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(54) **PHOSPHOR LAYERS FOR ELECTROLUMINESCENT PANELS AND METHODS OF THEIR MANUFACTURE**

LEUCHTSTOFFSCHICHTEN FÜR ELEKTROLUMINESZENZ-ANZEIGEN UND VERFAHREN ZU
DEREN HERSTELLUNG

COUCHES DE PHOSPHORE POUR PANNEAUX ELECTROLUMINESCENTS ET LEUR PROCEDE
DE FABRICATION

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(56) References cited:
GB-A- 2 017 140 US-A- 5 374 377

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Description

[0001] This invention relates to phosphor layers for electroluminescent panels and methods of their manufacture. It has particular application to ac electroluminescent panels.

[0002] An electroluminescent panel typically comprises a phosphor layer sandwiched between layers of conductive material which act as the electrodes and between which a voltage is applied. In the case of ac electroluminescent panels the voltage that is applied is an ac voltage. At least one of the electrodes is usually transparent. Since the phosphor material in the layer is usually in powder form it is necessary in manufacture to mix the powder with a suitable binder material. The binder material should be insulating, have a high dielectric constant and not be light restrictive. It should also have a high breakdown voltage. Typical binder materials that are used are plastics materials such as polystyrene, methyl methacrylate and polyvinyl chloride. Other binder materials are celluloses, such as cyanoethyl cellulose and intro cellulose, dissolved in organic solvents. Polymerised perfluorinated hydrocarbons can also be used. It is also known to use ceramic dielectrics, but these materials are characterised by low luminance compared to plastics and polymeric binders and do not provide the flexibility of polymeric materials. However even the polymeric materials have limited flexibility and all the above-mentioned binder materials are expensive. Additionally since the dielectric strength of the phosphor layer may not be sufficient additional dielectric layers, comprising for example barium titanate, may need to be included between the electrodes.

[0003] US-A-5374377 discloses a phosphorescent polyvinyl chloride (PVC) film which exhibits an intense and long-lived afterglow. The phosphorescent PVC film contains a polymerized PVC-based resin, a primary and secondary plasticizer, a primary and secondary stabilizer, and a phosphorescent pigment. The primary stabilizer is solely a zinc-based stabilizer (non-zinc metal stabilizers are not employed); the secondary stabilizer is a tertiary organic phosphite; the primary plasticizer is an epoxidized soybean oil; the secondary plasticizer is selected from phthalates, adipates, trimellitates, azelates and phosphates; and the phosphorescent pigment is preferably a zinc sulfide phosphor.

[0004] GB-A-2017140 discloses phosphor screens for converting X-rays to visible or near visible radiation. Stabilization of the X-ray intensifying screens against discoloration and hydrolysis of lanthanum or gadolinium oxyhalide phosphors is achieved by incorporating into the phosphor/binder formulation a compound containing free epoxy groups. The fluorescent layer may incorporate a plasticizer such as epoxidised soya bean oil.

[0005] It is an object of the invention to provide a phosphor layer for an electroluminescent panel which is flexible, has good electrical properties and makes use of binder materials which are not expensive.

[0006] According to the invention in one aspect a phosphor layer for an electroluminescent panel comprises a phosphor powder held in a binder comprising a mixture of two constituents, one constituent being one or more drying oils or semi drying oils or derivatives thereof and the other constituent being one or more sol-gel precursors.

[0007] According to the invention in another aspect a method of manufacturing a phosphor layer for an electroluminescent panel comprises mixing two constituents to form a binder, one constituent being one or more drying oils or semi drying oils or derivatives thereof and the other constituent being one or more sol-gel precursors, mixing a phosphor powder with the binder and then allowing the resulting mixture to dry.

[0008] The invention also comprises an electroluminescent panel comprising a pair of electrodes between which is sandwiched a phosphor layer manufactured as described above.

[0009] A drying oil is an oil that has a drying index of 70 or more. Examples of suitable drying oils are linseed oil, rape seed oil and sunflower oil. A semi drying oil has a drying index below 70, but such an oil can still be used to carry out the invention. An example of a semi drying oil is soyabean oil. Examples of derivatives of these oils are the alkyds thereof, which may be prepared by the monoglyceride process or the fatty acid process. Other derivatives, for example unsaturated organic compounds such as linolenic acid and other fatty acids may also be used.

[0010] Examples of particular compounds that are sol-gel precursors are tetraethyl orthosilicate, boron isopropoxide, aluminium sec-butoxide and titanium isopropoxide. Metal salts, for example metal alkoxides, metal acetates and metal nitrates, can be included with the sol-gel precursors. For example lead nitrate can be mixed with zirconium isopropoxide and with titanium isopropoxide to prepare multi-compound oxides such as lead zirconium titanium oxide.

