

Casting composition as diffusion barrier for water molecules

The invention relates to a casting composition based on a transparent epoxy or silicone resin, in particular for uses in an electroluminescent component, which preferably emits white light, and to a process for the preparation of casting compositions of this type. The casting composition here serves as diffusion barrier for water molecules through the use of glass or silica flakes.

Commercial white pc-LEDs consist of a chip which emits in the blue spectral region and a coating consisting of silicone or epoxy resin, in which one or more phosphors are located.

The phosphors are frequently based on silicate, sulfidic, nitridic or oxy-nitridic materials. These materials have the property of decomposing in the presence of extremely small traces of moisture.

In the case of ortho-silicate phosphors, this applies, in particular, to green phosphors comprising high concentrations of barium. The moisture present in the air diffuses through the silicone or epoxy resin matrix to the phosphor particles. This has the consequence that, due to decomposition of the phosphor, the luminance thereof decreases and degrades over time. This is associated with a drop in the performance of the white pc-LED: firstly, the colour point of the LED changes. Furthermore, reflectors present in the LED of the chip and the electrical connections are destroyed corrosively by the hydrolysis products of sulfidic or (oxy)nitridic phosphors.

The costs arising due to the requisite replacement of the LED hinder rapid substitution of incandescent bulbs, halogen lamps and fluorescent lamps, which are inefficient and have a short lifetime, by white LEDs.

EP 862794 discloses a wavelength-converting casting composition which consists of epoxy resin and comprises inorganic phosphor pigments. In

order to reduce agglomerate formation, the phosphor pigments may be provided with a silicone coating.

The object of the present invention is therefore to provide casting compositions which do not have one or more of the above-mentioned disadvantages.

Surprisingly, it has now been found that the decomposition of the phosphor, caused by traces of diffusing water, within the casting composition comprising a silicone or epoxy resin matrix can be prevented by the introduction of flake-form inorganic particles into the matrix. The flake-form particles, which consist of glass or silica, act as efficient diffusion barrier for the water molecules. Furthermore, the flake-form particles can be dispersed in the silicone or epoxy resin and can be applied directly to the phosphor coating of the LED as a separate diffusion barrier layer. (Figure 1 A or 1 B)

The present invention thus relates to a casting composition based on at least one transparent silicone or epoxy resin comprising inorganic phosphor particles and glass and/or silica particles, preferably in flake form, and a UV or blue light-emitting diode.

In a preferred embodiment, the glass or silica particles and the phosphor particles are homogeneously distributed in the casting composition (see Fig. 1 A)

In a further preferred embodiment, the flake-form glass or silica particles are dispersed and aligned in a plane-parallel manner in the casting composition and are arranged directly on an additional casting composition which comprises exclusively the phosphor particles as a separate diffusion barrier layer (see Fig. 1B)

The glass and silica particles preferably have a diameter of 5 to 20 μm and a thickness of 0.1 to 5 μm .

The average particle diameter d_{50} of the phosphor particles is preferably < 20 μm .

The effect of the flake-form glass and silica particles is based on the fact that the diffusion pathway of the water molecules is blocked in the casting composition comprising silicone or epoxy resin matrix. This occurs through the plane-parallel alignment of the particles in certain domains and through the offset arrangement of the flakes in the vertical direction. (see Fig. 2)

Owing to the fact that glass or silica particles have approximately the refractive index of the silicone or epoxy resin matrix in the range $n = 1.4 - 1.5$, the optical properties of the white LED are not adversely affected. Due to the slightly scattering properties of the flake-form particles (effect of the particle edges), the homogeneity of the luminance and colour temperature is improved over the angle range of the white LED

In order to improve the dispersibility of the flake-form glass and/or silica particles within the epoxy or silicone resin, the particles may be surface-coated. The flake-form particles are then coated with silicones/silanes by wet-chemical methods or by vapour deposition. These organosilicon compounds react with the surface OH groups of the flake-form particles. The desired hydrophobicity of the particles, structure of the oligomer/polymer chains and the coupling (physical and/or chemical) to the resin is controlled by modification of the organic chains of the silicon compounds.

