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(54) Title: RADIATION CURABLE COMPOSITION FOR WATER SCAVENGING LAYER, AND METHOD OF MANUFACTURING THE SAME

(57) Abstract: A radiation curable resin composition comprising: (A) metal oxide particles; (B) at least one photoinitiator, preferably a radical photoinitiator, or any mixture thereof; (C) at least one acrylate or methacrylate component with a Clog P higher than 2, preferably higher than 4, more preferably higher than 5,or any mixture thereof; (D) at least one monofunctional acrylate or methacrylate diluent component, preferably with a viscosity below 40 mPa•s at 20°C,or any mixture thereof; (E) at least one acrylate or methacrylate component with functionality equal or higher than 3, preferably 3 or 4,or any mixture thereof; can be advantageously used, for example,in multilayer barrier stack for the production of organic opto-electric or opto-electronic device, such as Organic Light Emitting Diode (OLED).

Radiation curable composition for water scavenging layer, and method of manufacturing the same

BACKGROUND OF THE INVENTION

Field of the invention

The present invention relates to a radiation curable or photocurable composition for water scavenging layer, to be advantageously used, for example, in a multilayer barrier stack, which may be employed, for instance, in the manufacturing of an organic opto-electric or opto-electronic device such as Organic Light Emitting Diode (OLED).

The present invention further relates to a method of manufacturing the radiation curable composition or photocurable composition, the water scavenging layer, the multilayer barrier stack and the organic opto-electric device or OLED itself.

Related Art

Exposure of moisture sensitive devices such as organic LEDs (both small molecule and polymer based), OPV, CI(G)S solar cells, to the ambient atmosphere results in loss of performance of the device. In the case of OLEDs, ingress of water or of other oxidizing materials can lead to degradation of the active organic layers leading to loss of efficiency mainly due to oxidation of the cathode, leading to local failure of the device.
Water ingress can come from two sides, from the anode side or the cathode side. Current state-of-the-art OLEDs are protected from water ingress by using glass as a substrate and glass or metal lids to encapsulate on the cathode side. Conventionally, encapsulation is performed with a coverlid glued at the edges. A getter is used to consume water that might penetrate through the glue. This encapsulation method is expensive and is not functional for large-area devices, especially flexible ones.
A more cost-effective alternative, which also will allow flexible devices to be manufactured, is the use of thin film barriers, which can be applied on a plastic foil to act as a substrate and which can be used as a final encapsulation.
In order to understand the issues with such kind of barrier, a brief explanation is given below about the mechanism of water ingress in an OLED.

The cathode in an OLED device most often consists of a thin (1-50 nm) layer of Ba (polymer LED) or LiF (small molecule OLED) covered with a relatively thick Al layer. Aluminum would be an excellent barrier against water, if not for the fact that it contains pinholes, of which most of them are caused by particles. Such particles originate from a plurality of causes and their presence is in practice difficult to avoid. Water from the ambient atmosphere is penetrating through pinholes in the cathode layer. Oxidation of metal at the cathode-polymer interface prevents electron injection from the cathode into the polymer during operation of the device, thus introducing a local spot without

emission, i.e. a black spot in the bright electroluminescent background. The evolution of the black spots is determined by the diffusion rate of water from the pinhole. The area of the resulting circular shaped spots increases linearly with time. Black spot formation and growth is a shelf effect, i.e. no current or voltage is necessary to drive the process. When an inorganic barrier layer is applied on top of the OLED, the majority of the particles is covered, resulting in a corresponding decrease in the number of black spots. Still the remaining black spot density is by far too large for any practical application. Increase of the thickness of the barrier layer hardly reduces the pinhole density. Once a pinhole is present in such a layer, it tends to propagate while depositing more of the same material.

Graff et al. describe in "Mechanisms of vapor permeation through multilayer barrier films: Lag time versus equilibrium permeation", J. of Applied Physics, Vol. 96, Nr. 4, pp. 1840-1849 a nowadays common strategy to interrupt the growth of pinholes by a barrier stack with organic layers. In this way, the pinholes in subsequent barrier layers are decoupled resulting in a tortuous path for water transport from the ambient atmosphere to the cathode in the device. Also other layers of different chemical composition, such as different inorganic materials are used for this purpose. Graff et al. investigated the use of polymer decoupling layers having a thickness in the range of 0.1 to 3 µm and suggested that even thinner polymer decoupling layers could result in further improvement.

US2009289549A describes an OLED display provided with a multi-layered protective barrier stack, wherein organic and inorganic layers are alternately stacked in a repeated manner and at least one moisture absorbing layer or water scavenging layer is interposed in the multi-layered protective layer. In particular, US2009289549A describes an embodiment wherein the multilayered protective layer comprises a first inorganic layer, a moisture absorbing layer (water scavenging layer), an organic layer and a second inorganic layer in this order. The presence of the moisture absorbing layer further reduces the ingress of water towards the opto-electric element. The moisture absorbing layer is formed of an organic metal compound solution and may contain additives such as a metal or a metal oxide. The moisture absorbing layer may have a thickness in the range of 3 to 50 nm. It is remarked in US2009289549A that the organic layer between the moisture absorbing layer and the second inorganic layer may have a thickness larger than the thickness of the moisture absorbing layer. The cited US patent does not disclose more specifically how much larger the thickness should be, but the drawing that is referred to suggests that the second organic layer is about two to three times thicker.

The deposition and manufacturing of a suitable moisture absorbing layer or water scavenging layer for opto-electrical devices has revealed exceptional technical difficulties from the point of view of the chemistry and of the required physical properties. No suitable materials have been found up to now, which fulfill all physical, mechanical, optical and processing requirements demanded by the industrial manufacturing of opto-electrical devices and OLED.

Calcium oxide is for example highly hygroscopic, and is useful as a moisture absorbent and a dehydrating agent, in particular in electronic enclosures where moisture decreases the device lifetime. From a viewpoint of handling in opto-electrical applications it would be however necessary to provide calcium oxide in the form of a homogeneous stable liquid, which could be coated or printed and cured on different substrates and at different thicknesses. From a viewpoint of processing in certain opto-electric applications, in

particular for making individual layouts and for on demand printing, it would be necessary to be able to deposit the hygroscopic material as a curable ink via inkjet printing, valve jet printing, and liquid dispensing methods. For patterning via gravure printing the viscosity of the ink must be lower than 200 mPa•s at 20°C, and for flexo printing the viscosity of the ink must be lower than 500 mPa•s at 20°C. These are among favoured roll to roll printing techniques. It can be also necessary to have access to medium and low viscosity resins exhibiting the water scavenging properties.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide a photocurable composition containing oxide particles for making water scavenging layers, which is stable and flowable, so that it can be easily dispensed or printed for example via inkjet/valve jet printing or via gravure and flexoprinting.

It is a further object of the present invention to provide a method of manufacturing such a photocurable composition, which is simple, fast and economically viable.

It is a further object of the present invention to provide a method of manufacturing a water scavenging layer, which is simple, fast, economically viable and suited for opto-electric devices and applications.

It is a further object of the present invention to provide a method for manufacturing a light-emitting device or opto-electric devices, in particular an organic light emitting diode (OLED), which is simple, fast, economically viable, whereby the light-emitting device, in particular the organic light emitting diode (OLED), remains protected by moisture and water for very long time, and exhibits an improved barrier against atmospheric substances.

According to a first aspect of the invention a radiation curable, preferably photocurable resin composition is provided comprising:
(A) metal oxide particles;
(B) at least one photo initiator, preferably a radical photoinitiator, or any mixture thereof;
(C) at least one acrylate or methacrylate component with a clogP higher than 2, preferably higher than 4, more preferably higher than 5, or any mixture thereof;
(D) at least one monofunctional acrylate or methacrylate diluent component, preferably with a viscosity below 40 mPa•s at 20°C, or any mixture thereof;
(E) at least one acrylate or methacrylate component with functionality equal or higher than 3, preferably 3 or 4, or any mixture thereof, wherein
Mica is excluded from the group of (A) metal oxide particles.

Such photocurable resin compositions are surprisingly stable and flowable and are surprisingly well suited for making water scavenging coatings that can be easily dispensed or printed via inkjet/valve jet printing or via gravure and flexoprinting. After curing, they give rise to water scavenging coatings characterized by exceptional water scavenging properties and transparency, and also by an exceptionally long life time. They are therefore surprisingly well suited for the manufacturing of water scavenging layers for opto-electric devices or light-emitting devices, in particular organic light emitting diodes (OLED).

Metal oxide particles can be also particle aggregates or agglomerates.

In order to avoid metal oxide (for example CaO) hydrolysis and the possibility of aggregation via hydrogen bonding, the curable matrix exhibits preferably a low water content - less than 1,000 ppm (by weight). For that reason, preferably compounds having a high hydrophobicity are used in order to prevent an elevated amount of internal water. A good indicator for the hydrophobicity is ClogP, i.e. the calculated logarithm of the octanol/water partition coefficient. A relatively high ClogP value indicates a relatively high hydrophobicity of the material. For the purpose of the present invention organic materials having a ClogP value of at least 2 are particularly suitable. The ClogP value is a well-known parameter and may be calculated for any given molecule from the knowledge of the structure of that molecule. There are a number of commercially-available computer programs performing this calculation. In the case of the present invention Osiris Property Explorer (http://www.organic-chemistry.org/prog/peo/.) was used, which is an integral part of Actelion's in-house substance registration system. The algorithm is implemented as an incremental system adding contributions of every atom, based on atom type, atom connectivity and chemical bonding. In addition, the curable matrix is preferably dried over activated 4A molecular sieves prior to the addition of the metal oxide or CaO particles.

The definition and way of calculation of ClogP can be found under the link http://en.wikipedia.org/wiki/Partition_coefficient; in Leo A, Hansch C, and Elkins D (1971) "Partition coefficients and their uses" Chem Rev 71 (6), 525–616; in Sangster, James (1997) Octanol-Water Partition Coefficients: Fundamentals and Physical Chemistry, Vol. 2 of Wiley Series in Solution Chemistry Chichester, John Wiley & Sons Ltd. pp. 178; in Hansch, Corwin Leo A (1979) Substituent Constants for Correlation Analysis in Chemistry and Biology New York, John Wiley & Sons Ltd. pp. 178; in Leo, Albert, Hoekman DH, Hansch C (1995) Exploring QSAR, Hydrophobic, Electronic, and Steric Constants Washington, DC, American Chemical Society.

In order to be flowable, and, in particular, for making inkjetable inks, which require very low viscosity resins (less than 30 mPa•s at printing temperature), a monofunctional acrylate or methacrylate diluent component (D) is used and the metal or calcium oxide concentration is preferably lower than 50% by weight, and more preferably lower than 20% by weight.

According to a preferred embodiment of the invention the photoinitiator is a radical photoinitiator.

According to a preferred embodiment of the invention the metal oxide particles are alkaline earth metal oxide particles, preferably CaO, BaO and/or MgO particles, and exhibit an average particle diameter of 10 to 1000 nm, preferably 15 to 500 nm, more preferably 20 to 350 nm, or even 50 to 250 nm.

The average particle diameter is calculated using the Dynamic Light Scattering technique. The apparatus used is a Malvern Zetasizer Nano ZS operating by Non Invasive Back Scatter mode for particle size measurement. Dynamic Light Scattering (also known as photon correlation spectroscopy or quasi-elastic light scattering) measures Brownian motion and relates this to the size of the particles using the Stokes-

Einstein equation. It operates by illuminating the particles with a laser and analyzing the intensity fluctuations in the scattered light.

Details of the used method to measure the average particle diameter in the present invention can be found under the link http://en.wikipedia.org/wiki/Dynamic_light_scattering, and in Berne, B.J.; Pecora, R. Dynamic Light Scattering, Courier Dover Publications (2000) ISBN 0-486-41155-9.

The metal oxide or CaO particle size is preferably in the nanometer range, in order to reduce sedimentation speed to a maximum, in particular for low viscosity resins. Nanometer range means calcium oxide fine particles having an average particle diameter (on volume basis) of 10 to 1000 nm, preferably 15 to 500 nm, more preferably 20 to 350 nm, and still more preferably 50 to 250 nm. In addition, a small particle size is highly desired for processes such as inkjet printing in order to avoid nozzle clogging, and also for making resins with a high degree of optical transparency. The problem is that the particles of calcium oxide are dried or prepared from a high temperature process (>500°C), and, as a consequence, are strongly agglomerated. A milling/grinding process has to be performed in order to pulverize the aggregates to the nanoscale. It is known from the grinding industry that nanoscale can be reached using very small milling balls. In our process, milling balls of 0.3-0.4 mm diameter were used. Smaller balls such as 50 µm or 100 µm would even be better suited, in particular for making transparent curable resins.

According to a preferred embodiment of the invention the photocurable resin composition does not comprise any urethane (meth)acrylate, polyester (meth)acrylate, or polyethylene glycol (PEG) (meth)acrylate.

Components capable of metal oxide or CaO complexation and hydrogen bonding have to be preferably avoided, or used at very low loadings in order to avoid clumping of CaO particles and the progressive formation (only a few hours needed) of a solid-like gel which does not flow anymore. This phenomenon is aggravated as the particle size is decreased, due to the increase in surface area. Urethane acrylate building blocks, PEG (polyethylene glycol) building blocks, alkoxylated (meth)acrylates, (meth)acrylates with acidic or alcohol functionalities, polyols functionalized with (meth)acrylates are therefore preferably avoided.

According to a preferred embodiment of the invention the photocurable resin composition exhibits a viscosity at 20°C below 500 mPa•s, preferably below 200 mPa•s, more preferably below 100 mPa•s, and/or exhibits a pot life at 60°C longer than 29 days, preferably longer than 43 days.

Pot life at a specific temperature is defined as the time after which the resin viscosity increases of 20% of the initial value of the resin viscosity, as measured at the time of the production of the resin.

The viscosity was measured using a Haake RS 80 rotational viscometer. This type of viscometer determines directly the absolute viscosity by measuring the resistance on a shaft rotating in the fluid of interest. The viscometer is composed of a cone attached to a rotating shaft. The cone is immerged in the fluid and rotated at a constant speed. The torque required to rotate the cone is measured and then related to the fluid viscosity.

The cone type used for our viscosity measurement was a 35 mm diameter with 2° angle, the rate was set at 100 s^{-1} and the measurement temperature was set at 20°C.

Details of the used method to determine the viscosity can be found under the link http://en.wikipedia.org/wiki/Viscometer#Rotational_viscometers and in the operating instructions of the used viscometer.

For making dispensable and printable inks (e.g. via gravure and flexoprinting), the viscosity must be lower than 500 mPa•s at 20°C, and preferably lower than 250 mPa•s for making dispensable inks. The curable resin has preferentially a viscosity lower than 60 mPa•s at 20°C for making inkjetable inks.

Non-flowable systems cannot be processed at all via printing techniques, such as inkjet, valve jet, gravure, and flexo printing or dispensing techniques, requiring low viscosity formulations.

Getter stickers are not practical for mass production at high speed compared to deposition of liquid resins.

It is very difficult to make thin coatings with high accuracy with high viscous pastes. A limited coating speed is achieved with viscous pastes, due to low levelling speed.

Thanks to the invention, dramatic advantages are therefore achieved in the field of the application of water scavenging materials, which were unimaginable according to the prior art.

According to another preferred embodiment of the invention the photocurable resin composition also comprises:
(F) a polybutadiene acrylate or methacrylate, a silicone acrylate or methacrylate, or a two-mole ethoxylated bisphenol A di(meth)acrylate, or any mixture thereof, whereby such component (F) exhibits preferably two (meth)acrylate functionalities.

Major components are preferably selected from polybutadiene (meth)acrylates, silicone (meth)acrylate, and other (meth)acrylate building blocks, preferably without PEG, acidic or alcohol functionalities.

According to a preferred embodiment of the invention
component (D) exhibits a ClogP higher than 2,
component (E) exhibits a ClogP higher than 1,
and/or component (F) exhibits a ClogP higher than 4, preferably higher than 6 or 7.

According to a preferred embodiment of the invention the component C is a 1,n-diol di(meth)acrylate of a diol of the formula $HO-(CH_2)_n-OH$, whereby n is higher than 3, preferably higher than 6, more preferably higher than 10.

According to an advantageous embodiment of the invention the photocurable resin composition, after curing, is transparent, preferably the cured resin, as a film of 20 micrometer thickness, has a light transmission at 600 nm of > 90%,
and/or exhibits a water uptake after storage for 80 hours at 40°C in 90% relative humidity of less than 2% of its initial weight.

According to a preferred embodiment of the invention, the resin composition comprises at least:
(A) 1 - 30 % by weight of CaO, BaO and/or MgO particles (component A);
(B) 0.1 - 10 % by weight of the photo initiator B;
(C) 30 - 80 % by weight of component C, which preferably exhibits two (meth)acrylate functionalities;
(D) 5 - 40 % by weight of the monofunctional (meth)acrylate diluent component D;
(E) 5 - 30 % by weight of the (meth)acrylate component E with functionality equal or higher than 3; and optionally
(F) 0.1 - 30 % by weight of component F;
based on the total weight of the composition.

According to a most preferred embodiment of the invention, the resin composition comprises at least:
(A) 4 - 20 % by weight of CaO, BaO and/or MgO particles (component A);
(B) 0.1 - 5 % by weight of the photo initiator B;
(C) 40 - 70 % by weight of component C, which exhibits preferably two (meth)acrylate functionalities;
(D) 10 - 30 % by weight of the monofunctional (meth)acrylate diluent component D;
(E) 7 - 20 % by weight of the (meth)acrylate component E with functionality equal or higher than 3; and optionally
(F) 0.3 - 25 % by weight of component F;
based on the total weight of the composition.

According to a second aspect of the invention a method is provided for preparing a photocurable resin according to the invention, comprising the steps of:

h) mixing and stirring together components C, D, E, and optionally F, in order to produce a mixture h, which is optionally dried;
i) incorporating optionally dehydrated calcium, barium and/or magnesium oxide (component A) into the produced mixture h, so as to obtain a mixture i;
j) Milling and/or grinding the produced mixture i, preferably via bead milling under dry nitrogen, in order to downsize the average diameter of calcium, barium and/or magnesium oxide particles, so as to produce a mixture j;
k) Adding the photoinitiator B to the produced mixture j, so as to obtain a mixture k, which is preferably stirred under dry nitrogen atmosphere.

