and included between said spaced electrodes, and additive ammonium fluoride included in said plastic dielectric material in amount of from 0.01% to 2% by weight of said plastic.

References Cited in the file of this patent

UNITED STATES PATENTS

2,698,915	Piper	Jan. 4, 1955
2,859,367	Larach	Nov. 4, 1958
2,887,601	Bain	May 19, 1959