The phosphor particles preferably consist of at least one of the following phosphor materials:

(Y, Gd, Lu, Sc, Sm, Tb)₃(Al, Ga)₅O₁₂:Ce (with or without Pr), (Ca, Sr, Ba)₂SiO₄:Eu, YSiO₂N:Ce, Y₂Si₃O₃N₄:Ce, Gd₂Si₃O₃N₄:Ce, (Y, Gd, Tb, Lu)₃Al_{5-x}Si_xO_{12-x}N_x:Ce, BaMgAl₁₀O₁₇:Eu, SrAl₂O₄:Eu, Sr₄Al₁₄O₂₅:Eu, (Ca, Sr, Ba)Si₂N₂O₂:Eu, SrSiAl₂O₃N₂:Eu, (Ca, Sr, Ba)₂Si₅N₈:Eu, CaAlSiN₃:Eu, zinc alkaline earth metal orthosilicates, copper alkaline earth metal orthosilicates, iron alkaline earth metal orthosilicates, molybdates, tungstates, vanadates, group III nitrides, oxides, in

each case individually or mixtures thereof with one or more activator ions, such as Ce, Eu, Mn, Cr and/or Bi.

Particularly preferred inorganic phosphor particles for the production of white-luminescent opto-electronic components are orthosilicates.

The starting materials for the production of the phosphor particle consist of the base material (for example salt solutions of yttrium, aluminium, gadolinium, etc.) and at least one dopant (for example cerium). Suitable starting materials are inorganic and/or organic substances, such as nitrates, halides, carbonates, hydrogencarbonates, phosphates, carboxylates, alcoholates, acetates, oxalates, sulfates, organometallic compounds, hydroxides and/or oxides of the metals, semimetals, transition metals and/or rare earths, which are dissolved and/or suspended in inorganic and/or organic liquids. Preference is given to the use of mixed nitrate solutions, chloride or hydroxide solutions which comprise the corresponding elements in the requisite stoichiometric ratio.

The object in accordance with the invention is furthermore achieved by a process for the preparation of a casting composition based on at least one transparent silicone or epoxy resin comprising inorganic phosphor particles and glass and/or silica particles and a UV or blue light-emitting diode, characterised by the process steps of:

- a) homogeneous mixing of inorganic phosphor particles with pulverulent glass and/or silica particles
- b) dispersal of the mixture of phosphors and glass or silica particles with the transparent silicone or epoxy resin.
- c) coating of the blue light-emitting diode with silicone or epoxy resin which comprises the phosphor and the glass and/or silica particles.
- d) curing of the coating.

The curing of the coating is carried out at temperatures between 120 and 180°C, preferably at 150°C

The production of the glass and silica particles is carried out by conventional processes via a belt process from the corresponding alkali metal salts (for example from a potassium or sodium water-glass solution for silica). The production process is described in detail in EP 763573, EP 608388 and DE 19618564.

The present invention furthermore relates to a process for the preparation of a casting composition based on at least one transparent silicone or epoxy resin comprising inorganic phosphor particles and glass and/or silica particles and a UV or blue light-emitting diode, characterised by the process steps of:

- a) dispersal of the inorganic phosphor particles with silicone or epoxy resin.
- b) coating of the light-emitting diode with the mixture of phosphor particles and silicone or epoxy resin.
- c) curing of the coating.
- d) dispersal of the glass and/or silica particles in silicone or epoxy resin.
- e) production of a diffusion barrier layer by coating the cured phosphor coating.
- f) curing of the diffusion barrier layer.

It is furthermore preferred for the flake-form glass or silica particles to be surface-coated with organosilicon compounds (such as silicones or silanes) by wet-chemical methods or by vapour deposition. As already mentioned, the coupling to the epoxy or silicone resin is improved by this coating.