Such method exhibits the exceptional surprising advantage that the photocurable resin according to the invention can be prepared with a one step milling process and without the use of any solvent, so that the preparation of the resin is simple, fast, inexpensive and practical.

The use of solvents and/or of a heating step for evaporating the solvent or for curing might not be compatible with the system in which the desiccant is applied. For instance, a heating step might be a critical issue when depositing the desiccant layer on a heat sensitive substrate, such as an OLED. Solvent residues might be trapped in the matrix and contaminate the system.

The dispersion of CaO in a solvent prior to dispensing the resin adds cost to the manufacturing process. In addition, it is not environmentally friendly.

The incorporation of CaO nanoparticles just before use requires the customer to be equipped with dispersing equipment, which is costly and requires expertise. A simple mixing step would not be sufficient to disperse the CaO particles to the nanometer scale.

A high number of preparation steps increases the risk of contamination of the CaO particles with humidity and, as a consequence, of the loss of water scavenging properties.

The method to prepare the photocurable composition according to the invention solves surprisingly all such problems and issues.

According to another preferred embodiment of the invention, during the milling step j) the average particle diameter of the CaO, BaO and/or MgO particles is reduced to the range of 10 to 1000 nm, preferably 15 to 500 nm, more preferably 20 to 350 nm or even 50 to 250 nm, and the produced photocurable resin k exhibits a water content less than 1000 ppm by weight.

Preferably, the CaO powder is dried, handled and milled with the resin under inert atmosphere (using inert gas with a water content of not more than 10 ppm (by mol)), in order to avoid CaO hydrolysis and the possibility of aggregation via hydrogen bonding. In the liquid curable matrix, the calcium oxide fine particles exhibit preferentially a calcium hydroxide content of less than 5% by weight and a calcium carbonate content of less than 1% by weight.

All the components have to be compatible for avoiding phase separation during the milling process.

According to a third aspect of the invention a method is provided for manufacturing a multi layer barrier stack (30) against water and oxygen penetration and diffusion, comprising the steps of:

m) Depositing a first inorganic layer (32), preferably silicon nitride or oxide, exhibiting preferably a thickness between 50 and 300 nm;
n) Depositing onto said first inorganic layer (32), preferably via ink jet printing, a first organic layer (34) of the photocurable resin according to the invention or produced with a method according to the invention;
o) exposing said first organic layer (34) to ultraviolet (UV) radiation, so as to solidify said first organic layer (34) and to produce a transparent layer exhibiting water scavenging properties;
p) applying onto said first solidified organic layer (34), preferably via ink jet printing, a second organic layer (36) of a photocurable resin not containing metal oxide particles;
q) exposing said second organic layer (36) to UV radiation, so as to solidify said second organic layer (36) and to produce a transparent layer exhibiting planarization properties;
r) Depositing onto said second solidified organic layer (36) a second inorganic layer (38), preferably silicon nitride or oxide, exhibiting preferably a thickness between 50 and 300 nm.

The first organic layer (34) exhibits advantageously a thickness between 10 and 100 micrometers, preferably between 20 and 80 micrometers.

The second organic layer (36) exhibits advantageously a thickness between 10 and 100 micrometers, preferably between 20 and 80 micrometers.

According to a fourth aspect of the invention a method is provided for manufacturing an opto-electric device, in particular an organic light emitting diode (OLED), comprising the steps of:

- providing an opto-electric element and/or layer (10),
- providing an encapsulation comprising a multi layer barrier stack (30) produced according to the method according to the invention.

According to a fifth aspect of the invention a multi layer barrier stack (30) or opto-electric device, in particular OLED, is provided, which is obtained by a method according the invention or a resin according to the invention.

Such organic opto-electric device or OLED comprises advantageously:

- an opto-electric element,
- a protective enclosure for protecting the opto-electric element against atmospheric substances, said protective enclosure comprising a multi-layered protective layer or multi layer barrier stack, in which a first inorganic layer, a first organic layer comprising a metal oxide, a second organic layer free from getter material and a second inorganic layer are stacked in the order named. The first organic layer is produced with the resin according to the invention or with a method according to the invention. The metal oxide is preferably CaO, BaO or MgO particles and is distributed advantageously in the first organic layer as nanometer sized particles with a density in the range of 4 to 20 wt%. The second organic layer has advantageously a thickness in the range of 10 to 100 micrometer.

Nanometer sized particles, hereinafter also denoted as nanoparticles, are understood to be particles having dimensions less than 100 nm. The getter-material distributed as nano-particles with a density in the range of 4 to 20 wt% provides for an efficient binding of moisture in the first organic layer of the OLED. In typical embodiments the density is in the range of 5 to 10 wt%, for example 5 wt%.

Despite the small size of the original getter particles, these particles tend to form clusters having a size of several micrometers. It has been surprisingly found that milling of the getter particles results in a distribution having a small average cluster size, so that the layer comprising the particles exhibit a good transparency and can be used in the manufacturing of a OLED for example. Transparency is a physical property necessary for films to be used in organic opto-electric devices or OLED. Despite such small average cluster size, it appeared that the presence of large clusters could not be fully ruled out. Accordingly, when applying a second organic layer over the first organic layer, having a conventional thickness in the range of 0.1 to 3 µm, these clusters may protrude through the second organic layer and the particles at the surface of the clusters tend to cause defects in the inorganic layer. The second organic layer has therefore advantageously a thickness substantially greater than the thickness that is conventionally applied. The first and the second inorganic layer encapsulate the first and the second organic layer so that a lateral ingress of moisture is prevented.

In a preferred embodiment the thickness of the second organic layer is at least 20 µm. This exhibits the advantage that even if tolerances in the manufacturing process cause variations in the thickness of the second organic layer then the remaining thickness is

still larger than the required minimum of 10 µm. For a flexible product it is preferred that the thickness of the second organic layer is less than 100 µm. In a typical embodiment the second organic layer exhibits a thickness of about 70 µm.

In an embodiment the first organic layer has a thickness in the range of 10 to 100 µm. A substantially smaller thickness, e.g. less than 5 µm, would exhibit an insufficient getter capacity, while a substantially larger thickness, e.g. more than 200 µm, would be undesirable for a flexible product.

In an embodiment the getter particles are of an alkaline earth metal oxide. Alkaline earth metal oxides, in particular CaO, provide for a very efficient binding of water.

In an embodiment the opto-electric element is an OLED, having an opto-electric layer arranged between a cathode and an anode, and the cathode faces the multi-layered protective layer. The cathode side of the OLED is the most vulnerable part to moisture, against which the multi-layered protective layer provides an efficient and still transparent protection. At the opposite side of the OLED another protective layer may be arranged, for example a metal foil. The metal foil may also serve as a conductor for the cathode or the anode. In another embodiment the opto-electric element has a multi-layered protective layer or stack as described above on both sides.

As explained, the first organic layer is produced by curing a photocurable resin according to the invention.

The advantage of using such photocurable resins to produce the described organic opto-electric device or OLED is that the resin is stable and flowable and can be easily applied in the form of a thin film with controlled thickness. Curing time is almost instantaneous by photocuring and layers can be produced with exceptional water scavenging properties and transparency.

COMPONENTS OF THE RESIN

The photocurable resin according to the invention comprises components (A), (B), (C), (D), (E) and optionally (F):

(A) metal oxide particles

The metal oxide particles with the function of getter are advantageously CaO, BaO or MgO particles, preferably CaO nanoparticles.

Also other getter materials may be used. Other alkaline earth metal oxides for this purpose which are particularly suitable are barium oxide (BaO), magnesium oxide (MgO) and strontium oxide (SrO). As an example, MgO nanopowder (Catalog Nr.12-1400) from Strem may be obtained having the following specifications: Specific Surface Area (BET): ≥ 230 m^2/g; True Density: 3.2 g/cc; Crystallite Size: ≤ 8 nm; Mean Aggregate Size: 3.3 µm; Average Pore Diameter: 50 Å; Loss on Ignition: ≤ 8%; Total Pore Volume: ≥ 0.2 cc/g; Moisture Content: ≤ 1%; Bulk Density: 0.6 g/cc Mg Content (Based on Metal): ≥ 95%.

(B) photoinitiator

In addition, the photocurable composition comprises at least one photoinitiator, preferably a free radical photoinitiator.
The free radical photoinitiator may be chosen from those commonly used to initiate radical photopolymerization. Examples of free radical photoinitiators include Irgacure ®369, benzoins, e.g., benzoin, benzoin ethers such as benzoin methyl ether, benzoin ethyl ether, benzoin isopropyl ether, benzoin phenyl ether, and benzoin acetate; acetophenones, e.g., acetophenone, 2,2-dimethoxyacetophenone, 2,2-dimethoxy-2-phenylacetophenone and 1,1-dichloroacetophenone; benzyl ketals, e.g., benzyl dimethylketal and benzyl diethyl ketal; anthraquinones, e.g., 2-methylanthraquinone, 2-ethylanthraquinone, 2-tertbutylanthraquinone, 1-chloroanthraquinone and 2-amylanthraquinone; triphenylphosphine; benzoylphosphine oxides, e.g., 2,4,6-trimethylbenzoy-diphenylphosphine oxide (Lucirin TPO); ethyl-2,4,6-trimethylbenzoylphenylphosphinate; bisacylphosphine oxides; benzophenones, e.g., benzophenone and 4,4'-bis(N,N'-dimethylamino)benzophenone; thioxanthones and xanthones; acridine derivatives; phenazine derivatives; quinoxaline derivatives; 1-phenyl-1,2-propanedione 2-O-benzoyl oxime; 4-(2-hydroxyethoxy)phenyl-(2-propyl)ketone (Irgacure® 2959); 2-methyl-1-[4-(methylthio)phenyl]-2-(4-morpholinyl)-1-propanone; 1-aminophenyl ketones or 1-hydroxy phenyl ketones, e.g., 1-hydroxycyclohexyl phenyl ketone, 2-hydroxyisopropyl phenyl ketone, phenyl 1-hydroxyisopropyl ketone, and 4-isopropylphenyl 1-hydroxyisopropyl ketone, and combinations thereof.

A content of the polymerization initiator is preferably within a range of from 0.01 to 10% by weight with respect to the total weight of the composition, more preferably from 0.5 to 7% by weight.

(C) (meth)acrylate with clogP > 2

In addition, the photocurable composition comprises one acrylate or methacrylate component with a ClogP higher than 2, preferably higher than 4, more preferably higher than 5, or any mixture thereof.

Examples of such (meth)acrylates are CD262 (= 1,12-dodecanediol dimethacrylate), methacrylate composed of a polyol and an ethylenically unsaturated acid include diester monomers each composed of a polyol and an ethylenically unsaturated carboxylic acid, such as 1,3-propanediol dimethacrylate, 1,4-butanediol dimethacrylate, 1,5-pentanediol diacrylate, 1,5-pentanediol dimethacrylate, 1,6-hexanediol diacrylate, 1,6-hexanediol dimethacrylate, 1,7-heptanediol diacrylate, 1,7-heptanediol dimethacrylate, 1,8-octanediol diacrylate, 1,8-octanediol dimethacrylate, 1,9-nonanediol diacrylate, 1,9-nonanediol dimethacrylate, 1,10-decanediol diacrylate, 1,10-decanediol dimethacrylate, 1,12-dodecanediol diacrylate, 1,12-dodecanediol dimethacrylate, 1,14-tetradecanediol diacrylate, 1,14-tetradecanediol dimethacrylate and the like.

(D) monofunctional (meth)acrylate diluent

In addition, the photocurable composition comprises a monofunctional acrylate or methacrylate diluent component, preferably with a low viscosity, for example below 40 mPa•s at 20°C, or any mixture thereof.

Specific examples of such mono functional (meth)acrylates include CHMA, CD421A, hexyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, tert-octyl (meth)acrylate, isoamyl (meth)acrylate, decyl (meth)acrylate, isodecyl (meth)acrylate, stearyl (meth)acrylate, isostearyl (meth)acrylate, cyclohexyl (meth)acrylate, 4-n-butylcyclohexyl (meth)acrylate, bornyl (meth)acrylate, isobornyl (meth)acrylate, benzyl (meth)acrylate, 2-ethylhexyl diglycol (meth)acrylate, butoxyethyl (meth)acrylate, 2-chloroethyl (meth)acrylate, 4-bromobutyl (meth)acrylate, butoxymethyl (meth)acrylate, 3-methoxybutyl (meth)acrylate, alkoxymethyl (meth)acrylate, alkoxyethyl (meth)acrylate, 2-(2-methoxyethoxy)ethyl (meth)acrylate, 2-(2-butoxyethoxy)ethyl (meth)acrylate, 2,2,2-trifluoroethyl (meth)acrylate, 1H,1H,2H,2H-perfluorodecyl (meth)acrylate, 4-butylphenyl (meth)acrylate, phenyl (meth)acrylate, 2,3,4,5-tetramethylphenyl (meth)acrylate, 4-chlorophenyl (meth)acrylate, phenoxymethyl (meth)acrylate, phenoxyethyl (meth)acrylate, glycidyl (meth)acrylate, glycidyloxybutyl (meth)acrylate, glycidyloxyethyl (meth)acrylate, glycidyloxypropyl (meth)acrylate, tetrahydrofurfuryl (meth)acrylate, hydroxyalkyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, 3-hydroxypropyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 2-hydroxybutyl (meth)acrylate, 4-hydroxybutyl (meth)acrylate, dimethylaminoethyl (meth)acrylate, diethylaminoethyl (meth)acrylate, dimethylaminopropyl (meth)acrylate, diethylaminopropyl (meth)acrylate, trimethoxysilylpropyl (meth)acrylate, trimethylsilylpropyl (meth)acrylate, polyethylene oxide monomethyl ether (meth)acrylate, oligoethylene oxide monomethyl ether (meth)acrylate, polyethylene oxide (meth)acrylate, oligoethylene oxide (meth)acrylate, oligoethylene oxide monoalkyl ether (meth)acrylate, polyethylene oxide monoalkyl ether (meth)acrylate, dipropylene glycol (meth)acrylate, polypropylene oxide monoalkyl ether (meth)acrylate, oligopropylene oxide monoalkyl ether (meth)acrylate, 2-methacryloyloxyethylsuccinic acid, 2-methylacryloyloxyhexahydrophthalic acid, 2-methacryloyloxyethyl-2-hydroxypropyl phthalate, butoxydiethylene glycol (meth)acrylate, trifluoroethyl (meth)acrylate, perfluorooctylethyl (meth)acrylate, 2-hydroxy-3-phenoxypropyl (meth)acrylate, EO-denatured phenol (meth)acrylate, EO-denatured cresol (meth)acrylate, EO-denatured nonylphenol (meth)acrylate, PO-denatured nonylphenol (meth)acrylate, and EO-denatured 2-ethylhexyl (meth)acrylate.

(E) (meth)acrylate with functionality ≥ 3

In addition, the photocurable composition comprises an acrylate or methacrylate component with functionality equal or higher than 3, preferably 3 or 4, or any mixture thereof.

Specific examples of trifunctional (meth)acrylate include SR351, trimethylolpropane tri(meth)acrylate, trimethylolethane tri(meth)acrylate, alylene oxide-denatured tri(meth)acrylate of trimethylolpropane, pentaerythritol tri(meth)acrylate, dipentaerythritol tri(meth)acrylate, trimethylolpropane tris((meth)acryloyloxypropyl)ether, alkylene-denatured tri(meth)acrylate of isocyanuric acid, dipentaerythritol propionate tri(meth)acrylate, tris((meth)acryloyloxyethyl)isocyanurate, hydroxypivalyl aldehyde-

denatured dimethylolpropane tri(meth)acrylate, sorbitol tri(meth)acrylate, propoxylated trimethylolpropane tri(meth)acrylate, and ethoxylated glycerin triacrylate.

Specific examples of tetrafunctional (meth)acrylate include pentaerythritol tetra(meth)acrylate, sorbitol tetra(meth)acrylate, ditrimethylolpropane tetra(meth)acrylate, dipentaerythritol propionate tetra(meth)acrylate, and ethoxylated pentaerythritol tetra(meth)acrylate.

Specific examples of pentafunctional (meth)acrylate include sorbitol penta(meth)acrylate, and dipentaerythritol penta(meth)acrylate.

Specific examples of hexafunctional (meth)acrylate include dipentaerythritol hexa(meth)acrylate, sorbitol hexa(meth)acrylate, alkylene oxide-denatured hexa(meth)acrylate of phosphazene, and caprolactone-denatured dipentaerythritol hexa(meth)acrylate.

(F) additional (meth)acrylate

In addition, the photocurable composition may optionally comprise a polybutadiene acrylate or methacrylate, a silicone acrylate or methacrylate, or a two-mole ethoxylated bisphenol A di(meth)acrylate, or any mixture thereof, whereby such component (F) exhibits preferably two (meth)acrylate functionalities.

Examples of such (meth)acrylates are polydiene (meth)acrylates like polybutadiene (meth)acrylate, polydiene di(meth)acrylates like polybutadiene di(meth)acrylate as SR307 and CN301 from Sartomer, polyisoprene diacrylate and the like, 2 mole alkoxylated bisphenol A di(meth)acrylate as 2 mole ethoxylated bisphenol A di(meth)acrylate as SR348L, silicone (meth)acrylates and silicone di(meth)acrylates like CN9800.

Preferably, the inventive compositions should not comprise urethane (meth)acrylates, polyester (meth)acrylates, polyethylene glycol (PEG) (meth)acrylates. Such compounds may destroy the water scavenging properties of the film and may react with the CaO nanoparticles.

A dispersant may be added, in order to increase the dispersibility of getter particles into the organic matrix. The dispersant may be a low molecular weight organic dispersant, a high molecular weight organic dispersant, a low molecular weight organic/inorganic complex dispersant, a high molecular weight organic/inorganic complex dispersant, an organic/inorganic acid, or the like. The dispersant serves to disperse the getter particles homogeneously in the organic layer, for example, by avoiding aggregation, and thus minimizes the size of the getter particles, which remains few nm, so as to produce a transparent moisture absorption layer.

The photocurable composition may additionally include other components, for example, stabilizers, modifiers, toughenors, antifoaming agents, leveling agents, thickening agents, flame retardants, antioxidants, pigments, dyes, fillers, and combinations thereof.

BRIEF DESCRIPTION OF THE DRAWINGS

Some aspects of the present invention are described in more detail in the drawing.

FIG. 1 shows in detail a cross-section of a first embodiment of an opto-electric device according to an aspect of the invention.