[0011] Phosphor layers embodying the invention have the property that they are sufficiently strong and flexible to be peeled from the substrate on which they are prepared without damaging the layer. They are also readily patternable. The peeled sheet can be cut to any desired pattern and then placed between electrodes to function as an electroluminescent panel. They also have good uniformity and high dielectric strength. It is therefore possible to dispense with additional dielectric layers between the electrodes.

[0012] In order that the invention may be more fully understood reference will now be made to the examples described below.

Example 1

[0013] 20 ml of linseed oil was injected into a stoppered glass vial and flushed with dry nitrogen. Titanium isopropoxide was injected into the vial to give a mixture of

10% by weight. The mixture was mixed on a roller for 1 hour and then slurried with an electroluminescent phosphor powder in the ratio of 2:7 w:w to the binder. The phosphor powder that was used was zinc sulphide doped with a high concentration of copper. The slurry was then doctor bladed onto an indium tin oxide (ITO) glass substrate using one layer of adhesive tape to hold the blade above the substrate. The coated panel was covered and allowed to cure in air overnight. The panel was then dried in air at 130°C for 1 hour. On cooling the film thickness was measured by subtraction of the substrate thickness from the total thickness. The thickness of the film was found to be 30 microns. A micrometer was used for these measurements.

[0014] 1gm of barium titanate was mixed with 0.3 gm of the binder precursor and the resulting paste was then applied over the phosphor layer using a doctor blade with two layers of adhesive tape. The panel was then allowed to dry overnight in air and then finally dried in an oven at 130°C for 1 hour. The resulting layer of barium titanate acts as a reflective coating.

Example 2

[0015] A phosphor slurry was prepared as described above in Example 1 but with a phosphor to binder ratio of 1:3 w:w. The slurry was then patterned onto a conducting substrate using a K-Bar printer. A second electrode was added by the sublimation of aluminium onto the free surface of the phosphor layer.

Example 3

[0016] This example corresponds in all respects to Example 1 except that the amount of titanium iso-propoxide that was injected into the vial was reduced to give a mixture of 5% by weight to the linseed oil. It was found that the resulting slurry was slightly too thin to doctor blade evenly.

Example 4

[0017] This example corresponds in all respects to Example 1 except that the amount of titanium iso-propoxide that was injected into the vial was increased to give a mixture of 20% by weight to the linseed oil. It was found that the resulting slurry was slightly too dry to doctor blade evenly.

Claims

1. A phosphor layer for an electroluminescent panel comprising a phosphor powder held in a binder comprising a mixture of two constituents, one constituent being one or more drying oils or semi drying oils or derivatives thereof and the other constituent being one or more sol-gel precursors

2. A phosphor layer as claimed in claim 1 in which the said one constituent comprises one or more drying oils selected from linseed oil, rape seed oil and sunflower oil.
3. A phosphor layer as claimed in claim 1 in which said one constituent comprises soyabean oil.
4. A phosphor layer as claimed in claim 1 in which the said one constituent comprises an alkyd of a drying oil or a semi drying oil.
5. A phosphor layer as claimed in claim 1 in which the said one constituent comprises linolinic acid.
6. A phosphor layer as claimed in claim 1 in which the said other constituent comprises one or more compounds selected from tetraethyl orthosilicate, boron iso-propoxide, aluminium sec-butoxide and titanium iso-propoxide.
7. A phosphor layer as claimed in any one of the preceding claims in which the said other constituent includes one or more compounds selected from metal alkoxides, metal acetates or metal nitrates.
8. A phosphor layer as claimed in any one of the preceding claims in which the ratio by weight of the said other constituent to the said one constituent lies between 5% and 20%.
9. A method of manufacturing a phosphor layer for an electroluminescent panel comprising mixing two constituents to form a binder, one constituent being one or more drying oils or semi drying oils or derivatives thereof and the other constituent being one or more sol-gel precursors, mixing a phosphor powder with the binder and then allowing the resulting mixture to dry.

Patentansprüche

1. Phosphorschicht für eine Elektrolumineszenz-Anzeige, mit einem Phosphorpulver, welches in einem Bindemittel gehalten ist, das eine Mischung aus zwei Bestandteilen umfasst, wobei einer der Bestandteile durch eines oder mehr trocknende Öle oder halbtrocknende Öle oder Derivate derselben gebildet ist, und der andere Bestandteil durch ein oder mehr Sol-Gel-Vorläuferstoffen gebildet ist.
2. Phosphorschicht nach Anspruch 1, bei welcher der eine Bestandteil ein oder mehr trocknende Öle umfasst, die unter Leinsamenöl, Rapsöl und Sonnenblumenöl ausgewählt sind.
3. Phosphorschicht nach Anspruch 1, bei welcher der

eine Bestandteil Sojaöl umfasst.