Light-scattering particles, so-called diffusers (such as, for example, CaF_2), may additionally be added to the casting composition. This advantageously

enables the colour impression and the emission characteristics of the semiconductor component to be optimised further.

In addition, the casting composition may also comprise adhesion promoters, hydrophobicising agents, processing assistants and/or thixotropic agents. Thixotropic agents which can be used are, for example, pyrogenic silicic acid. The thixotropic agent serves for thickening of the epoxy resin in order to prevent sedimentation of the phosphor particles. Suitable processing assistants are, for example, glycol ethers.

Adhesion promoters which can be employed are, for example, functional alkoxysiloxanes which improve the adhesion between phosphor particles and resin.

Hydrophobicising agents which can be employed are, for example, liquid silicone wax, which likewise serves for modification of the phosphor particle surface.

The UV or blue light-emitting diode according to the invention is a light source comprising a luminescent indium aluminium gallium nitride, in particular of the formula $\text{In}_i\text{Ga}_j\text{Al}_k\text{N}$, where $0 \leq i$, $0 \leq j$, $0 \leq k$, and $i+j+k=1$.

Possible forms of light sources of this type are known to the person skilled in the art. These may be light-emitting LED chips of various structure.

The following examples are intended to clarify the present invention. However, they should in no way be regarded as limiting. All compounds or components which can be used in the preparations are either known and commercially available or can be synthesised by known methods. The temperatures indicated in the examples are always in °C. It furthermore goes without saying that, both in the description and in the examples, the added amounts of the components in the compositions always add up to a total of 100%. Percentage data given should always be regarded in the given con-

text. However, they usually always relate to the weight of the part amount or total amount indicated.

Examples

Example 1: Coating of flake-form glass or silica particles with functional groups

1. A) Silanisation for epoxy polymers:

100 g of the silica or glass particles are suspended in 1350 ml of deionised water with vigorous stirring. The pH of the suspension is adjusted to pH = 6.5 using 5 wt-% of H₂SO₄, and the suspension is heated to 75°C. 4.0 g of a 1:1 mixture of Silquest A-186 [beta-(3,4-epoxycyclohexyl)ethyltrimethoxysilane] and Silquest A-1310 [gamma-isocyanatopropyltriethoxysilane] are subsequently metered into the suspension over the course of 60 min with moderate stirring. When the addition is complete, the mixture is subsequently stirred for 15 min in order to complete the coupling of the silanes to the surface. The pH is corrected to 6.5 by means of 5 wt-% H₂SO₄.

The suspension is subsequently filtered, and the filter cake is washed with deionised water until salt-free. The drying is carried out at 130°C for 20 h. The powder obtained in this way is then sieved by means of a 40 µm sieve.

1. B) Silanisation for silicone resin coupling:

100 g of the silica or glass particles are suspended in 1350 ml of deionised water with vigorous stirring. The pH of the suspension is adjusted to pH = 6.5 using 5 wt-% H₂SO₄, and the suspension is heated to 75°C. 6.0 g of a 1:2 mixture of Silquest A-1110 [gamma-aminopropyltrimethoxysilane] and

Silquest A-1524 [γ -ureapropyltrimethoxysilane] are subsequently metered into the suspension over the course of 75 min with moderate stirring. When the addition is complete, the mixture is subsequently stirred for 15 min in order to complete the coupling of the silanes to the surface. The pH is corrected to 6.5 by means of 5 wt-% H_2SO_4 .

The suspension is subsequently filtered, and the filter cake is washed with deionised water until salt-free. The drying is carried out at 140°C for 20 h. The powder obtained in this way is then sieved by means of a $40\ \mu\text{m}$ sieve.