DETAILED DESCRIPTION OF EMBODIMENTS

COMPONENTS

Table I describes components A, B, C, D, E and F used for the manufacture of the photocurable compositions according to the present invention.

PREPARATION OF THE RESINS

The raw materials - except for the photoinitiators - were mixed together and stirred for 1h at 340 rpm at 25°C. The mixture was dried over 4A molecular sieves during 24 hours (sieves dried at 150°C under vacuum during 2 hours), then filtered prior to mixing with dry CaO powder.

The CaO particles were obtained from Strem Chemicals (Catalog #20-1400) and had the following product specifications: Specific Surface Area (BET): ≥ 20 m2/g; Bulk Density: 0.5 g/cc; Crystallite Size: ≤ 40 nm; True Density: 3.3 g/cc; Average Pore Diameter: 165Å; Mean Aggregate Size: 4 µm; Total Pore Volume: ≥ 0.1 cc/g; Ca Content (Based on Metal): > 99.8%. The particle size distribution was measured with a dynamic light scattering tool (DLS), a Zetasizer Nano of Malvern Instruments. The distribution was a three-modal distribution having a first maximum at about 60 nm, a second peak at about 550 nm and a third peak at about 5 µm.

CaO was dehydrated for 1 hour at 900°C in air, then slowly cooled down to 200°C, and transferred quickly to a dry nitrogen filled enclosure, where it was ultimately cooled to room temperature prior incorporation into the curable matrix. As evident from SEM pictures, the CaO particles are strongly aggregated after and even before the calcination process, with particles aggregates up to 10 micrometers in size. Such SEM pictures highlight the necessity to perform a milling/grinding step for downsizing the particles to the nanometer scale.

In order to determine calcium oxide purity, the calcium hydroxide content and calcium carbonate content were determined via Thermogravimetric analysis (TGA measurements and elemental analyses). Quantitative analysis is carried out on combustion. The used measurement method can be found under the link http://en.wikipedia.org/wiki/Thermogravimetric_analysis or in Mansfield, E.; Kar, A.; Quinn, T. P.; Hooker, S. A. (2010). "Quartz Crystal Microbalances for Microscale Thermogravimetric Analysis". Analytical Chemistry 82 (24). Calcium carbonate decomposes into calcium oxide at high temperatures (above 750°C) and calcium hydroxide decomposes into calcium oxide above 400°C. More than 98% purity was obtained after the drying process.

A steel milling chamber filled with 85% (in volume) of yttrium stabilized zirconium oxide milling beads of 0.3-0.4 mm was used for the milling process (in a Dynomill KDL equipment with a gap seal of 0.1 mm). The milling equipment was connected to a reactor to allow recirculation of the mixture, and the complete system was put under dry nitrogen flow for keeping it protected from moisture. A cryostat was used for cooling the reactor and maintaining the milling chamber temperature at 21°C (± 3°C) during the milling process. The recirculation and milling were stopped once the desired particle size was reached.

In case of example 18 (F18 in Table 2), the CaO particles were shaken into the curable matrix under dry nitrogen during 2 hours with a Retch PM100 ball milling equipment using a 250 ml zirconium oxide bowl and 10 mm diameter zirconium oxide milling balls.

The resin milled via bead milling was diluted by 100 times with the curable matrix (without photoinitiator) for determining the particle size distribution using a Zeta Sizer Nano ZS from Malvern Instruments. Particle size distribution measurements were only taken on stable resins, because aggregation phenomena were interfering with signal resulting from "brownian motion" of particles of different sizes.

In order to finalize the formulation preparation, the photoinitiator was added to the curable matrix after the milling process, and the composition was stirred for 1h at 340 rpm at room temperature - all steps being performed under a dry nitrogen atmosphere. The photoinitiator was added after the milling process because it may induce problems during the particle size measurements via dynamic light scattering : resin curing might occur upon laser exposure.

EXAMPLES

Table II a and b show the compositions of the photocurable resins (examples F1 - F20).

ClogP of the components is indicated.

The viscosity of the resins at 20°C - determined immediately after preparation - is indicated.

The stability of the resins at 25°C and at 60°C, and the appearance after 4 days at 60°C is indicated. A resin is considered stable, if it has a pot life at 60°C of longer than 29 days, preferably longer than 43 days, meaning that the viscosity increase of the resin is less than 20% compared to its initial viscosity. At the same time, no solid like gel formation or sedimentation of the particles is detected.

The resins which fulfill said stability requirements and exhibits a good transparency after curing can be advantageously used to produce water scavenging layers for opto-electric devices, in particular OLED.

Tables II a and b also indicate the measured average particle diameter (z) and the polydispersity (PDI) of the produced compositions.
From Table II it is evident that only the inventive compositions F1, F3, F15, F16, F17, F19 and F20 fulfill the necessary stability requirements and are suited to produce water

scavenging layers for opto-electric devices, in particular OLED. Said compositions exhibit a white liquid appearance after 4 days at 60°C, and become transparent after curing. They are stable at 25°C and at 60°C, and flowable with an initial viscosity less than 100 mPa ·s.

In said compositions component A are CaO nanoparticles, component B is Irgacure 369, component C is CD262, component D is CHMA or CD421A, component E is SR351, component F is SR348L, CN9800, CN301 or SR307.

Table II shows that the inventive compositions do not comprise urethane (meth)acrylates, polyester (meth)acrylates, polyethylene glycol (PEG) (meth)acrylates. Such compounds may destroy the water scavenging properties of the film and may react with the CaO nanoparticles. Actually, the negative effects produced by such compounds are exemplified by the non-inventive examples in Table II.
The above mentioned inventive photocurable compositions are well suited to produce water scavenging layers for multilayer thin film barrier stacks used for protecting moisture and oxygen sensitive devices, such as organic LEDs, OPV, CIGS solar cells, liquid crystal displays, electrophoretic displays, electrochromic displays, thin film batteries etc.

Said inventive photocurable compositions exhibit the advantage that the preparation process is carried out in one step, without the need to pre-process the CaO particles prior to their addition into the resin.

Curable and printable inks can be prepared using such inventive photocurable compositions, which is of considerable interest in printed electronic applications, such as the manufacturing of organic light emitting diodes, lithium ion batteries, and the like. No drying step or heating step is needed, since there is no solvent to evaporate, so that sensitive electronic devices are not damaged during the application of the inventive resins.

Said inventive photocurable compositions can be supplied as a liquid one-component system, which remains stable for days or months.

Said inventive photocurable compositions provide flowable and curable inks with an elevated dehydrating power, because they hardly contains any calcium hydroxide and calcium carbonate, which are inactive in dehydration.

Since the CaO particles are milled to the nanoscale, curable inks with an exceptionally high degree of optical transparency can be prepared.

TEST RESULTS FOR THE RESIN OF EXAMPLE 20

The uncured liquid resin of example 20 exhibits the physical properties indicated in Table III:

Table III

PROPERTIES	UNITS	VALUES
Appearance		White, low viscosity liquid
Surface tension	mN/m	28.7-31.6 at 22-25 °C *(2 tests, 2 batches)*
Refractive index	24.2 °C	1.475 *(2 tests, 2 batches)*
Density (ISO1183-3)	g/cm^3	0.998-0.999 *(2 batches - 2 tests each)*
Viscosity @ 20 °C	mPa s	40-50
Viscosity @ 60 °C	mPa s	9-13
Typical particle diameter – z avera	nm	150-350
Particle size distribution - PDI		≤ 0.3
Outgassing at 1 mbar for 5 h	Weight %	≤ 0.2 *(2 tests, 2 batches)*

The uncured liquid resin exhibits a pot life longer than 4 months (viscosity increase ≤20%).

The resin of example 20 was applied by inkjet printing on a silicon nitride substrate in conditions of low humidity (< 30 ppm) with a layer thickness of 10-40 μm and then cured in the UV (ultraviolet) wavelength range 250-400 nm (by LED curing) with a UV dose of 1 J/cm2 under conditions of no oxygen (< 20 ppm) and low humidity (< 30 ppm). Table IV shows the measured physical and mechanical properties of the obtained cured film (UV exposure, 1 J/cm^2).

Table IV

MEASUREMENT	TEST METHOD	VALUES
E Modulus at 20°C on thin films (50-100 μm)	Non-ISO via DMTA[1]	1.3-1.5 GPa *(2 tests, 2 batches)*
E Modulus at 60°C on thin films (50-100 μm)	Non-ISO via DMTA[1]	590-690 MPa *(2 tests, 2 batches)*
E Modulus at 100°C on thin films (50-100 μm)	Non-ISO via DMTA[1]	230-282 MPa *(2 tests, 2 batches)*
E Modulus at 120°C on thin films (50-100 μm)	Non-ISO via DMTA[1]	158-186 MPa *(2 tests, 2 batches)*
Refractive index	23.9°C - 100 μm film	1.51 *(2 tests, 2 batches)*
UV-Visible transmission (400, 600, 800 nm)	UV-Visible spectroscopy – 20 μm	81%, 97%, 99% *(2 tests, 2 batches)*
Hardness	Pencil hardness, 24°C/40%RH - 20 μm on glass	1H-2H *(2 tests, 2 batches)*
Mean surface roughness	Profilometry - 1,5 mm scan Length - 2 μm tip radius	Ra ≤ 10 nm *(1 test, 1 batch)*
Surface energy	Sessile drop method	Total: 42-45 mN/m *(2 tests, 2 batches)*
		Polar: 0.00-0.02 mN/m
		Disperse: 42-45 mN/m
Water uptake at saturation (WU)	40°C/90% RH	2% ≥ WU ≥ 1.8%

[1] Dynamic Thermal Analysis Measurements (DMTA) performed on visco-analyser Metravib VA-3000. Modulus is recorded in tension during thermal scanning from -30 °C to 150°C at 3°C/min (x2) under a static load, 1Hz frequency, 15 μm displacement. The reported values correspond to the first scan.

The Water uptake at saturation (WU) has been measured as the weight increase in % by moisture absorption after 80 hours at 40°C and humidity 90% RH. A saturation of the weight increase is reached after such ageing time. The weight increase of the specimen

after said ageing time is comprised between 1.8% and 2% of the initial weight of the specimen.

Table IV demonstrates that the obtained mechanical properties, in particular the elastic modulus, the obtained optical properties, in particular the light transmission, and the obtained low water uptake make the produced film very well suited as a water scavenging layer for an opto-electric device.

MANUFACTURING OF THE OPTO-ELECTRIC DEVICE

In the following, the materials, methods, and examples are illustrative only and not intended to be limiting.

It will be understood that when an element or layer is referred to as being "on", "connected to" or "coupled to" another element or layer, it can be directly on, connected or coupled to the other element or layer or intervening elements or layers may be present. In contrast, when an element is referred to as being "directly on," "directly connected to" or "directly coupled to" another element or layer, there are no intervening elements or layers present.

FIG. 1 schematically shows a cross-section of an inventive opto-electric device comprising the inventive multi-layered protective barrier stack.

The organic opto-electric device shown in FIG. 1 comprises an opto-electric element 10, that is enclosed by a protective enclosure for protecting the opto-electric element against atmospheric substances in particular water vapor. The protective enclosure comprises a multi-layered protective layer or barrier stack 30, in which a first inorganic layer 32, a first organic layer 34 comprising a metal oxide, a second organic layer 36 free from getter material and a second inorganic layer 38 are stacked in the order named. In the embodiment shown the multilayer protective layer 30 has a further organic layer 40.

The material of the organic layers exhibits preferably a low specific water vapor transmission rate and a high hydrophobicity.

The first organic layer 34 has been produced by curing a photocurable resin according to the invention or by a method according to the invention. In particular, composition F20 has been experimentally used.

The metal oxide is distributed in the first organic layer 34 as nanometer sized particles with a density in the range of 4 to 20 wt%. The second organic layer 36 has a thickness in the range of 10 to 100 micrometer.

In the embodiment shown the metal oxide is an alkaline earth metal oxide. In particular, the selected alkaline earth metal oxide is calcium oxide.

As explained, the organic material experimentally used for the first organic layer 34 is a cured inventive composition, in particular resin composition F20. The second organic layer 36 and the further organic layer 40 may be obtained by curing a photocurable resin according to the invention, which, however, does not comprise any metal oxide, CaO,

BaO or MgO particle. Such resin would exhibit therefore the same composition as the inventive resins, but without any getter particle. The function of the second organic layer 36 (planarization layer) is not to protect from water or oxygen, but to create a plane smooth surface, deprived of any asperity or metal oxide particle, onto which a continuous resistant thin layer of silicone nitride or oxide absolutely free of any discontinuity can be created. In particular, a resin composition corresponding to F20, but without any addition of CaO particles, has been experimentally used to produce the second organic layer 36.

The organic layers may be applied by all kinds of coatings techniques, such spin coating, slot-die coating, kiss-coating, hot-melt coating, spray coating, etc. and all kinds of printing techniques, such as inkjet printing, gravure printing, flexographic printing, screen printing, rotary screen printing, etc.

The second organic layer 36 as well can be deposited by ink-jet printing, for example. For such second organic layer 36, the same organic resin was used as the organic resin used for the first organic layer, deprived however of any metal oxide particle. Alternatively, a different photocurable resin may be used, without metal oxide particles.

Curing or drying may exemplary occur by irradiation of the wet material, pure, or suitably formulated with a photo- or heat-sensitive radical initiator, with UV-light, visible light, infrared light or heat, E-beam, gamma-rays or any combination of the aforementioned.

The first and the second organic layer were both cured experimentally by radiation with a Dymax Flood Lamp at a power density of 33mW/cm^2 during 90 s.

The inorganic layer(s) 32, 38 may be formed by any ceramic, including but not limited to metal oxides, metal nitrides and metal carbides. Suitable materials therefore are for example silicon nitride, silicon oxide (SiO_2), aluminum oxide (Al_2O_3), titanium oxide (TiO_2), indium oxide (In_2O_3), tin oxide (SnO_2), indium tin oxide (ITO, In_2O_3+SnO_2), SiC, silicon oxynitride (SiON) and combinations thereof.

The inorganic layers 32 and 38 have a water vapor transmission rate of at most 10^{-4} g.m^{-2}.day^{-1}. The inorganic layer(s) are in practice substantially thinner than the organic layers. The inorganic layers should have a thickness in the range of 10 to 1000 nm, preferably in the range of 100 to 300 nm. An inorganic layer with a thickness less than 10 nm exhibits in practice insufficient barrier properties. Deposition of an inorganic layer with a thickness of at least 100 nm is preferred in that relatively large tolerances in the manufacturing process are allowed without having consequences for the quality of the product. For flexible products the thickness of the inorganic layers preferably does not exceed 300 nm. A thickness larger than 1000 nm does not further improve the barrier properties of the inorganic layer, while the duration of the deposition process is economically unattractive.

In the experimentally manufactured opto-electric device, the first and the second inorganic layers 32, 38 are silicone nitride layers having a thickness of 150 nm. The first organic layer 34 comprises 5 wt% CaO particles embedded in a matrix of resins according to the invention (F20) and has a thickness of about 80 µm.

The second organic layer 36 is a layer of a resin according to the invention (F20) free from metal oxide particles and having a thickness of about 70 µm. The further organic

layer 40, forming the top-layer of the multilayer protective layer 30 is also a layer of resins according to the invention (F20) free from metal oxide particles and having a thickness of about 50 µm.

As illustrated in FIG. 1, in practice the inorganic layers 32, 38 exhibit defects 32a, 38A, such as pinholes. The organic layers 34 and 36 serve to decouple the pinholes of the layers 32 and 38, to reduce a flow of atmospheric substances towards the opto-electric element 10. The first organic layer 34 comprising the nanometer sized metal oxide particles captures a significant portion of these substances that flow through the second inorganic layer 38. The second organic layer 36, having a thickness of at least 10 µm, prevents that clusters of these metal oxide particles can damage the second inorganic layer 38.

In the embodiment shown the second organic layer 36 extends laterally beyond the first organic layer 34.

In the embodiment shown, the multilayered protective layer 30 exhibits a top layer 40 of a further organic material.

The inorganic layers 32, 38 extend beyond the organic layers 34, 36 and form an encapsulation of the organic layers 34, 36, so that also a lateral ingress of atmospheric substances into the organic layers 34, 36 is prevented.

The first organic layer 34 covers the area defined by the opto-electric element 10 completely. Furthermore, the second organic layer 36 extends laterally beyond the area of the first organic layer 34. In particular, the second organic layer 36 extends laterally over its full circumference beyond the area of the first organic layer 34.

The lateral dimensions of the inorganic layers 32, 38 extend beyond the opto-electric element 10, and the organic layers 34, 36. In particular, the inorganic layers 32, 38 encapsulate the organic layers 34, 36. The multilayer protective layer 30 (barrier stack) forms part of a protective encapsulation of the opto-electric element 10. The encapsulation may comprise a further multilayer protective layer or another type of layer that has sufficient barrier properties, such as a glass plate, a metal foil etc.

In the depicted embodiment, the opto-electric element 10 is an OLED. The OLED has a light emitting layer arranged between a cathode and an anode. In case the device has a metal substrate, the latter may function as an electrode. For an improved functionality the OLED typically has additional functional layers, such as a hole injection layer, a hole transport layer, an electron injection layer, an electron injection layer etc.

Although the present invention is specifically explained with reference to an OLED, the invention is equally applicable to opto-electric devices having another opto-electric element, such as an electrochromic device, or a photovoltaic device.

As used herein, the terms "comprises," "comprising," "includes," "including," "has," "having" or any other variation thereof, are intended to cover a non-exclusive inclusion.