4. Phosphorschicht nach Anspruch 1, bei welcher der eine Bestandteil ein Alkyd eines trocknenden Öls oder eines halbtrocknenden Öls aufweist.
5. Phosphorschicht nach Anspruch 1, bei welcher der eine Bestandteil Linolensäure umfasst.
6. Phosphorschicht nach Anspruch 1, bei welcher der andere Bestandteil eine oder mehr Zusammensetzungen aufweist, die unter Tetraethylorthosilicat, Borisopropylat, Aluminium-sec-butoxid und Titanisopropylat ausgewählt sind.
7. Phosphorschicht nach einem der vorhergehenden Ansprüche, bei welcher der andere Bestandteil eine oder mehr Zusammensetzungen umfasst, welche unter Metallalkoxiden, Metallacetaten oder Metallnitraten ausgewählt sind.
8. Phosphorschicht nach einem der vorhergehenden Ansprüche, bei welcher das Gewichtsverhältnis des anderen Bestandteils zu dem einen Bestandteil zwischen 5% und 20% liegt.
9. Verfahren zur Herstellung einer Phosphorschicht für eine Elektroluminiszenz-Anzeige, umfassend: das Mischen zweier Bestandteile zur Bildung eines Bindemittels, wobei ein Bestandteil aus einem oder mehr trocknenden Ölen oder halbtrocknenden Ölen oder Derivaten derselben besteht und der andere Bestandteil aus einem oder mehr Sol-Gel-Vorläuferstoffen besteht, das Mischen eines Phosphorpulvers mit dem Bindemittel, und das Trocknenlassen der sich ergebenden Mischung.

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4. Couche de substance luminescente selon la revendication 1 dans laquelle ledit premier composant comporte un alkyde d'une huile siccative ou d'une huile semi-siccative.

5. Couche de substance luminescente selon la revendication 1 dans laquelle ledit premier composant comprend de l'acide linoléique.

6. Couche de substance luminescente selon la revendication 1 dans laquelle ledit second composant comporte un ou plusieurs composés sélectionné(s) à partir de l'orthosilicate de tétraéthyle, de l'iso-propoxyde de bore, de sec-butoxyde d'aluminium et de l'iso-propoxyde de titane.

7. Couche de substance luminescente selon l'une quelconque des revendications précédentes dans laquelle ledit second composant comporte un ou plusieurs composé(s) sélectionné(s) à partir d'alkoxydes métalliques, d'acétates de métal ou de nitrates de métal.

8. Couche de substance luminescente selon l'une quelconque des revendications précédentes dans laquelle le rapport en poids dudit second composant audit premier composant se situe entre 5% et 20%.

9. Procédé de fabrication d'une couche de substance luminescente destinée à un panneau électroluminescent consistant à mélanger deux composants pour former un liant, un composant étant une ou plusieurs huile(s) siccative(s) ou huile(s) semi-siccative(s) ou leurs dérivés et le second composant étant un ou plusieurs précurseur(s) sol-gel, à mélanger une poudre de substance luminescente avec le liant et ensuite à mettre à sécher le mélange résultant.

Revendications

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1. Couche de substance luminescente destinée à des panneaux électroluminescents comportant une poudre de substance luminescente maintenue dans un liant comprenant un mélange de deux composants, un composant étant une ou plusieurs huile(s) siccative(s) ou huile(s) semi-siccative(s) ou des dérivés de celles-ci et l'autre composant étant un ou plusieurs précurseur(s) sol-gel.
2. Couche de substance luminescente selon la revendication 1 dans laquelle ledit premier composant comporte une ou plusieurs huile(s) siccative(s) sélectionnée(s) à partir de l'huile de lin, de l'huile de graines de colza et de l'huile de tournesol.
3. Couche de substance luminescente selon la revendication 1 dans laquelle ledit premier composant comprend de l'huile de graines de soja.

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REFERENCES CITED IN THE DESCRIPTION

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- US 5374377 A [0003]
- GB 2017140 A [0004]

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摘要(译)

用于电致发光面板的荧光粉层包括保持在粘合剂中的荧光粉。粘合剂包含两种成分的混合物，其中一种是干性油或半干性油或衍生物，另一种成分是溶胶 - 凝胶前体。合适的油的实例是亚麻子油，菜籽油，向日葵油和大豆油。合适的溶胶 - 凝胶前体的实例是原硅酸四乙酯，异丙醇硼，仲丁醇铝和异丙醇钛。金属盐如金属醇盐，金属乙酸盐和金属硝酸盐可与溶胶 - 凝胶前体混合。