1. C) Silanisation with a vinylsilane for silicone resin coupling:

100 g of the silica or glass particles are suspended in 1350 ml of deionised water with vigorous stirring. The pH of the suspension is adjusted to pH = 6.8 using 5 wt-% H_2SO_4 , and the suspension is heated to 75°C . 6.0 g of a 1:2 mixture of Silquest A-174 [γ -methacryloxypropyltrimethoxysilane] and Silquest A-151 [vinyltriethoxysilane] are subsequently metered into the suspension over the course of 90 min with moderate stirring. When the addition is complete, the mixture is subsequently stirred for 15 min in order to complete the coupling of the silanes to the surface. The pH is corrected to 6.5 by means of 5 wt-% H_2SO_4 .

The suspension is subsequently filtered, and the filter cake is washed with deionised water until salt-free. The drying is carried out at 140°C for 20 h. The powder obtained in this way is then sieved by means of a $40\ \mu\text{m}$ sieve.

Example 2: Production of an LED

A) Mixture of phosphor with flake-form particles

The following mixtures are prepared in a Speedmixer ® (speed 3000 rpm, duration: 5 min, room temperature):

50 ml of each of the two resin components JCR 6122 a and b are admixed with 4% by weight of one of the green orthosilicate phosphors and 2% of uncoated glass or silica particles or the flake-form particles which have been compatibilised in accordance with Example 1 A, B, or C. The flake-form particles have an average diameter of 5 μm to 20 μm and a thickness distribution from 0.1 μm to 5 μm . The two resin mixtures are combined, stirred and degassed. 10 ml are then introduced into the storage vessel of a jet dispenser or screw metering valve dispenser. Bonded COB (chip on board) crude LED packages are placed beneath the dispensing valve. Glob tops of the resin mixture are then placed dropwise on the chips of the crude LED packages using the dispenser. These coated LEDs are conditioned in a drying cabinet at 150°C for 1 hour, during which the resin (= casting composition) cures.

B) Separate diffusion barrier layer

The following mixtures are prepared in a Speedmixer ® (speed 3000 rpm, duration: 5 min, room temperature):

50 ml of each of the two resin components JCR 6122 a and b are admixed with 4% by weight of a green orthosilicate phosphor. The two resin mixtures are combined, stirred and degassed. 10 ml are then introduced into the storage vessel of a jet dispenser or screw metering valve dispenser.

Bonded COB (chip on board) crude LED packages are placed beneath the dispensing valve. Glob tops of the resin mixture are then placed dropwise on the chips of the crude LED packages using the dispenser. These coated LEDs are conditioned in a drying cabinet at 150°C for 1 hour, during which the resin (= casting composition) cures.

50 ml of the two resin components JCR 6122 a and b are subsequently again mixed with 4% by weight of the uncoated glass or silica particles or the flake-form glass and/or silica particles which have been compatibilised in accordance with Example 1 A, B, or C. The two resin mixtures are com-

bined, stirred and degassed. 10 ml are then introduced into the storage vessel of a jet dispenser or screw metering valve dispenser. The coated LEDs are placed beneath the dispensing valve. The diffusion barrier layers consisting of the resin mixture and the flake-form particles are then applied to the coated LEDs using the dispenser. These coated LEDs are then conditioned in a drying cabinet at 150°C for 1 hour, during which the resin of the diffusion barrier layer cures.

Figures

The invention will be explained in greater detail below with reference to a number of illustrative embodiments, in which:

Fig. 1 shows a homogeneous distribution of the glass or silica flakes in the silicone or epoxy resin matrix. 1: silicone / epoxy resin, 2: glass or silica flakes, 3: LED chip, 4: phosphor particles; B) separate diffusion barrier layer; 5: diffusion barrier layer consisting of silicone / epoxy resin matrix which comprises only the flake-form particles; 6: water diffusing in.

Fig. 2: 1: glass or silica particles. The flake-form particles are aligned parallel and overlap in the vertical direction, effectively preventing the diffusion of water.

Fig. 3: 1: average of the measurements of the light flux of 50 LEDs which have a separate water diffusion barrier layer.