Table I

Trade Name	Supplier	Chemical Name	CAS number	Structure
CD262	Sartomer	1,12 dodecanediol dimethacrylate	Proprietary	
SR351	Sartomer	Trimethylolpropanetriacrylate	15625-89-5	
CHMA	BASF	Cyclohexylmethacrylate	101-43-9	
SR348C	Sartomer	Three-mole ethoxylated bisphenol A dimethacrylate	Not available	
SR348L	Sartomer	Two-mole ethoxylated bisphenol A dimethacrylate	Not available	
SR307	Sartomer	Poly(butadiene) Diacrylate	Not assigned	
CN301	Sartomer	Poly(butadiene) Dimethacrylate	Not assigned	
CN981	Sartomer	Aliphatic polyester/polyether based urethane diacrylate oligomer	Proprietary	Proprietary
Art resin 106S30B	Huntsman	Mixture of acrylates and polyethylene glycol acrylates	Proprietary	Proprietary
Genomer 4205	Rahn	Aliphatic urethane methacrylate	Not available	Proprietary

FIT 852	Esstech	Urethane dimethacrylate	72869-86-4 + 868-77-9	
SR480	Sartomer	10 mole ethoxylated bisphenol A dimethacrylate	41637-38-1	
CN972	Sartomer	Aromatic polyether based urethane triacrylate oligomer	Proprietary	Proprietary
CN9800	Sartomer	Difunctional aliphatic silone acrylate oligomer	Proprietary	Proprietary
SR610	Sartomer	Polyethylene glycol (600) diacrylate	26570-48-9	
Ebecryl 837	Cytec	Multifunctional polyester acrylate	Proprietary	Proprietary
ACMO	Rahn	Acryloyl morpholine	5117-12-4	
NVC	BASF	N-Vinyl Caprolactam	2235-00-9	
Ebecryl 210	Cytec	Aromatic difunctional urethane acrylate	Proprietary	Proprietary
Irgacure 369	BASF	2-Benzyl-2-dimethylamino-4-morpholinobutyrophenone	119313-12-1	

RAW MATERIALS	ClogP	F1 (wt%)	F2 (wt%)	F3 (wt%)	F4 (wt%)	F5 (wt%)
Desiccant						
CaO		5	5	5	5	5
(Meth)acrylates						
CD262	6.38	48.45	48.45	48.45	48.45	48.45
SR351	1.58	9.12	9.12	9.12	9.12	9.12
CHMA	2.71	20	20	20	20	20
SR348L	> 4	16.44				
SR348C	> 4		16.44			
CN9800	>2			16.44		
CN981	CD				16.44	
Art resin 106S30B	CD					16.44
Genomer 4205	CD					
FIT 852	>3					
SR480	4.58					
SR610	<1					
Ebecryl 210	CD					
Photoinitiator						
Irgacure 369		0.95	0.95	0.95	0.95	0.95
TOTAL		100	100	100	100	100
Process		Bead-milling	Bead-milling	Bead-milling	Bead-milling	Bead-milling
Viscosity at 20°C (mPa.s)		26-27	23-24	19-20	34	58
Miscibility at 25°C		OK	OK	OK	OK	OK
Stability at 25°C		> 43 days - <20% increase in viscosity	> 43 days - <20% increase in viscosity	> 43 days - <20% increase in viscosity	1-2 days - Solid like gel formation	1-2 days - Solid like gel formation
Stability at 60°C		> 43 days - <20% increase in viscosity	4 days - PS	> 43 days - <20% increase in viscosity	1 day - Solid like gel formation	1 day - Solid like gel formation
Appearance after 4 days at 60°C		White liquid	PS + bottom layer = solid like gel containing CaO	White liquid	Solid like gel formation	Solid like gel formation
z average (r. nm)		290	208	435	NM	NM
PDI		0.13	0.11	0.16	NM	NM

NM: Not Measurable
PS:Phase Separation
CD: Cannot be determined – molecular structure kept confidential by supplier

Table II a

RAW MATERIALS	ClogP	F6 (wt%)	F7 (wt%)	F8 (wt%)	F9 (wt%)	F10 (wt%)
Desiccant						
CaO		5	5	5	5	5
(Meth)acrylates						
CD262	6.38	48.45	48.45	48.45	48.45	48.45
SR351	1.58	9.12	9.12	9.12	9.12	9.12
CHMA	2.71	20	20	20	20	20
SR348L	> 4					
SR348C	> 4					
CN9800	>2					
CN981	CD					
Art resin 106S30B	CD					
Genomer 4205	CD	16.44				
FIT 852	>3		16.44			
SR480	4.58			16.44		
SR610	<1				16.44	
Ebecryl 210	CD					16.44
Photoinitiator						
Irgacure 369		0.95	0.95	0.95	0.95	0.95
TOTAL		100	100	100	100	100
Process		Bead-milling	Bead-milling	Bead-milling	Bead-milling	Bead-milling
Viscosity at 20°C (mPa.s)		38-39	49-50	32-33	40-41	65-66
Miscibility at 25°C		OK	OK	OK	OK	OK
Stability at 25°C		1-2 days - Solid like gel formation	1-2 days - Solid like gel formation	1-2 days - Solid like gel formation	1-2 days - Solid like gel formation	1-2 days - Solid like gel formation
Stability at 60°C		1 day - Solid like gel formation	1 day - Solid like gel formation	1 day - Solid like gel formation	1 day - Solid like gel formation	1 day - Solid like gel formation
Appearance after 4 days at 60°C		Solid like gel formation	Solid like gel formation	Solid like gel formation	Solid like gel formation	Solid like gel formation
z average (r. nm)		NM	NM	NM	NM	NM
PDI		NM	NM	NM	NM	NM

NM: Not Measurable
PS:Phase Separation
CD: Cannot be determined – molecular structure kept confidential by supplier

Table II b

RAW MATERIALS	ClogP	F11 (wt%)	F12 (wt%)	F13 (wt%)	F14 (wt%)	F15 (wt%)
Desiccant						
CaO		5	5	5	5	5
(Meth)acrylates						
CD262	6.38	48.45	48.45	48.45	48.45	48.45
SR351	1.58	9.12	9.12	9.12	9.12	9.12
CHMA	2.71	20	20	20	20	20
CD421A						
CN972	CD	16.44				
ACMO	0.32		16.44			
NVC	1.64			16.44		
Ebecryl 837	CD				16.44	
CN301	>8					16.44
SR307	>7					
Photoinitiator						
Irgacure 369		0.95	0.95	0.95	0.95	0.95
TOTAL		100	100	100	100	100
Process		Bead-milling	Bead-milling	Bead-milling	Bead-milling	Bead-milling
Viscosity at 20°C (mPa.s)		13-14	70-71	23-24	30	83-84
Miscibility at 25°C		PS	OK	PS	PS	OK
Stability at 25°C		PS + bottom layer = solid like gel containing CaO	1-2 days - Solid like gel formation	PS + bottom layer = solid like gel containing CaO	PS + bottom layer = solid like gel containing CaO	> 43 days - <20% increase in viscosity
Stability at 60°C		PS + bottom layer = solid like gel containing CaO	1 day - Solid like gel formation	PS + bottom layer = solid like gel containing CaO	PS + bottom layer = solid like gel containing CaO	> 43 days - <20% increase in viscosity
Appearance after 4 days at 60°C		PS + bottom layer = solid like gel containing CaO	Solid like gel formation	PS + bottom layer = solid like gel containing CaO	PS + bottom layer = solid like gel containing CaO	White liquid
z average (r. nm)		NM	NM	NM	NM	168
PDI		NM	NM	NM	NM	0.075

Table II c

RAW MATERIALS	ClogP	F16 (wt%)	F17 (wt%)	F18 (wt%)	F19 (wt%)	F20 (wt%)
Desiccant						
CaO		5	5	5	10	5
(Meth)acrylates						
CD262	6.38	64.45	48.45	64.89	45.9	48.45
SR351	1.58	9.12	9.12	9.12	8.7	9.12
CHMA	2.71	20	20	20		
CD421A					18.9	20
CN972	CD					
ACMO	0.32					
NVC	1.64					
Ebecryl 837	CD					
CN301	>8	0.44				
SR307	>7		16.44		15.6	16.44
Photoinitiator						
Irgacure 369		0.95	0.95	0.95	0.9	0.95
TOTAL		100	100	100	100	100
Process		Bead-milling	Bead-milling	Ball shaking	Bead-milling	Bead-milling
Viscosity at 20°C (mPa.s)		16-17	40-41	41-42	45-50	40-41
Miscibility at 25°C		OK	OK	OK	OK	OK
Stability at 25°C		> 43 days - <20% increase in viscosity	> 43 days - <20% increase in viscosity	3 days - CaO sedimentation	> 29 days - <20% increase in viscosity	> 43 days - <20% increase in viscosity
Stability at 60°C		> 43 days - <20% increase in viscosity	> 43 days - <20% increase in viscosity	1 day - CaO sedimentation	> 29 days - <20% increase in viscosity	> 43 days - <20% increase in viscosity
Appearance after 4 days at 60°C		White liquid	White liquid	All CaO sedimented at the bottom	White liquid	White liquid
z average (r. nm)		417	233	NM	270	268
PDI		0.13	0.05	NM	0.1	0.05

Table II d

CLAIMS

1. A radiation curable resin composition comprising:
(A) metal oxide particles;
(B) at least one photoinitiator, preferably a radical photoinitiator, or any mixture thereof;
(C) at least one acrylate or methacrylate component with a ClogP higher than 2, preferably higher than 4, more preferably higher than 5, or any mixture thereof;
(D) at least one monofunctional acrylate or methacrylate diluent component, preferably with a viscosity below 40 mPa•s at 20°C, or any mixture thereof;
(E) at least one acrylate or methacrylate component with functionality equal or higher than 3, preferably 3 or 4, or any mixture thereof; wherein
Mica is excluded from the group of (A) metal oxide particles.

2. A resin composition according to claim 1, wherein metal oxide particles A are alkaline earth metal oxide particles, preferably CaO, BaO and/or MgO particles,
and exhibit an average particle diameter of 10 to 1000 nm, preferably 15 to 500 nm, more preferably 20 to 350 nm, or even 50 to 250 nm.

3. A photocurable resin composition according to any of the preceding claims, which does not comprise any urethane (meth)acrylate, polyester (meth)acrylate, or polyethylene glycol (PEG) (meth)acrylate.

4. A photocurable resin composition according to any of the preceding claims, which exhibits a viscosity at 20°C below 500 mPa•s, preferably below 200 mPa•s, more preferably below 100 mPa•s,
and/or which exhibits a pot life at 60°C longer than 29 days, preferably longer than 43 days.

5. A photocurable resin composition according to any of the preceding claims, which also comprises:
(F) a polybutadiene acrylate or methacrylate, a silicone acrylate or methacrylate, or a two-mole ethoxylated bisphenol A di(meth)acrylate, or any mixture thereof,
whereby such component (F) exhibits preferably two (meth)acrylate functionalities.

6. A photocurable resin composition according to any of the preceding claims, wherein component (D) exhibits a ClogP higher than 2,
component (E) exhibits a ClogP higher than 1,
and/or component (F) exhibits a ClogP higher than 4, preferably higher than 6 or 7.

7. A photocurable resin composition according to any of the preceding claims, wherein component C is a 1,n-diol di(meth)acrylate of a diol of the formula $HO-(CH_2)_n-OH$, whereby n is higher than 3, preferably higher than 6, more preferably higher than 10.

8. A photocurable resin composition according to any of the preceding claims, which, after curing, is transparent, preferably the cured resin, as a film of 20 micrometer thickness, has a light transmission at 600 nm of > 90%,
and/or exhibits a water uptake after storage for 80 hours at 40°C in 90% relative humidity of less than 2% of its initial weight.

9. A resin composition according to any of the preceding claims comprising at least:
(A) 1 - 30 % by weight of CaO, BaO and/or MgO particles (component A);
(B) 0.1 - 10 % by weight of the photo initiator B;
(C) 30 - 80 % by weight of component C, which preferably exhibits two (meth)acrylate functionalities;
(D) 5 - 40 % by weight of the monofunctional (meth)acrylate diluent component D;
(E) 5 - 30 % by weight of the (meth)acrylate component E with functionality equal or higher than 3; and optionally
(F) 0.1 - 30 % by weight of component F;
based on the total weight of the composition.

10. A resin composition according to any of the preceding claims comprising at least:
(A) 4 - 20 % by weight of CaO, BaO and/or MgO particles (component A);
(B) 0.1 - 5 % by weight of the photo initiator B;
(C) 40 - 70 % by weight of component C, which exhibits preferably two (meth)acrylate functionalities;
(D) 10 - 30 % by weight of the monofunctional (meth)acrylate diluent component D;
(E) 7 - 20 % by weight of the (meth)acrylate component E with functionality equal or higher than 3; and optionally
(F) 0.3 - 25 % by weight of component F;
based on the total weight of the composition.

11. Method for preparing a photocurable resin according to any of the claims 1 to 10, comprising the steps of:

h) mixing and stirring together components C, D, E, and optionally F, in order to produce a mixture h. which is optionally dried;
i) incorporating optionally dehydrated calcium, barium and/or magnesium oxide (component A) into the produced mixture h, so as to obtain a mixture i;
j) Milling and/or grinding the produced mixture i, preferably via bead milling under dry nitrogen, in order to downsize the average diameter of calcium, barium and/or magnesium oxide particles, so as to produce a mixture j;
k) Adding the photoinitiator B to the produced mixture j, so as to obtain a mixture k, which is preferably stirred under dry nitrogen atmosphere.

12. Method for preparing a photocurable resin according to claim 11, wherein during the milling step j) the average particle diameter of the CaO, BaO and/or MgO particles is reduced to the range of 10 to 1000 nm, preferably 15 to 500 nm, more preferably 20 to 350 nm or even 50 to 250 nm, and/or
wherein the produced photocurable resin k exhibits a water content less than 1000 ppm by weight.

13. Method for manufacturing a multi layer barrier stack (30) against water and oxygen penetration and diffusion, comprising the steps of:

m) Depositing a first inorganic layer (32), preferably silicon nitride or oxide, exhibiting preferably a thickness between 50 and 300 nm;
n) Depositing onto said first inorganic layer (32), preferably via ink jet printing, a first organic layer (34) of the photocurable resin according to the invention or produced with a method according to the invention;
o) exposing said first organic layer (34) to ultraviolet (UV) radiation, so as to solidify said first organic layer (34) and to produce a transparent layer exhibiting water scavenging properties;

p) applying onto said first solidified organic layer (34), preferably via ink jet printing, a second organic layer (36) of a photocurable resin not containing metal oxide particles;
q) exposing said second organic layer (36) to UV radiation, so as to solidify said second organic layer (36) and to produce a transparent layer exhibiting planarization properties;
r) Depositing onto said second solidified organic layer (36) a second inorganic layer (38), preferably silicon nitride or oxide, exhibiting preferably a thickness between 50 and 300 nm.

14 . Method for manufacturing a multi layer barrier stack (30) according to claim 13, whereby the first organic layer (34) exhibits a thickness between 10 and 100 micrometers, preferably between 20 and 80 micrometers, and/or
whereby the second organic layer (36) exhibits a thickness between 10 and 100 micrometers, preferably between 20 and 80 micrometers.

15 . A method for manufacturing an opto-electric device, in particular an organic light emitting diode (OLED), comprising the steps of:
- providing an opto-electric element and/or layer (10),
- providing an encapsulation comprising a multi layer barrier stack (30) produced according to the method of claim 13 or 14.

16 . A multi layer barrier stack (30) or opto-electric device, in particular OLED, obtained by a method according to claim 13, 14 or 15.

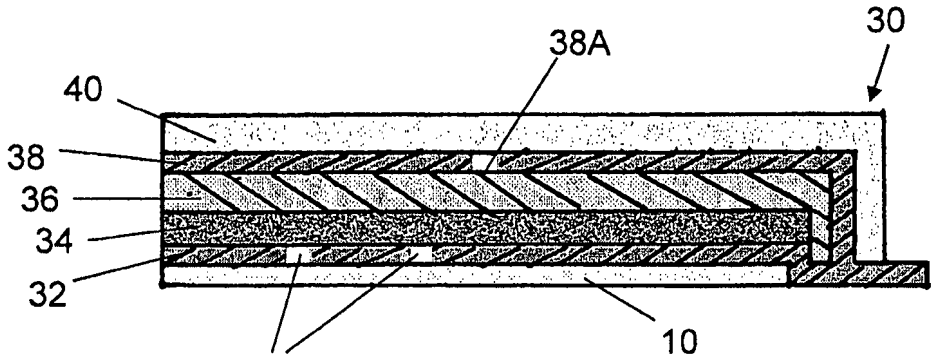

FIG. 1

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/065012

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08K3/22 C08K5/09 H01L51/52
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08K H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Week 200941 Thomson Scientific, London, GB; AN 2009-J14796 XP002687068, & CN 101 423 675 A (UNIV SICHUAN) 6 May 2009 (2009-05-06) abstract -----	1,3,4, 6-8,11, 12
X	US 2004/195967 A1 (PADIYATH RAGHUNATH [US] ET AL) 7 October 2004 (2004-10-07) paragraphs [0002], [0042], [0066] - [0068]; claims; figures; examples -----	13-16
X	WO 02/46323 A2 (PRINTAR LTD [IL]; ZOHAR RON [IL]; MOZEL JACOB [IL]; SAMUEL JOSHUA [IL]) 13 June 2002 (2002-06-13) claims; example 1 -----	1,4-8
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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

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Name and mailing address of the ISA/	Authorized officer
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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	US 2005/227114 A1 (TANAKA SATOSHI [JP] ET AL) 13 October 2005 (2005-10-13) paragraph [0003]; claims; examples	1-16
A	EP 2 445 029 A1 (TNO [NL]; KONINKL PHILIPS ELECTRONICS NV [NL]; HUNTSMAN ADV MAT SWITZE) 25 April 2012 (2012-04-25) paragraphs [0005] - [0008], [0090] - [0092]; claims	1-16

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
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H01L 51/52(2006.01)

权利要求书2页 说明书24页 附图1页

(54)发明名称

用于水清除层的可辐射固化的组合物及其制备方法

(57)摘要

一种可辐射固化的树脂组合物，包含：(A)金属氧化物颗粒；(B)至少一种光引发剂，优选自由基光引发剂，或它们的任何混合物；(C)至少一种具有大于2、优选大于4、更优选大于5的ClogP的丙烯酸酯或甲基丙烯酸酯组分，或它们的任何混合物；(D)至少一种单官能丙烯酸酯或甲基丙烯酸酯稀释剂组分，优选在20℃下具有小于40mPa·s的粘度，或它们的任何组合物；(E)至少一种具有等于或大于3，优选3或4的官能度的丙烯酸酯或甲基丙烯酸酯组分，或它们的任何混合物；其例如可以有利地用于制造有机光电或光电子器件(例如有机发光二极管(OLED))的多层阻隔叠层。

CN 104704035 A

1. 一种可辐射固化的树脂组合物，包含：

(A) 金属氧化物颗粒；

(B) 至少一种光引发剂，优选自由基光引发剂，或它们的任何混合物；

(C) 至少一种具有大于 2、优选大于 4、更优选大于 5 的 ClogP 的丙烯酸酯或甲基丙烯酸酯组分，或它们的任何混合物；

(D) 至少一种单官能丙烯酸酯或甲基丙烯酸酯稀释剂组分，优选在 20℃下具有小于 40mPa·s 的粘度，或它们的任何混合物；

(E) 至少一种具有等于或大于 3、优选 3 或 4 的官能度的丙烯酸酯或甲基丙烯酸酯组分，或它们的任何组合物；其中

云母被排除在 (A) 金属氧化物颗粒之外。

2. 根据权利要求 1 的树脂组合物，其中金属氧化物颗粒 A 是碱土金属氧化物颗粒，优选 CaO、BaO 和 / 或 MgO 颗粒，并且显示出 10-1000nm 的平均粒径，优选 15-500nm，更优选 20-350nm，或甚至 50-250nm。

3. 根据前述权利要求任一项的树脂组合物，其不包含任何聚氨酯 (甲基) 丙烯酸酯，聚酯 (甲基) 丙烯酸酯，或聚乙二醇 (PEG)(甲基) 丙烯酸酯。

4. 根据前述权利要求任一项的树脂组合物，其在 20℃下显示出小于 500mPa·s 的粘度，优选小于 200Pa·s，更优选小于 100Pa·s，和 / 或其在 60℃下显示出长于 29 天的贮存期，优选长于 43 天。

5. 根据前述权利要求任一项的树脂组合物，其还包含 (F) 聚丁二烯丙烯酸酯或甲基丙烯酸酯、硅氧烷丙烯酸酯或甲基丙烯酸酯，或两摩尔乙氧基化双酚 A 二 (甲基) 丙烯酸酯，或它们的任何混合物，其中这种组分 (F) 优选显示出两个 (甲基) 丙烯酸酯官能团。

6. 根据前述权利要求任一项的树脂组合物，其中组分 (D) 显示出大于 2 的 ClogP，组分 (E) 显示出大于 1 的 ClogP，和 / 或组分 (F) 显示出大于 4、优选大于 6 或 7 的 ClogP。

7. 根据前述权利要求任一项的树脂组合物，其中组分 C 是式 $HO-(CH_2)_n-OH$ 的二醇的二 (甲基) 丙烯酸 1，n- 二醇酯，其中 n 大于 3，优选大于 6，更优选大于 10。

8. 根据前述权利要求任一项的树脂组合物，其在固化后是透明的，优选作为 20 微米厚的膜的固化的树脂在 600nm 下具有 > 90% 的透光率，和 / 或在 90% 相对湿度中在 40℃下存储 80 小时后显示出小于其初始重量 2% 的吸水量。

9. 根据前述权利要求任一项的树脂组合物，至少包含：

(A)1-30wt% 的 CaO、BaO 和 / 或 MgO 颗粒 (组分 A)；

(B)0.1-10wt% 的光引发剂 B；

(C)30-80wt% 的组分 C，其优选显示出两个 (甲基) 丙烯酸酯官能团；

(D)5-40wt% 的单官能 (甲基) 丙烯酸酯稀释剂组分 D；

(E)5-30wt% 的具有等于或大于 3 的官能度的 (甲基) 丙烯酸酯组分 E；和任选地

(F)0.1-30wt% 的组分 F；

基于所述组合物的总重量。

10. 根据前述权利要求任一项的树脂组合物，至少包含：

(A)4-20wt% 的 CaO、BaO 和 / 或 MgO 颗粒 (组分 A)；

(B)0.1-5wt% 的光引发剂 B；

(C)40-70wt%的组分C,其优选显示出两个（甲基）丙烯酸酯官能团；

(D)10-30wt%的单官能（甲基）丙烯酸酯稀释剂组分D；

(E)7-20wt%的具有等于或大于3的官能度的（甲基）丙烯酸酯组分E；和任选地

(F)0.3-25wt%的组分F；

基于所述组合物的总重量。

11.制备权利要求1-10任一项的树脂组合物的方法,包括以下步骤：

h)将组分C、D、E和任选的F混合并且一起搅拌以制备混合物h,任选地将其干燥；

i)将任选地脱水的氧化钙、氧化钡和/或氧化镁（组分A）引入到所制备的混合物h中,以获得混合物i；

j)在干燥氮气下,优选通过球磨,研磨和/或碾磨制备的混合物i以缩小氧化钙、氧化钡和/或氧化镁颗粒的平均直径,以制备混合物j；

k)将光引发剂B加入到所制备的混合物j中,以获得混合物k,其优选在干燥氮气气氛下搅拌。

12.根据权利要求11的制备树脂组合物的方法,其中在研磨步骤j)期间,CaO、BaO和/或MgO颗粒的平均粒径被降低至10-1000nm的范围,优选15-500nm,更优选20-350nm或甚至50-250nm,和/或其中制备的树脂k显示出小于1000ppm重量的水含量。

13.制造耐水和氧渗透及扩散的多层阻隔叠层(30)的方法,包括以下步骤：

m)沉积第一无机层(32),优选为氮化硅或氧化硅,其优选显示出50-300nm的厚度；

n)优选通过喷墨打印,将本发明或根据本发明的方法制备的树脂组合物的第一有机层(34)沉积在所述第一无机层(32)上；

o)将所述第一有机层(34)曝光于紫外(UV)辐射,以固化所述第一有机层(34)并且制备显示出水清除性能的透明层；

p)优选通过喷墨印刷,将不包含金属氧化物颗粒的可光固化的树脂的第二有机层(36)施加到所述第一固化的有机层(34)上；

q)将所述第二有机层(36)曝光于UV辐射以固化所述第二有机层(36)并且制备显示出平面化性能的透明层；

r)将第二无机层(38)沉积在所述第二固化的有机层(36)上,其中第二无机层(38)优选氮化硅或氧化硅和其优选显示出50-300nm的厚度。

14.根据权利要求13的制造多层阻隔叠层(30)的方法,其中所述第一有机层(34)显示10-100微米的厚度,优选20-80微米,和/或其中第二有机层(36)显示出10-100微米的厚度,优选20-80微米的厚度。

15.一种制造光电器件的方法,其中光电器件特别是有机发光二极管(OLED),包括以下步骤：

-提供光电元件和/或层(10),

-提供包含根据权利要求13或14的方法制备的多层阻隔叠层(30)的封装。

16.通过权利要求13、14或15的方法获得的多层阻隔叠层(30)或光电器件,特别是OLED。

用于水清除层的可辐射固化的组合物及其制备方法

[0001] 发明背景

发明领域

[0002] 本发明涉及一种用于水清除层的可辐射固化或可光固化的组合物，所述水清除层例如有利地用在多层阻隔叠层中，所述多层阻隔叠层例如可以用于有机光电或光电子器件（例如有机发光二极管（OLED））的制造中。

[0003] 本发明进一步涉及制造所述可辐射固化的组合物或可光固化的组合物、所述水清除层、所述多层阻隔叠层和所述有机光电器件或 OLED 本身的方法。

[0004] 相关技术

[0005] 湿气敏感性器件例如有机 LED（基于小分子和聚合物二者）、OPV、CI(G)S 太阳能电池暴露于环境气氛导致器件性能的损失。在 OLED 的情况下，水或其它氧化性材料的进入可以导致活性有机层的降解，导致效率的损失，这主要是由于阴极的氧化，导致器件的局部失效。水的进入可以来自两侧，从阳极侧或从阴极侧。目前现有技术 OLED 通过使用玻璃作为基板和玻璃或金属盖以封装在阴极侧上防止水的进入。常规地，使用在边缘胶黏的覆盖盖进行封装。使用吸气剂（getter）消耗可能渗透通过胶的水。该封装方法是昂贵的并且对于大面积器件是无效的，尤其是柔性器件。也将允许制造柔性器件的更成本有效的替代品是使用薄膜阻隔，其可以施加到塑料箔上充当基板并且可以用作最后的封装。为了理解使用这种阻隔的问题，以下给出了关于水进入 OLED 机理的简要解释。

[0006] 在 OLED 器件中的阴极最通常由覆盖有相对厚 Al 层的 Ba（聚合物 LED）或 LiF（小分子 OLED）的薄层（1-50nm）构成。如果不是其含有针孔的事实（其中其大部分由颗粒造成），铝将会是耐水优异的阻隔。这些颗粒来源于多种原因并且它们的存在在实践中难以避免。来自周围气氛的水在阴极层中通过针孔渗透。在阴极 - 聚合物界面处金属的氧化在器件操作期间防止电子从阴极注入到聚合物中，从而引入局部点而不发射，即在明亮的电致发光背景中的黑点。黑点的演化由水从针孔的扩散速率决定。所得圆形点的面积随着时间线性增加。黑点形成和生长是货架效应，即不需要电流或电压来驱动过程。当将无机阻隔层施加到 OLED 的顶部时，大部分颗粒被覆盖，导致黑点数量的相应减少。仍然保留的黑点密度目前对于任何实际应用都太大。阻隔层的厚度的增加难以降低针孔密度。一旦在这种层中存在针孔，则其趋于增殖，同时沉积更多的相同材料。

[0007] Graff 等在" Mechanisms of vapor permeation through multilayer barrier films :Lag time versus equilibrium permeation"，J.of Applied Physics, Vol.96, Nr.4, pp.1840-1849 中描述了通过具有有机层的阻隔叠层阻断针孔生长的目前通常的策略。以这种方式，在后续阻隔层中的针孔被去偶联，导致水由环境气氛传输到器件的阴极的曲折路径。不同化学组合物（例如不同的无机材料）的其它层也被用于这一目的。Graff 等研究了使用具有 0.1-3 μm 厚度的聚合物去偶联层，并且提出甚至更薄的聚合物去偶联层可以导致进一步的改善。

[0008] US2009289549A 描述了提供有多层保护性阻隔叠层的 OLED 显示器，其中有机和无

机层以重复的方式交替叠加并且将至少一个吸湿层或水清除层插在多层保护性层中。特别地，US2009289549A 描述了一个实施方案，其中多层保护性层按顺序包含第一无机层、吸湿层（水清除层）、有机层和第二无机层。吸湿层的存在进一步降低了水进入到光电元件。所述吸湿层由有机金属化合物溶液形成并且可以包含诸如金属或金属氧化物的添加剂。吸湿层可以具有 3-50nm 范围的厚度。在 US2009289549A 中标记了在吸湿层和第二无机层之间的有机层可以具有大于吸湿层厚度的厚度。所引用的 US 专利未更具体地公开厚度应当大多少，但是被引用的附图表明第二有机层为约 2-3 倍厚。

[0009] 用于光电器件的合适的吸湿层或水清除层的沉积和制造已经表明了从化学和所需的物理性能的角度特殊的技术难度。至今未发现合适的材料，其满足所有工业制造光电器件和 OLED 所需的物理、机械、光学和加工要求。

[0010] 例如氧化钙是高度吸湿性的并且可用作吸湿和脱水剂，特别是在其中湿气降低器件寿命的电子外壳中。从在光电应用中处理的角度，然而有必要以均匀稳定液体的形式提供氧化钙，其可以涂覆或印刷并且固化在不同的基板上并且以不同的厚度。从在某些光电应用中处理的角度，特别是用于个体布局和按需印刷方面，有必要能够通过喷墨印刷、阀喷射印刷和液体分配方法将吸湿性材料作为可固化的油墨沉积。为了通过凹版印刷图案化，油墨的粘度在 20℃下必须低于 200mPa·s，并且对于柔性版印刷油墨的粘度在 20℃下必须低于 500mPa·s。这些对于卷对卷印刷技术是有利的。获得显示出水清除性能的中和低粘度树脂也可能是必须的。

[0011] 发明概述

[0012] 本发明的目的在于提供用于制备水清除层的含有氧化物颗粒的可光固化的组合物，其是稳定的并且是可流动的，使得其可以例如容易地通过喷墨 / 阀喷射印刷或通过凹版印刷和柔性版印刷分配或印刷。

[0013] 本发明另一个目的是提供制备这种可光固化的组合物的方法，其是简单、快速和经济上可行的。

[0014] 本发明的另一个目的是提供制备水清除层的方法，其是简单、快速、经济上可行的并且适用于光电器件和应用。

[0015] 本发明的另一个目的是提供制造发光器件或光电器件（特别是有机发光二极管(OLED)）的方法，其是简单、快速、经济上可行的，其中发光器件，特别是有机发光二极管(OLED) 保持被湿气和水保护非常长的时间，并且对环境物质显示出改善的阻隔。

[0016] 根据本发明的第一方面，提供了一种可辐射固化的（优选可光固化的）树脂组合物，其包含：

[0017] (A) 金属氧化物颗粒；

[0018] (B) 至少一种光引发剂，优选自由基光引发剂，或它们的任何混合物；

[0019] (C) 至少一种具有大于 2、优选大于 4、更优选大于 5 的 ClogP 的丙烯酸酯或甲基丙烯酸酯组分，或它们的任何混合物；

[0020] (D) 至少一种单官能丙烯酸酯或甲基丙烯酸酯稀释剂组分，优选在 20℃下具有小于 40mPa·s 的粘度，或它们的任何混合物；

[0021] (E) 至少一种具有等于或大于 3，优选 3 或 4 官能度的丙烯酸酯或甲基丙烯酸酯组分，或它们的任何混合物；其中

[0022] 云母被排除在 (A) 金属氧化物颗粒之外。

[0023] 这种可光固化的树脂组合物令人意外地稳定并且可流动，并且令人意外地适用于制备可以容易地通过喷墨 / 阀喷射印刷或通过凹版印刷和柔性版印刷分配或印刷的水清除涂层。在固化之后，它们产生了以优异的水清除性能和透明性以及以优异的长寿命为特征的水清除涂层。因此，它们令人意外地适用于制造用于光电器件或发光器件（特别是有机发光二极管 (OLED)）的水清除层。

[0024] 金属氧化物颗粒也可以是颗粒聚集体或团聚体。

[0025] 为了避免金属氧化物（例如 CaO）水解和通过氢键聚集的可能性，可固化的基质优选显示出低水含量 - 小于 1000ppm（以重量计）。出于这种原因，优选使用具有高疏水性的化合物以避免内水量的升高。疏水性的良好指示剂是 ClogP，即辛醇 / 水分配系数的计算对数值。相对高的 ClogP 值表明材料相对高的疏水性。出于本发明的目的，具有至少 2 的 ClogP 值的有机材料是特别合适的。ClogP 值是众所周知的参数并且可以通过该分子结构的知识对于任何给定分子进行计算。存在大量可商购的计算机程序进行该计算。在本发明的情况下，使用了 Osiris Property Explorer (http ://www.organic-chemistry.org/prog/peo/.)，其是 Actelion 内部物质登记系统的组成部分。作为增量系统实施该算法，基于原子类型、原子连接性和化学键，添加每一个原子的贡献。此外，可固化基质优选在加入金属氧化物或 CaO 颗粒之前在活化的 4A 分子筛上干燥。

[0026] ClogP 的定义和计算方法可以在以下链接中找到 :http ://en.wikipedia.org/wiki/Partition_coefficient ;Leo A, Hansch C, and Elkins D(1971) " Partition coefficients and their uses " Chem Rev71(6),525-616 ;Sangster, James(1997) Octanol-Water Partition Coefficients :Fundamentals and Physical Chemistry, Vol.2of Wiley Series in Solution Chemistry Chichester, John Wiley&Sons Ltd. pp.178 ;Hansch,Corwin Leo A(1979)Substituent Constants for Correlation Analysis in Chemistry and Biology New York, John Wiley&Sons Ltd.pp.178 ;Leo, Albert, Hoekman DH, Hansch C(1995)Exploring QSAR, Hydrophobic, Electronic, and Steric Constants Washington, DC, American Chemical Society.

[0027] 为了是可流动的，并且特别是为了制备可喷墨的油墨（其要求非常低粘度的树脂，在印刷温度下小于 30mPa • s)，使用单官能丙烯酸酯或甲基丙烯酸酯稀释剂组分 (D) 并且金属氧化物或氧化钙的浓度优选小于 50wt%，并且更优选小于 20wt%。

[0028] 根据本发明一个优选的实施方案，所述光引发剂是自由基光引发剂。

[0029] 根据本发明一个优选的实施方案，金属氧化物颗粒是碱土金属氧化物颗粒，优选 CaO、BaO 和 / 或 MgO 颗粒，并且显示出 10-1000nm 的平均粒径，优选 15-500nm，更优选 20-350nm，或甚至 50-250nm。

[0030] 使用动态光散射技术计算平均粒径。所使用的装置是用于粒径测量的通过非侵入背散射模式操作的 Malvern Zetasizer Nano ZS。动态光散射（也称为光子相关光谱法或准弹性光散射）测量布朗运动并且使用 Stokes-Einstein 方程将其与颗粒的尺寸相关联。其通过使用激光照射颗粒并且分析散射光中的强度波动操作。

[0031] 在本发明中测量平均颗粒直径所使用方法的细节可以在以下链接中找到 :http ://en.wikipedia.org/wiki/Dynamic_light_scattering 和 Berne, B.J. ;

Pecora, R. Dynamic Light Scattering, Courier Dover Publications(2000)ISBN 0-486-411155-9。

[0032] 所述金属氧化物或 CaO 粒径优选在纳米范围，以最大降低沉降速度，特别是对于低粘度树脂。纳米范围是指氧化钙细小颗粒具有 10-1000nm，优选 15-500nm，更优选 20-350nm，和仍然更优选 50-250nm 的平均颗粒直径（基于体积）。此外，对于例如喷墨印刷的方法小粒径是高度想要的以避免喷嘴堵塞并且对于制造具有高度光学透明的树脂小粒径也是高度想要的。问题是氧化钙颗粒被干燥或由高温方法（＞500℃）制备，并且作为结果，其是强烈团聚的。必须进行研磨 / 碾磨工艺以将聚集体粉碎至纳米尺度。碾磨工业已知可以使用非常小的研磨球实现纳米尺度。在我们的方法中，使用了 0.3-0.4mm 直径的研磨球。更小的球例如 50μm 或 100μm 甚至将更适合，特别是用于制备透明的可固化树脂。

[0033] 根据本发明一个优选的实施方案，所述可光固化的树脂组合物不包含任何聚氨酯（甲基）丙烯酸酯，聚酯（甲基）丙烯酸酯，或聚乙二醇 (PEG)（甲基）丙烯酸酯。

[0034] 优选必须避免能够与金属氧化物或 CaO 络合以及氢键结合的组分，或者以非常小的负载量使用以避免 CaO 颗粒结块以及不再流动的固体状凝胶的逐渐形成（仅需要数小时）。随着粒径的降低该现象恶化，这是因为表面积的增加所致。因此优选避免聚氨酯丙烯酸酯结构单元、PEG（聚乙二醇）结构单元、烷氧基化的（甲基）丙烯酸酯、具有酸或醇官能团的（甲基）丙烯酸酯、用（甲基）丙烯酸酯官能化的多醇。