2: average of the measurements of the light flux of 50 LEDs which have a water diffusion barrier. The green orthosilicate phosphor has been mixed with flake-form particles here.

3: average of the measurements of the light flux of 50 LEDs which have no water diffusion barrier.

Patent Claims

1. Casting composition based on at least one transparent silicone or epoxy resin comprising inorganic phosphor particles and glass and/or silica particles and a UV or blue light-emitting diode, characterised in that the glass and/or silica particles have a diameter of 5 to 20 μm , have a thickness of 0.1 to 5 μm and are in flake-form.
2. Casting composition according to Claim 1, characterised in that the glass and/or silica particles and the phosphor particles are homogeneously distributed in the casting composition.
3. Casting composition according to Claim 1, characterised in that the glass and/or silica particles and the phosphor particles are each located within separate layers of the casting composition.
4. Casting composition according to Claim 3, characterised in that the glass and/or silica particles are dispersed and each aligned in a plane substantially parallel to and opposite a tangent to a curved face of the phosphor particle containing layer of the casting composition and wherein the glass and/or silica particles containing layer of the casting composition overlie the phosphor particle containing layer.
5. Casting composition according to one or more of Claims 1 to 4, characterised in that the average particle diameter d_{50} of the phosphor particles is $<20 \mu\text{m}$.
6. Casting composition according to one or more of Claims 1 to 5, characterised in that the inorganic phosphor particles are selected from the following group:
 $(\text{Y, Gd, Lu, Sc, Sm, Tb})_3 (\text{Al, Ga})_5 \text{O}_{12}:\text{Ce}$ (with or without Pr), $(\text{Ca, Sr Ba})_2 \text{SiO}_4:\text{Eu}$, $\text{YSiO}_2\text{N}:\text{Ce}$, $\text{Y}_2\text{SiO}_3\text{N}_4:\text{Ce}$, $\text{Gd}_2\text{Si}_3\text{O}_3\text{N}_4:\text{Ce}$, $(\text{Y, Gd, Tb, Lu})_3 \text{Al}_{5-x} \text{Si}_x \text{O}_{12-x} \text{N}_x:\text{Ce}$, $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}$, $\text{SrAl}_2\text{O}_4:\text{Eu}$, $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}$,

(Ca,Sr,Ba)Si₂N₂O₂:Eu, SrSiAl₂O₃N₂:Eu, (Ca,Sr,Ba)₂Si₅N₈:Eu, CaAlSiN₃:Eu, zinc alkaline earth metal orthosilicates, copper alkaline earth metal orthosilicates, iron alkaline earth metal orthosilicates, molybdates, tungstates, vanadates, group III nitrides, oxides, in each case individually or mixtures thereof with one or more activator ions, such as Ce, Eu, Mn, Cr and/or Bi.

7. Casting composition according to Claim 6, characterised in that the inorganic phosphor particles are orthosilicates.
8. Process for the preparation of a casting composition according to one or more of Claims 1 to 7, characterised by the process steps of:
 - a) homogeneous mixing of inorganic phosphor particles with pulverulent glass and/or silica particles;
 - b) dispersal of the mixture of phosphors and glass and/or silica particles with the transparent silicone or epoxy resin;
 - c) coating of the blue light-emitting diode with silicone or epoxy resin which comprises the phosphor and the glass and/or silica particles;
 - d) curing of the coating.
9. Process for the preparation of a casting composition according to one or more of Claims 1 to 7, characterised by the process steps of:
 - a) dispersal of the inorganic phosphor particles with silicone or epoxy resin;
 - b) coating of the light-emitting diode with the mixture of phosphor particles and silicone or epoxy resin;
 - c) curing of the coating;
 - d) dispersal of the glass or silica particles in silicone or epoxy resin;
 - e) production of a diffusion barrier layer by coating the cured phosphor coating;
 - f) curing of the diffusion barrier layer.
10. Process according to Claim 8 and/or 9, characterised in that the glass and/or silica particles are surface-coated with organosilicon compounds.