[0035] 根据本发明一个优选的实施方案，所述可光固化的树脂组合物在 20℃下显示出 500mPa·s 以下的粘度，优选 200mPa·s 以下，更优选 100mPa·s 以下，和 / 或其在 60℃下显示出长于 29 天的贮存期，优选长于 43 天。

[0036] 在特定温度下的贮存期被定义为在制备树脂的时间中测量的树脂粘度增加该树脂粘度起始值的 20％的时间。

[0037] 使用 Haake RS 80 旋转粘度仪测量粘度。这种类型的粘度计通过在感兴趣流体中测量对于轴旋转的阻力直接测量绝对粘度。所述粘度仪由连接到旋转轴的锥体组成。该锥体被浸没在流体中并且以恒定的速度旋转。测量旋转该锥体所需的扭矩并且随后相关于流体粘度。

[0038] 用于我们粘度测量所使用的锥体类型是具有 2° 角的 35mm 直径，速率设定为 $100s^{-1}$ 并且测量温度设置在 20℃。

[0039] 测量粘度所使用方法的细节可以在以下链接和所使用粘度仪的操作手册中找到：http://en.wikipedia.Org/wiki/Viscometer#Rotational viscometers。

[0040] 为了制备可分配和可印刷的油墨（例如通过凹版和柔性版印刷），在 20℃下的粘度必须低于 500mPa·s，并且优选低于 250mPa·s 以制备可分配的油墨。所述可固化树脂优选在 20℃下具有小于 60mPa·s 的粘度以制备可喷墨的油墨。

[0041] 通过要求低粘度制剂的印刷技术，例如喷墨、阀喷射、凹版和柔性版印刷或分配技术，根本不能加工非可流动性体系。

[0042] 相比于液体树脂的沉积，吸气贴纸对于高速下的大规模生产是不实际的。

[0043] 使用高粘的糊状物制备具有高精确性的薄涂层是非常困难的。由于低的流平速度，使用粘的糊状物实现了限制的涂覆速度。

[0044] 由于本发明，因此在水清除材料的应用领域中实现了显著的优点，其根据现有技

术是无法想象的。

[0045] 根据本发明另一个优选的实施方案，所述可光固化的树脂组合物还包含：(F) 聚丁二烯丙烯酸酯或甲基丙烯酸酯、硅氧烷丙烯酸酯或甲基丙烯酸酯，或两摩尔乙氧基化双酚 A 二（甲基）丙烯酸酯，或它们的任何混合物，其中这种组分 (F) 优选具有两个（甲基）丙烯酸酯官能团。

[0046] 主要组分优选选自聚丁二烯（甲基）丙烯酸酯，硅氧烷（甲基）丙烯酸酯和其它（甲基）丙烯酸酯结构单元，优选不含 PEG、酸或醇官能团。

[0047] 根据本发明一个优选的实施方案

[0048] 组分 (D) 显示出大于 2 的 ClogP，

[0049] 组分 (E) 显示出大于 1 的 ClogP，

[0050] 和 / 或组分 (F) 显示出大于 4，优选大于 6 或 7 的 ClogP。

[0051] 根据本发明一个优选的实施方案，其中组分 C 是式 $HO-(CH_2)_n-OH$ 的二醇的二（甲基）丙烯酸 1，n- 二醇酯，其中 n 大于 3，优选大于 6，更优选大于 10。

[0052] 根据本发明一个有利的实施方案，所述可光固化的树脂组合物在固化后是透明的，优选作为 20 微米厚的膜的固化的树脂在 600nm 下具有＞ 90％的透光率，和 / 或在 90％相对湿度中在 40℃下存储 80 小时后显示出小于其初始重量 2％的吸水量。

[0053] 根据本发明一个优选的实施方案，所述树脂组合物至少包含：

[0054] (A) 1-30wt％的 CaO、BaO 和 / 或 MgO 颗粒（组分 A）；

[0055] (B) 0.1-10wt％的光引发剂 B；

[0056] (C) 30-80wt％的组分 C，其优选具有两个（甲基）丙烯酸酯官能团；

[0057] (D) 5-40wt％的单官能（甲基）丙烯酸酯稀释剂组分 D；

[0058] (E) 5-30wt％的具有等于或大于 3 的官能度的（甲基）丙烯酸酯组分 E；和任选地

[0059] (F) 0.1-30wt％的组分 F；

[0060] 基于组合物的总重量。

[0061] 根据本发明最优选的实施方案，所述树脂组合物至少包含：

[0062] (A) 4-20wt％的 CaO、BaO 和 / 或 MgO 颗粒（组分 A）；

[0063] (B) 0.1-5wt％的光引发剂 B；

[0064] (C) 40-70wt％的组分 C，其优选显示出两个（甲基）丙烯酸酯官能团；

[0065] (D) 10-30wt％的单官能（甲基）丙烯酸酯稀释剂组分 D；

[0066] (E) 7-20wt％的具有等于或大于 3 的官能度的（甲基）丙烯酸酯组分 E；和任选地

[0067] (F) 0.3-25wt％的组分 F；

[0068] 基于组合物的总重量。

[0069] 根据本发明的第二个方面，提供了用于制备根据本发明的可光固化的树脂的方法，包括以下步骤：

[0070] h) 将组分 C、D、E 和任选的 F 混合并且一起搅拌，以制备混合物 h，其任选地被干燥；

[0071] i) 将任选地脱水的氧化钙、氧化钡和 / 或氧化镁（组分 A）引入到所制备的混合物 h 中，以获得混合物 i；

[0072] j) 在干燥氮气下，优选通过球磨，研磨和 / 或碾磨制备的混合物 i，以降低氧化钙、

氧化钡和 / 或氧化镁颗粒的平均直径，以制备混合物 j ；

[0073] k) 将光引发剂 B 加入到制备的混合物 j 中，以获得混合物 k，其优选在干燥氮气气氛下搅拌。

[0074] 这种方法显示了优异的令人惊异的优点是，本发明的可光固化的树脂可以使用一步研磨方法和不使用任何溶剂制备，使得该树脂的制备简单、快速、廉价并且实用。

[0075] 溶剂的使用和 / 或用于蒸发溶剂或用于固化的加热步骤的使用与其中施加干燥剂的系统可能不相容。例如，当在热敏感性基板（例如 OLED）上沉积干燥剂层时，加热步骤可能是重要的问题。溶剂残余物可能被捕获在基质中并且污染体系。

[0076] 在分配树脂之前在溶剂中分散 CaO 增加了制备方法的成本。此外，其不是环境友好的。

[0077] 刚好在使用之前引入 CaO 纳米颗粒要求用户装备有分散设备，其是昂贵的并且需要专业知识。简单的混合步骤对于将 CaO 颗粒分散至纳米尺度将不是充分的。

[0078] 大量的制备步骤增加了湿度污染 CaO 颗粒的风险，并且结果增加了丧失水清除性能的风险。

[0079] 令人意外地，根据本发明制备可光固化的组合物的方法解决了所有这些问题。

[0080] 根据本发明另一个优选的实施方案，在研磨步骤 j) 期间，CaO、BaO 和 / 或 MgO 颗粒的平均粒径被降低至 10-1000nm 的范围，优选 15-500nm，更优选 20-350nm 或甚至 50-250nm，和制备的可光固化的树脂 k 显示出小于 1000ppm 重量的水含量。

[0081] 优选地，在惰性气氛下（使用水含量不超过 10ppm（以摩尔计）的惰性气体）干燥、处理并且使用树脂研磨 CaO 粉末，以避免 CaO 水解和通过氢键聚集的可能性。在液体可固化基质中，氧化钙细小颗粒优选显示出小于 5wt％的氢氧化钙含量和小于 1wt％的碳酸钙含量。

[0082] 所有的组分必须相容以避免研磨工艺期间的相分离。

[0083] 根据本发明的第三个方面，提供了用于制造耐水和氧气渗透和扩散的多层阻隔叠层 (30) 的方法，包括以下步骤：

[0084] m) 沉积第一无机层 (32)，优选为氮化硅或氧化硅，其优选显示出 50-300nm 的厚度；

[0085] n) 优选通过喷墨打印，将本发明或根据本发明的方法制备的可光固化的树脂的第一有机层 (34) 沉积在所述第一无机层 (32) 上；

[0086] o) 将所述第一有机层 (34) 曝光于紫外 (UV) 辐射，以固化所述第一有机层 (34) 并且制备显示出水清除性能的透明层；

[0087] p) 优选通过喷墨印刷，将所述不包含金属氧化物颗粒的可光固化的树脂的第二有机层 (36) 施加到所述第一固化有机层 (34) 上；

[0088] q) 将所述第二有机层 (36) 曝光于 UV 辐射以固化所述第二有机层 (36) 并且制备显示出平面化性能的透明层；

[0089] r) 将第二无机层 (38) 沉积在所述第二固化有机层 (36) 上，其中第二无机层 (38) 优选氮化硅或氧化硅，其优选显示出 50-300nm 的厚度。

[0090] 第一有机层 (34) 有利地显示出 10-100 微米的厚度，优选 20-80 微米。

[0091] 第二有机层 (36) 有利地显示出 10-100 微米的厚度，优选 20-80 微米。

[0092] 相据本发明的第四个方面，提供了用于制造光电器件（特别是有机发光二极管(OLED)）的方法，包括以下步骤：

[0093] -提供光电元件和/或层(10)，

[0094] -提供包含根据本发明的方法制备的多层阻隔叠层(30)的封装。

[0095] 根据本发明的第五个方面，提供了多层阻隔叠层(30)或光电器件，特别是OLED，其通过本发明的方法或本发明的树脂获得。

[0096] 这种有机光电器件或OLED有利地包括：

[0097] -光电元件

[0098] -用于保护光电元件免于环境物质的保护性外壳，所述保护性外壳包括多层保护性层或多层阻隔叠层，其中第一无机层、包含金属氧化物的第一有机层、不含吸气材料的第二有机层和第二无机层以所述顺序堆叠。所述第一有机层是使用本发明的树脂或根据本发明的方法制备。

[0099] 金属氧化物优选为CaO、BaO或MgO颗粒并且作为纳米尺寸的颗粒有利地分布在第一有机层中，其密度在4-20wt%的范围。第二有机层有利地具有10-100微米的厚度。

[0100] 纳米尺寸的颗粒（以下称为纳米颗粒）应被理解为是具有小于100nm尺寸的颗粒。作为具有4-20wt%密度的纳米颗粒分布的吸气材料提供了OLED的第一有机层中湿气的有效结合。在典型的实施方案中，密度是5-10wt%，例如5wt%。

[0101] 尽管原始吸气颗粒是小尺寸，但这些颗粒趋于形成具有几微米尺寸的簇。已经令人惊讶地发现，吸气颗粒的研磨导致具有小平均簇尺寸的分布，使得包含颗粒的层显示出良好的透明性，并且可以例如用于OLED的制造中。透明性是用于有机光电器件或OLED中膜所需的物理性能。尽管这些小平均簇尺寸，但似乎大簇的存在不可能完全被排除。因此，当在第一有机层上施加第二有机层时，其具有0.1-3μm范围的常规厚度，这些簇可能伸出通过第二有机层且在簇表面的颗粒趋于引起无机层中的缺陷。因此，第二有机层有利地具有实质上大于常规施加的厚度的厚度。第一和第二无机层封装了第一和第二有机层，使得防止湿气的侧向进入。

[0102] 在一个优选的实施方案中，第二有机层的厚度为至少20μm。这显示了以下优点：即使制备工艺中的误差引起了第二有机层厚度的变化，那么剩余的厚度仍然大于所要求的最小值10μm。对于柔性产品，优选第二有机层的厚度小于100μm。在典型的实施方案中，第二有机层显示了约70μm的厚度。

[0103] 在一个实施方案中，第一有机层具有10-100μm范围的厚度。实质上更小的厚度，例如小于5μm将显示出不足的吸气能力，而实显著更大的厚度，例如大于200μm，对于柔性产品将是不希望的。

[0104] 在一个实施方案中，吸气颗粒是碱土金属氧化物。碱土金属氧化物，特别是CaO，提供了非常有效的水结合。

[0105] 在一个实施方案中，光电元件是OLED，其具有在阴极和阳极之间设置的光电层，并且阴极面对多层保护性层。OLED的阴极侧是对于湿气最脆弱的部分，针对此多层保护性层提供了有效并且仍然透明的保护。在OLED的相反侧，可以设置另一个保护层，例如金属箔。所述金属箔也可以充当阴极或阳极的导体。在另一个实施方案中，光电元件在两侧上具有如上所述的多层保护性层或叠层。

[0106] 如所解释的，第一有机层是通过固化本发明的可光固化的树脂制备。

[0107] 使用这种可光固化的树脂以制备所描述的有机光电器件或 OLED 的优点是，所述树脂是稳定的并且可流动以及可以容易地以具有受控厚度的薄膜形式施加。通过光固化的固化时间几乎是瞬间的，并且可以制备具有优异的水清除性能和透明性的层。

[0108] 树脂的组分

[0109] 根据本发明的可光固化的树脂包含组分 (A)、(B)、(C)、(D)、(E) 和任选地 (F)：

[0110] (A) 金属氧化物颗粒

[0111] 具有吸气功能的金属氧化物颗粒有利地为 CaO、BaO 或 MgO 颗粒，优选是 CaO 纳米颗粒。

[0112] 也可以使用其它吸气材料。特别适合用于此目的其它碱土金属氧化物为氧化钡 (BaO)、氧化镁 (MgO) 和氧化锶 (SrO)。作为一个实例，可以获得来自 Strem 的 MgO 纳米粉末 (产品目录 Nr. 12-1400)，其具有以下规格：比表面积 (BET)：≥ 230m^2/g；真实密度：3.2g/cc；晶粒尺寸：≤ 8nm；平均聚集体尺寸：3.3 μm；平均孔直径：50Å；烧失重：≤ 8%；总孔体积：≥ 0.2cc/g；湿气含量：≤ 1%；堆密度：0.6g/cc；Mg 含量 (基于金属)：≥ 95%。

[0113] (B) 光引发剂

[0114] 此外，所述可光固化的组合物包含至少一种光引发剂，优选自由基光引发剂。

[0115] 自由基光引发剂可以选自通常用于引发自由基光聚合的那些。自由基光引发剂的实例包括Irgacure®369，安息香类，例如，安息香，安息香醚如安息香甲基醚，安息香乙基醚，安息香异丙基醚，安息香苯基醚，和安息香乙酸酯；苯乙酮类，例如苯乙酮，2,2- 二甲氧基苯乙酮，2,2- 二甲氧基 -2- 苯基苯乙酮和 1,1- 二氯苯乙酮；苄基缩酮，例如苄基二甲基缩酮和苄基二乙基缩酮；蒽醌类，例如 2- 甲基蒽醌，2- 乙基蒽醌，2- 叔丁基蒽醌，1- 氯蒽醌和 2- 戊基蒽醌；三苯基膦；苯甲酰膦氧化物，例如 2,4,6- 三甲基苯甲酰 - 二苯基膦氧化物 (Lucirin TPO)；乙基 -2,4,6- 三甲基苯甲酰苯基次磷酸酯；二酰基氧化膦；二苯甲酮类，例如，二苯甲酮和 4,4′ - 双 (N,N′ - 二甲基氨基) 二苯甲酮；噻吨酮和呫吨酮类；吖啶衍生物；吩嗪衍生物；喹喔啉衍生物；1- 苯基 -1,2- 丙烷二酮 2-O- 苯甲酰肟；4-(2- 羟基乙氧基) 苯基 -(2- 丙基) 酮(Irgacure® 2959)；2- 甲基 -1-[4-(甲基硫化) 苯基]-2-(4- 吗啉基)-1- 丙酮；1- 氨基苯基酮或 1- 羟基苯基酮，例如 1- 羟基环己基苯基酮，2- 羟基异丙基苯基酮，苯基 1- 羟基异丙基酮和 4- 异丙基苯基 1- 羟基异丙基酮和它们的组合。

[0116] 聚合引发剂的含量相对于组合物的总重量优选为 0.01-10wt%，更优选 0.5-7wt%。

[0117] (C) 具有＞ 2 的 clogP 的 (甲基) 丙烯酸酯

[0118] 此外，所述可光固化的组合物包含一种具有大于 2、优选大于 4、更优选大于 5 的 ClogP 的丙烯酸酯或甲基丙烯酸酯组分，或它们的任何混合物。

[0119] 这些 (甲基) 丙烯酸酯的实例是 CD262(＝1,12- 十二烷二醇二甲基丙烯酸酯)，由多醇和乙烯基不饱和酸组成的甲基丙烯酸酯包括各自由多醇和乙烯基不饱和羧酸组成的二酯单体，如 1,3- 丙二醇二甲基丙烯酸酯，1,4- 丁二醇二甲基丙烯酸酯，1,5- 戊二醇二丙烯酸酯，1,5- 戊二醇二甲基丙烯酸酯，1,6- 己二醇二丙烯酸酯，1,6- 己二醇二甲基丙烯酸酯，1,7- 庚二醇二丙烯酸酯，1,7- 庚二醇二甲基丙烯酸酯，1,8- 辛二醇二丙烯酸酯，1,8- 辛

二醇二甲基丙烯酸酯，1,9- 壬二醇二丙烯酸酯，1,9- 壬二醇二甲基丙烯酸酯，1,10- 癸二醇二丙烯酸酯，1,10- 癸二醇二甲基丙烯酸酯，1,12- 十二烷二醇二丙烯酸酯，1,12- 十二烷二醇二甲基丙烯酸酯，1,14- 十四烷二醇二丙烯酸酯，1,14- 十四烷二醇二甲基丙烯酸酯等。

[0120] (D) 单官能（甲基）丙烯酸酯稀释剂

[0121] 此外，所述可光固化的组合物包含单官能丙烯酸酯或甲基丙烯酸酯稀释剂组分，其优选具有低粘度，例如在 20℃下小于 40mPa·s，或它们的任何混合物。

[0122] 这种单官能（甲基）丙烯酸酯的具体实例包括 CHMA，CD421A，己基（甲基）丙烯酸酯，2- 乙基己基（甲基）丙烯酸酯，叔辛基（甲基）丙烯酸酯，异戊基（甲基）丙烯酸酯，癸基（甲基）丙烯酸酯，异癸基（甲基）丙烯酸酯，硬脂基（甲基）丙烯酸酯，异硬脂基（甲基）丙烯酸酯，环己基（甲基）丙烯酸酯，4- 正 - 丁基环己基（甲基）丙烯酸酯，冰片基（甲基）丙烯酸酯，异冰片基（甲基）丙烯酸酯，苄基（甲基）丙烯酸酯，2- 乙基己基二乙二醇（甲基）丙烯酸酯，丁氧基乙基（甲基）丙烯酸酯，2- 氯乙基（甲基）丙烯酸酯，4- 溴丁基（甲基）丙烯酸酯，丁氧基甲基（甲基）丙烯酸酯，3- 甲氧基丁基（甲基）丙烯酸酯，烷氧基甲基（甲基）丙烯酸酯，烷氧基乙基（甲基）丙烯酸酯，2-(2- 甲氧基乙氧基）乙基（甲基）丙烯酸酯，2-(2- 丁氧基乙氧基）乙基（甲基）丙烯酸酯，2,2,2- 三氟乙基（甲基）丙烯酸酯，1H,1H,2H,2H- 全氟癸基（甲基）丙烯酸酯，4- 丁基苯基（甲基）丙烯酸酯，苯基（甲基）丙烯酸酯，2,3,4,5- 四甲基苯基（甲基）丙烯酸酯，4- 氯苯基（甲基）丙烯酸酯，苯氧基甲基（甲基）丙烯酸酯，苯氧基乙基（甲基）丙烯酸酯，缩水甘油基（甲基）丙烯酸酯，缩水甘油基氧基丁基（甲基）丙烯酸酯，缩水甘油基氧基乙基（甲基）丙烯酸酯，缩水甘油基氧基丙基（甲基）丙烯酸酯，四氢糠基（甲基）丙烯酸酯，羟基烷基（甲基）丙烯酸酯，2- 羟基乙基（甲基）丙烯酸酯，3- 羟基丙基（甲基）丙烯酸酯，2- 羟基丙基（甲基）丙烯酸酯，2- 羟基丁基（甲基）丙烯酸酯，4- 羟基丁基（甲基）丙烯酸酯，二甲基氨基乙基（甲基）丙烯酸酯，二乙基氨基乙基（甲基）丙烯酸酯，二甲基氨基丙基（甲基）丙烯酸酯，二乙基氨基丙基（甲基）丙烯酸酯，三甲氧基甲硅烷基丙基（甲基）丙烯酸酯，三甲基甲硅烷基丙基（甲基）丙烯酸酯，聚氧化乙烯单甲基醚（甲基）丙烯酸酯，寡氧化乙烯单甲基醚（甲基）丙烯酸酯，聚氧化乙烯（甲基）丙烯酸酯，寡氧化乙烯（甲基）丙烯酸酯，寡氧化乙烯单烷基醚（甲基）丙烯酸酯，聚氧乙烯单烷基醚（甲基）丙烯酸酯，二丙二醇（甲基）丙烯酸酯，聚氧丙烯单烷基醚（甲基）丙烯酸酯，寡氧化丙烯单烷基醚（甲基）丙烯酸酯，2- 甲基丙烯酰氧基乙基琥珀酸，2- 甲基丙烯酰氧基六氢邻苯二甲酸，2- 甲基丙烯酰氧基乙基 -2- 羟基丙基邻苯二甲酸酯，丁氧基二乙二醇（甲基）丙烯酸酯，三氟乙基（甲基）丙烯酸酯，全氟辛基乙基（甲基）丙烯酸酯，2- 羟基 -3- 苯氧基丙基（甲基）丙烯酸酯，EO- 变性苯酚（甲基）丙烯酸酯，EO- 变性甲酚（甲基）丙烯酸酯，EO- 变性壬基苯酚（甲基）丙烯酸酯，PO- 变性壬基苯酚（甲基）丙烯酸酯和 EO- 变性 2- 乙基己基（甲基）丙烯酸酯。

[0123] (E) 具有≥ 3 官能度的（甲基）丙烯酸酯

[0124] 此外，所述可光固化的组合物包含具有等于或大于 3，优选 3 或 4 官能度的丙烯酸酯或甲基丙烯酸酯组分，或它们的任何混合物。

[0125] 三官能（甲基）丙烯酸酯的具体实施例包括 SR351、三羟甲基丙烷三（甲基）丙烯酸酯，三羟甲基乙烷三（甲基）丙烯酸酯，氧化烯 - 变性的三羟甲基丙烷的三（甲基）丙烯酸酯，季戊四醇三（甲基）丙烯酸酯、二季戊四醇三（甲基）丙烯酸酯、三羟甲基丙烷三

((甲基)丙烯酰氧基丙基)醚,烯烃-变性异氰尿酸的三(甲基)丙烯酸酯,二季戊四醇丙酸脂三(甲基)丙烯酸酯,三((甲基)丙烯酰氧基乙基)异氰尿酸酯,羟基三甲基乙酰基醛-变性的二羟甲基丙烷三(甲基)丙烯酸酯,山梨糖醇三(甲基)丙烯酸酯,丙氧基化的三羟甲基丙烷三(甲基)丙烯酸酯,和乙氧基化的甘油三丙烯酸酯。

[0126] 四官能(甲基)丙烯酸酯的具体实例包括季戊四醇四(甲基)丙烯酸酯,山梨糖醇四(甲基)丙烯酸酯,二三羟甲基丙烷四(甲基)丙烯酸酯,二季戊四醇丙酸脂四(甲基)丙烯酸酯和乙氧基化的季戊四醇四(甲基)丙烯酸酯。

[0127] 五官能(甲基)丙烯酸酯的具体实例包括山梨糖醇五(甲基)丙烯酸酯,和二季戊四醇五(甲基)丙烯酸酯。

[0128] 六官能(甲基)丙烯酸酯的具体实例包括二季戊四醇六(甲基)丙烯酸酯,山梨糖醇六(甲基)丙烯酸酯,氧化烯-变性的磷腈的六(甲基)丙烯酸酯,和己内酯变性的二季戊四醇六(甲基)丙烯酸酯。

[0129] (F)另外的(甲基)丙烯酸酯

[0130] 此外,所述可光固化的组合物可以任选地包含聚丁二烯丙烯酸酯或甲基丙烯酸酯、硅氧烷丙烯酸酯或甲基丙烯酸酯,或两摩尔乙氧基化双酚A二(甲基)丙烯酸酯,或它们的任何混合物,其中这种组分(F)优选显示出两个(甲基)丙烯酸酯官能团。

[0131] 这种(甲基)丙烯酸酯的实例为聚二烯(甲基)丙烯酸酯如聚丁二烯(甲基)丙烯酸酯,聚二烯二(甲基)丙烯酸酯如聚丁二烯二(甲基)丙烯酸酯如Sartomer的SR307和CN301,聚异戊二烯二丙烯酸酯等,2摩尔烷氧基化双酚A二(甲基)丙烯酸酯如2摩尔乙氧基化的双酚A二(甲基)丙烯酸酯如SR348L,硅氧烷(甲基)丙烯酸酯和硅氧烷二(甲基)丙烯酸酯如CN9800。

[0132] 优选地,本发明的组合物应当不包含聚氨酯(甲基)丙烯酸酯,聚酯(甲基)丙烯酸酯,聚乙二醇(PEG)(甲基)丙烯酸酯。这类化合物可能破坏膜的水清除性能并且可能与CaO纳米颗粒反应。

[0133] 可以加入分散剂,以增加吸气颗粒分散至有机基质的分散性。所述分散剂可以是低分子量有机分散剂,高分子量有机分散剂,低分子量有机/无机复合分散剂,高分子量有机/无机复合分散剂,有机/无机酸等。分散剂的作用是例如通过避免聚集将吸气颗粒均匀地分散至有机层中,并且从而最小化吸气颗粒的尺寸,其保持在几nm以制造透明湿气吸收层。

[0134] 所述可光固化的组合物可以另外地包括其它组分,例如稳定剂、改性剂、增韧剂、消泡剂、流平剂、增稠剂、阻燃剂、抗氧化剂、颜料、染料、填料,以及它们的组合。

[0135] 附图简要说明

[0136] 本发明的一些方面被更详细地描述在附图中。

[0137] 图1详细显示了根据本发明的一个方面的光电器件的第一实施方案的横截面。

具体实施方式

[0138] 组分

[0139] 表I描述了用于制备根据本发明的可光固化的组合物的组分A、B、C、D、E和F。

[0140] 树脂的制备

[0141] 将各原料（除了光引发剂）混合在一起并且在25℃下以340rpm搅拌1h。将混合物在4A分子筛上干燥24小时（在真空150℃下干燥筛2小时），随后过滤，之后与干燥CaO粉末混合。

[0142] CaO颗粒由Strem Chemicals获得（产品目录#20-1400）并且具有以下产品规格：比表面积(BET)：≥20m^2/g；堆密度：0.5g/cc；晶粒尺寸：≤40nm；真实密度：3.3g/cc；平均孔径：165Å；平均聚集尺寸：4μm；总孔体积：≥0.1cc/g；Ca含量（基于金属）：＞99.8%。使用动态光散射工具(DLS)，Malvern Instruments的Zetasizer Nano测量粒径分布。分布是三峰分布，其在约60nm具有第一最大峰，在约550nm具有第二峰和在约5μm具有第三峰。

[0143] 将CaO在900℃空气中脱水1小时，随后缓慢冷却至200℃，并且快速转移至干燥氮气填充的封闭件，在其中将其最终冷却至室温，之后合并入可固化基质中。从SEM照片可以明显看出，在焙烧过程之后和甚至在焙烧过程之前，CaO颗粒强烈聚集，颗粒聚集至10微米的尺寸。这些SEM图片突出说明了进行研磨/碾磨步骤以降低颗粒尺寸至纳米尺度的必要性。

[0144] 为了确定氧化钙的纯度，通过热重分析(TGA测量和元素分析）确定氢氧化钙含量和碳酸钙含量。燃烧进行定量分析。所使用的测量方法可以在以下链接http://en.wikipedia.org/wiki/Thermoqravimetric analysis 或 Mansfield, E.; Kar, A.; Quinn, T.P.; Hooker, S.A.(2010)." Quartz Crystal Microbalances for Microscale Thermogravimetric Analysis". Analytical Chemistry 82(24)中找到。在高温下(750℃以上）将碳酸钙分解成氧化钙，并且在400℃以上将氢氧化钙分解成氧化钙。在干燥过程之后获得了超过98%的纯度。

[0145] 使用填充有85%（以体积计）的0.3-0.4mm的钇稳定的氧化锆磨珠的钢磨室用于研磨工艺（在具有0.1mm间隙密封的Dynomill KDL设备中）。将研磨设备连接至反应器以允许混合物再循环，并且将整个系统置于干燥氮气流下以保持其免于湿气。使用低温恒温器用于冷却反应器并且在研磨工艺期间保持研磨室温度在21℃（±3℃）下。一旦达到了理想的粒径则停止再循环和研磨。

[0146] 在实施例18的情况下（表2中的F18），在2小时期间在干燥氮气下将CaO颗粒摇动入可固化基质中，使用Retch PM100球磨设备，其使用250ml氧化锆碗和10mm直径氧化锆研磨球。

[0147] 使用可固化基质（不含光引发剂）将通过球磨研磨的树脂稀释100倍以使用Malvern Instruments的Zeta Sizer Nano ZS测定粒径分布。仅在稳定树脂上取粒径分布测量，因为聚集现象干扰不同尺寸的颗粒的“布朗运动”获得的信号。

[0148] 为了完成配制剂制备，在研磨工艺之后将光引发剂加入到可固化基质中，并且将组合物在室温下以340rpm搅拌1h-所有的步骤在氮气气氛下进行。在研磨工艺之后加入光引发剂，因为其在通过动态光散射的粒径测量期间可能引发问题：可能在激光曝光下发生树脂固化。

实施例

[0149] 表IIa和b显示了可光固化的树脂的组合物（实施例F1-F20）。表明了组分的

ClogP。

[0150] 表明了在 20℃下树脂的粘度（在制备之后立即测定）。

[0151] 表明了 25℃和 60℃下树脂的稳定性，和在 60℃下 4 天之后的外观。如果，其在 60℃下具有大于 29 天，优选大于 43 天的贮存期，则认为树脂是稳定的，意味着与其初始粘度相比，树脂的粘度增加小于 20%。同时，未检测到类似固体凝胶的形成或颗粒的沉积。

[0152] 满足所述稳定性要求并且在固化后显示出良好透明性的树脂可以有利地用于制造光电器件（特别是 OLED）的水清除层。

[0153] 表 IIa 和 b 还表明了所制备的组合物的测量的平均颗粒直径 (z) 和多分散度 (PDI)。

[0154] 由表 II 可以明显看出仅本发明的组合物 F1、F3、F15、F16、F17、F19 和 F20 满足了必要的稳定性要求，并且适于制造光电器件（特别是 OLED）的水清除层。所述组合物在 60℃下 4 天后显示了白色液体外观，并且在固化后变得透明。它们在 25℃和 60℃下是稳定的，并且是可流动的，初始粘度小于 100mPa s。

[0155] 在所述组合物中，组分 A 是 CaO 纳米颗粒，组分 B 是 Irgacure 369，组分 C 是 CD262，组分 D 是 CHMA 或 CD421A，组分 E 是 SR351，组分 F 是 SR348L、CN9800、CN301 或 SR307。

[0156] 表 II 显示了本发明的组合物不包含聚氨酯（甲基）丙烯酸酯、聚酯（甲基）丙烯酸酯、聚乙二醇 (PEG)（甲基）丙烯酸酯。这些化合物可能破坏膜的水清除性能并且可以与 CaO 纳米颗粒反应。实际上，这些化合物制造的负面作用通过表 II 中的非本发明的实施例得以例证。

[0157] 上述本发明的可光固化的组合物非常适合于制备用于保护湿气和氧敏感性器件（例如有机 LED、OPV、CIGS 太阳能电池、液晶显示器、电泳显示器、电致变色显示器、薄膜电池等）的多层薄膜阻隔叠层的水清除层。

[0158] 所述本发明的可光固化的组合物显示了以下优点：制备方法在一步中进行，在将它们添加到树脂中之前无需预处理 CaO 颗粒。

[0159] 可以使用本发明的可光固化的组合物制备可固化和可印刷油墨，其在印刷电子应用例如制造有机发光二极管、锂离子电池等中是相当令人感兴趣的。无需干燥步骤或加热步骤，因为不存在溶剂蒸发，使得在应用本发明的树脂期间不损害敏感性电子器件。

[0160] 所述本发明的可光固化的组合物可以作为液体单组分系统供应，其保持稳定数日或数月。

[0161] 所述本发明的可光固化的组合物提供了具有提高脱水能力的可流动和可固化的油墨，因为它们几乎不包含任何氢氧化钙和碳酸钙，其在脱水中是惰性的。

[0162] 因为 CaO 颗粒被研磨至纳米尺度，可以制备具有非常高程度光透明性的可固化油墨。

[0163] 实施例 20 的树脂的测试结果

[0164] 实施例 20 的未固化的液体树脂显示了表 III 中表明的物理性能：

[0165] 表 III

[0166]

性能	单位	值
外观		白色低粘度液体
表面张力	mN/m	在 22-25℃下 28.7-31.6（2 次测试，2 批次）
折射率	24.2℃	1.475（2 次测试，2 个批次）
密度（ISO1183-3）	g/cm^3	0.998-0.999（2 批次-每次 2 次测试）
粘度@20℃	mPa s	40-50
粘度@60℃	mPa s	9-13
典型颗粒直径-z 均	nm	150-350
粒径分布-PDI		≤0.3
在 1mbar 下脱气 5 小时	重量%	≤0.2（2 次测试，2 个批次）

[0167] 未固化的液体树脂显示出大于 4 个月的贮存期（粘度增加≤ 20%）。

[0168] 在低湿度（＜ 30ppm）的条件下通过喷墨印刷将实施例 20 的树脂施加在氮化硅基板上，层厚度为 10-40 μm，并且随后使用 $1J/cm^2$的 UV 剂量在无氧气（＜ 20ppm）和低湿度（＜ 30ppm）的条件下在 UV（紫外）波长范围 250-400nm 中固化（通过 LED 固化）。

[0169] 表 IV 显示了所获得的固化膜的测量的物理和机械性能（UV 曝光，$1J/cm^2$）。

[0170] 表 IV

[0171]

测量	测试方法	值
在 20 ℃下薄膜（50-100μm）上的 E 模量	通过 DMTA[1] 的非-ISO	1.3-1.5GPa（2 次测试，两个批次）
在 60 ℃下薄膜（50-100μm）上的 E 模量	通过 DMTA[1] 的非-ISO	590-690MPa（2 次测试，两个批次）
在 100 ℃下薄膜（50-100μm）上的 E 模量	通过 DMTA[1] 的非-ISO	230-282MPa（2 次测试，两个批次）
在 120 ℃下薄膜（50-100μm）上的 E 模量	通过 DMTA[1] 的非-ISO	158-186MPa（2 次测试，两个批次）
折光率	23.9℃-100μm 膜	1.51（2 次测试，2 个批

[0172]

		次）
UV- 可见光透射率（400, 600, 800nm）	UV-可见光光谱-20μm	81%, 97%, 99%（2 次测试，2 个批次）
硬度	铅笔硬度，24℃/40%RH-在玻璃上 20μm	1H-2H（2 次测试，2 个批次）
平均表面粗糙度	轮廓测定-1.5mm 扫描长度-2μm 曲率半径	Ra ＜ 10nm（1 次测试，1 个批次）
表面能	座滴法	总共：42-45mN/m（2 次测试，2 个批次）
		极性：0.00-0.02mN/m
		分散：42-45mN/m
饱和下的吸水（WU）	40℃/90%RH	2% ≥ WU ≥ 1.8%

[0173] [1]动态热分析测试（DMTA）是在 visco-analyser Metravib VA-3000 上进行。在热扫描期间记录拉伸模量，所述热扫描由 -30℃至 150℃，以 3℃ /min(x2)，在静态负载，1Hz 频率，15μm 位移下进行。记录的值对应于第一扫描。

[0174] 饱和下吸水（WU）已经作为在 40℃和湿度 90% RH 下 80 小时后以%计的水分吸收的重量增加测量。在这种老化时间之后达到了重量增加的饱和。在所述老化时间之后样品的重量增加包含在样品初始重量的 1.8%和 2%之间。

[0175] 表 IV 证明了所获得的机械性能（特别是弹性模量）、所获得的光学性能（特别是光透射率）和所获得的低吸水使得制备的膜非常适于作为光电器件的水清除层。

[0176] 光电器件的制造

[0177] 以下材料、方法和实施例仅是解释说明性的并且不旨在限制。

[0178] 应当理解，当一个要素或层被称为“在另一个元件或层之上”、“连接至另一个元件或层”或“结合至另一个元件或层”，其可以直接在另一个元件或层上，连接到另一个元件或层上或结合到另一个元件或层上，或可以存在中间元件或层。与之相反，当一个元件被称为“直接在另一个元件或层上”、“直接连接至另一个元件或层上”或“直接结合至另一个元件或层上”，则不存在中间元件或层。

[0179] 图 1 示例性地显示了本发明的光电器件的横截面，所述器件包括本发明的多层保护性阻隔叠层。

[0180] 在图 1 中所示的有机光电器件包括光电元件 10，其被保护性外壳封闭以保护光电元件避免环境物质，特别是水蒸气。所述保护性外壳包含多层保护性层或阻隔叠层 30，其中第一无机层 32，包含金属氧化物的第一有机层 34，不含吸气材料的第二有机层 36 和第二无基层 38 以所述顺序堆叠。在所示的实施方案中，多层保护性层 30 具有另外的有机层 40。

[0181] 有机层的材料优选显示出低比水蒸气透过率和高疏水性。

[0182] 第一有机层 34 是通过固化本发明的可光固化的树脂或根据本发明的方法制备。

特别地，实验使用了组合物 F20。

[0183] 金属氧化物作为纳米尺寸的颗粒分布在第一有机层 34 中，密度为 4-20wt％的范围。第二有机层 36 具有 10-100 微米范围的厚度。

[0184] 在所示的实施方案中，金属氧化物是碱土金属氧化物。特别地，所选择的碱土金属氧化物是氧化钙。

[0185] 如所解释的，实验性地用于第一有机层 34 的有机材料是固化的本发明的组合物，特别是树脂组合物 F20。所述第二有机层 36 和另外的有机层 40 可以通过固化本发明的可光固化的树脂获得，然而其不包含任何金属氧化物、CaO、BaO 或 MgO 颗粒。因此该树脂将显示出与本发明树脂相同的组分，但不含任何吸气颗粒。第二有机层 36（平面化层）的功能不是保护避免水或氧，而是产生平的光滑表面，剥夺任何凹凸或金属氧化物颗粒，在其上可以产生绝对不含任何不连续性的氮化硅或氧化硅的连续抗性薄层。特别地，对应于 F20 但不添加任何 CaO 颗粒的树脂组合物已经实验性地用于制备第二有机层 36。

[0186] 所述有机层可以通过所有种类的涂覆技术（例如旋涂、槽模涂布、吻涂、热熔涂布、喷涂等）和所有种类的印刷技术（例如喷墨印刷、凹版印刷、柔性版印刷、丝网印刷、旋转丝网印刷等）施加。

[0187] 所述第二有机层 36 例如也可以通过喷墨印刷沉积。对于该第二有机层 36，使用与第一有机层所使用的有机树脂相同的有机树脂，然而剥夺任何金属氧化物颗粒。或者，可以使用不同的可光固化的树脂，其不含金属氧化物颗粒。

[0188] 固化或干燥可以示例性地通过使用 UV- 光、可见光、红外光或热、电子束、γ - 射线或前述的任意组合来辐射湿物质发生，所述湿物质是纯的或合适的配制有光 - 或热 - 敏感性自由基引发剂。

[0189] 第一和第二有机层均是通过使用 Dymax Flood Lamp 的辐射实验性的固化 90s，功率密度为 33mW/cm^2。

[0190] 无机层 32、38 可以通过任何陶瓷形成，所述陶瓷包括但不限于金属氧化物、金属氮化物和金属碳化物。因此合适的材料例如是氮化硅、氧化硅（SiO_2）、氧化铝（Al_2O_3）、氧化钛（TiO_2）、氧化铟（In_2O_3）、氧化锡（SnO_2）、氧化铟锡（ITO，In_2O_3+SnO_2）、SiC、氮氧化硅（SiON）和它们的组合。

[0191] 无机层 32 和 38 具有最多 10^{-4}g.m^{-2}. 天 $^{-1}$的水蒸气透过率。无机层实际基本上比有机层更薄。无机层应当具有 10-1000nm 范围的厚度，优选 100-300nm。厚度小于 10nm 的无机层实际上显示出不足的阻隔性能。至少 100nm 厚度的无机层的沉积是优选的，因为允许制造过程中相对大的偏差而不对产品的质量产生影响。对于柔性产品，无机层的厚度优选不超过 300nm。大于 1000nm 的厚度不进一步改善无机层的阻隔性能，同时沉积过程的持续时间在经济上是没有吸引力的。

[0192] 在实验上制造的光电器件中，第一和第二无机层 32、38 是具有 150nm 厚度的氮化硅层。第一有机层 34 包含包埋在本发明树脂基质（F20）中的 5wt％的 CaO 颗粒，并且具有约 80 μm 的厚度。

[0193] 第二有机层 36 是根据本发明的树脂（F20）层，其不含金属氧化物颗粒并且具有约 70 μm 的厚度。另外的有机层 40（形成多层保护性层 30 的顶层）也是根据本发明的树脂（F20）层，其不含金属氧化物颗粒并且具有约 50 μm 的厚度。

[0194] 如在图 1 中所示，实际上无机层 32、38 显示出缺陷 32a、38A，例如针孔。有机层 34 和 36 起到了分离层 32 和 38 的针孔的作用以降低环境物质向光电元件 10 的流动。包含纳米尺寸的金属氧化物颗粒的第一有机层 34 捕获流动通过第二无机层 38 的大部分的这些物质。具有至少 10μm 厚度的第二有机层 36 防止这些金属氧化物颗粒的簇破坏第二无机层 38。

[0195] 在所示的实施方案中，第二有机层 36 横向延伸超过第一有机层 34。

[0196] 在所示的实施方案中，多层保护性层 30 显示出另外有机材料的顶层 40。

[0197] 无机层 32、38 延伸超过有机层 34、36 并且形成有机层 34、36 的封装，也使得防止环境物质向有机层 34、36 的侧向进入。

[0198] 第一有机层 34 完全覆盖由光电元件 10 定义的区域。此外，第二有机层 36 横向延伸超过第一有机层 34 的区域。特别地，第二有机层 36 横向延伸在其整个圆周上超过第一有机层 34 的区域。

[0199] 无机层 32、38 的横向尺寸延伸超过光电元件 10 和有机层 34、36。特别地，无机层 32、38 封装有机层 34、36。多层保护层 30（阻隔叠层）形成了光电元件 10 的保护性封装部分。该封装可以包含另外的多层保护性层或另一类型具有足够阻隔性能的层，例如玻璃板，金属箔等。

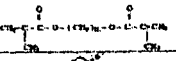
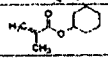
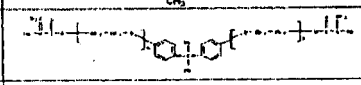
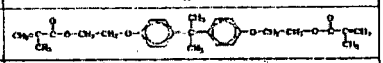
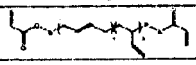
[0200] 在描述的实施方案中，光电元件 10 是 OLED。所述 OLED 具有在阴极和阳极之间设置的发光层。在所述器件具有金属基板的情况下，后者可以用作电极。为了改善的功能性，OLED 通常具有另外的功能层，例如空穴注入层、空穴传输层、电子注入层、电子传输层等。

[0201] 虽然本发明具体参考 OLED 进行解释，但本发明同样可用于具有另一种光电元件的光电器件，例如电致变色器件或者光伏器件。

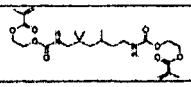
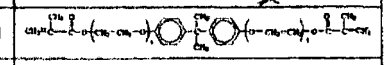
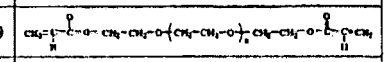
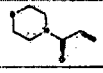
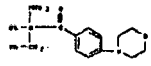
[0202] 如本文所使用的，术语“包含”、“包含”、“包括”、“包括”、“具有”、“具有”或其任何其它变体旨在覆盖非排他的包含。

[0203] 表 1

[0204]

商品名	供应商	化学名	CAS号	结构
CD262	Sartomer	1,12-十二烷基二醇二甲基丙烯酸酯	专有	
SR351	Sartomer	三羟甲基丙烷三丙烯酸酯	15625-89-5	
CHMA	BASF	环己烷甲基丙烯酸酯	101-43-9	
SR348C	Sartomer	三摩尔乙氧基化双酚A二甲基丙烯酸酯	不可获得	
SR348L	Sartomer	两摩尔乙氧基化双酚A二甲基丙烯酸酯	不可获得	
SR307	Sartomer	聚(丁二烯)二丙烯酸酯	未分配	
CN301	Sartomer	聚(丁二烯)二甲基丙烯酸酯	未分配	
CN981	Sartomer	脂肪族聚酯/聚醚基的聚氨酯二丙烯酸酯低聚物	专有	专有
Art resin 106S30B	Huntsman	丙烯酸酯和聚乙二醇丙烯酸酯的混合物	专有	专有
Genomer 4205	Rahn	脂肪族聚氨酯甲基丙烯酸酯	不可获得	专有

[0205]

FIT 852	Esstech	聚氨酯二甲基丙烯酸酯	72869-86-4 + 868-77-9	
SR480	Sartomer	10mol乙氧基化双酚A二甲基丙烯酸酯	41637-38-1	
CN972	Sartomer	芳族聚醚基的聚氨酯三丙烯酸酯低聚物	专有	专有
CN9800	Sartomer	二官能脂肪族硅氧烷丙烯酸酯低聚物	专有	专有
SR610	Sartomer	聚乙二醇(600)二丙烯酸酯	26570-48-9	
Ebecryl 837	Cytec	多官能聚酯丙烯酸酯	专有	专有
ACMO	Rahn	丙烯酰吗啉	5117-12-4	
NVC	BASF	N-乙烯基己内酰胺	2235-00-9	
Ebecryl 210	Cytec	芳族二官能聚氨酯丙烯酸酯	专有	专有
Irgacure 369	BASF	2-苄基-2-二甲基氨基-4-吗啉代丁酰苯类	119313-12-1	

[0206]

原料	ClogP	F1 (wt%)	F2 (wt%)	F3 (wt%)	F4 (wt%)	F5 (wt%)
干燥剂						
CaO		5	5	5	5	5
(甲基)丙烯酸酯						
CD262	6.38	48.45	48.45	48.45	48.45	48.45
SR351	1.58	9.12	9.12	9.12	9.12	9.12
CHMA	2.71	20	20	20	20	20
SR348L	>4	16.44				
SR348C	>4		16.44			
CN9800	>2			16.44		
CN981	CD				16.44	
Art 树脂 106S30B	CD					16.44
Genomer 4205	CD					

[0207]

FIT 852	>3					
SR480	4.58					
SR610	<1					
Ebecryl 210	CD					
光引发剂						
Irgacure 369		0.95	0.95	0.95	0.95	0.95
总共		100	100	100	100	100
方法		球磨	球磨	球磨	球磨	球磨
在20℃下粘度(mPa.s)		26-27	23-24	19-20	34	58
25℃下的混溶性		OK	OK	OK	OK	OK
25℃下的稳定性		>43天-<20%的粘度增加	>43天-<20%的粘度增加	>43天-<20%的粘度增加	1-2天-类似固体凝胶形成	1-2天-类似固体凝胶形成
60℃下的稳定性		>43天-<20%的粘度增加	4天-PS	>43天-<20%的粘度增加	1天-类似固体凝胶形成	1天-类似固体凝胶形成
60℃下4天后的外观		白色液体	PS+底层=包含CaO的类似固体凝胶	白色液体	类似固体凝胶形成	类似固体凝胶形成
Z均(r.nm)		290	208	435	NM	NM
PDI		0.13	0.11	0.16	NM	NM

[0208] NM:不可测量

[0209] PS:相分离

[0210] CD:不能检测-分子结构供应商保密

[0211] 表II a

[0212]

原料	ClogP	F6 (wt%)	F7 (wt%)	F8 (wt%)	F9 (wt%)	F10 (wt%)
干燥剂						
CaO		5	5	5	5	5
(甲基)丙烯酸酯						
CD262	6.38	48.45	48.45	48.45	48.45	48.45
SR351	1.58	9.12	9.12	9.12	9.12	9.12
CHMA	2.71	20	20	20	20	20
SR348L	>4					
SR348C	>4					
CN9800	>2					
CN981	CD					
Art 树脂 106S30B	CD					
Genomer 4205	CD	16.44				
FIT 852	>3		16.44			
SR480	4.58			16.44		
SR610	<1				16.44	
Ebecryl 210	CD					16.44
光引发剂						
Irgacure 369		0.95	0.95	0.95	0.95	0.95
总共		100	100	100	100	100

[0213]

方法		球磨	球磨	球磨	球磨	球磨
在20℃下粘度(mPa.s)		38-39	49-50	32-33	40-41	65-66
25℃下的混溶性		OK	OK	OK	OK	OK
25℃下的稳定性		1-2天-类似固体凝胶形成	1-2天-类似固体凝胶形成	1-2天-类似固体凝胶形成	1-2天-类似固体凝胶形成	1-2天-类似固体凝胶形成
60℃下的稳定性		1天-类似固体凝胶形成	1天-类似固体凝胶形成	1天-类似固体凝胶形成	1天-类似固体凝胶形成	1天-类似固体凝胶形成
60℃下4天后的外观		类似固体凝胶形成	类似固体凝胶形成	类似固体凝胶形成	类似固体凝胶形成	类似固体凝胶形成
Z均(r.nm)		NM	NM	NM	NM	NM
PDI		NM	NM	NM	NM	NM

[0214] NM:不可测量

[0215] PS:相分离

[0216] CD:不能检测-分子结构供应商保密

[0217] 表II b

[0218]

原料	ClogP	F11	F12	F13	F14	F15
		(wt%)	(wt%)	(wt%)	(wt%)	(wt%)
干燥剂						
CaO		5	5	5	5	5
(甲基)丙烯酸酯						

[0219]

CD262	6.38	48.45	48.45	48.45	48.45	48.45
SR351	1.58	9.12	9.12	9.12	9.12	9.12
CHMA	2.71	20	20	20	20	20
CD421A						
CN972	CD	16.44				
ACMO	0.32		16.44			
NVC	1.64			16.44		
Ebecryl 837	CD				16.44	
CN301	>8					16.44
SR307	>7					
光引发剂						
Irgacure 369		0.95	0.95	0.95	0.95	0.95
总共		100	100	100	100	100
方法		球磨	球磨	球磨	球磨	球磨
在20℃下粘度(mPa.s)		13-14	70-71	23-24	30	83-84
25℃下的混溶性		PS	OK	PS	PS	OK
25℃下的稳定性		PS+底层=包含CaO的类似固体凝胶	1-2天-类似固体凝胶形成	PS+底层=包含CaO的类似固体凝胶	PS+底层=包含CaO的类似固体凝胶	>43天-<20%的粘度增加
60℃下的稳定性		PS+底层=包含CaO的类似固体凝胶	1天-类似固体凝胶形成	PS+底层=包含CaO的类似固体凝胶	PS+底层=包含CaO的类似固体凝胶	>43天-<20%的粘度增加

[0220]

60℃下4天后的外观		PS+底层=包含CaO的类似固体凝胶	类似固体凝胶形成	PS+底层=包含CaO的类似固体凝胶	PS+底层=包含CaO的类似固体凝胶	白色液体
Z均(r.nm)		NM	NM	NM	NM	168
PDI		NM	NM	NM	NM	0.075

[0221] 表II c

[0222]

原料	ClogP	F16 (wt%)	F17 (wt%)	F18 (wt%)	F19 (wt%)	F20 (wt%)
干燥剂						
CaO		5	5	5	10	5
(甲基)丙烯酸酯						
CD262	6.38	64.45	48.45	64.89	45.9	48.45
SR351	1.58	9.12	9.12	9.12	8.7	9.12
CHMA	2.71	20	20	20		
CD421A					18.9	20
CN972	CD					
ACMO	0.32					
NVC	1.64					
Ebecryl 837	CD					
CN301	>8	0.44				
SR307	>7		16.44		15.6	16.44
光引发剂						
Irgacure 369		0.95	0.95	0.95	0.9	0.95

[0223]

总共		100	100	100	100	100
方法		球磨	球磨	球磨	球磨	球磨
在20℃下粘度(mPa.s)		16-17	40-41	41-42	45-50	40-41
25℃下的混溶性		OK	OK	OK	OK	OK
25℃下的稳定性		>43天-<20%的粘度增加	>43天-<20%的粘度增加	3天-CaO沉积	>29天-<20%的粘度增加	>43天-<20%的粘度增加
60℃下的稳定性		>43天-<20%的粘度增加	>43天-<20%的粘度增加	1天-CaO沉积	>29天-<20%的粘度增加	>43天-<20%的粘度增加
60℃下4天后的外观		白色液体	白色液体	所有CaO沉积在底部	白色液体	白色液体
Z均(r.nm)		417	233	NM	2.70	268
PDI		0.13	0.05	NM	0.1	0.05

[0224] 表II d

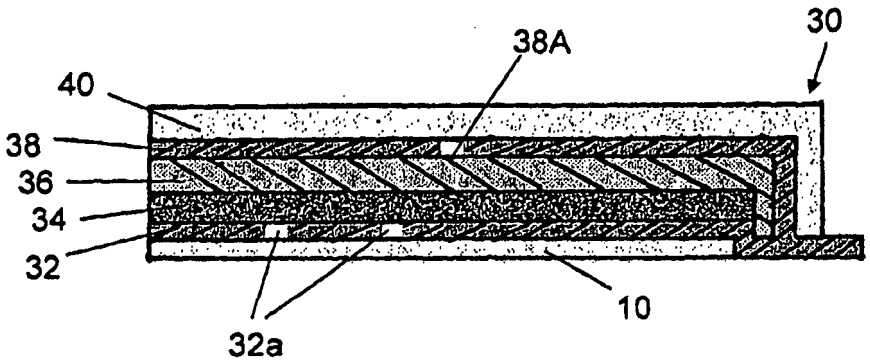


图 1