${\bf (19) \ World \ Intellectual \ Property \ Organization}$

International Bureau



. I TERRE BURNER IN BURNER HER BERKE BERKE BERKE HER HER HER BURNER BURNER BURNER BURNER BERKE HER HER HER HER

(43) International Publication Date 8 November 2007 (08.11,2007)

(10) International Publication Number WO 2007/126561 A1

(51) International Patent Classification: *C09K 11/08* (2006.01) *H05B 33/04* (2006.01) *H01L 33/00* (2006.01)

(21) International Application Number:

PCT/US2007/006076

(22) International Filing Date: 9 March 2007 (09.03.2007)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:

11/391,021 28 March 2006 (28.03.2006) US

(71) Applicant (for all designated States except US): LUMI-NATION LLC [US/US]; 6180 Halle Drive, Valley View, OH 44125-4635 (US).

(71) Applicant and

(72) Inventor (for all designated States except US): HAITKO, Deborah, Ann [US/US]; 1041 Lexington Avenue, Schenectady, NY 12309 (US).

(72) Inventor; and

(75) Inventor/Applicant (for US only): LEHMAN, John, T.

[US/US]; 1256 Dorwaldt Avenue, Niskayuna, NY 12309 (US).

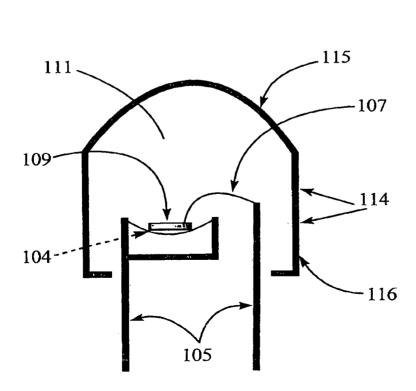
(74) Agent: McCOLLISTER, Scott, A.; Fay Sharpe LLP, 1100 Superior Avenue, 7th Floor, Cleveland, OH 44114-2579 (US).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

[Continued on next page]

(54) Title: Q SILICONE-CONTAINING COMPOSITION, OPTOELECTRONIC ENCAPSULANT THEREOF AND DEVICE THEREOF



(57) Abstract: The invention provides a composition comprising a phosphor and a Q-containing silicone: an encapsulant formulation comprising a phosphor and a Q-containing silicone; and a device including an optoelectronic device such as LED, a phosphor, and a Q-containing silicone. The Q-containing silicone passes thermal shock condition of up to 150°C, and has many suitable properties such as transparency and viscosity to function as a phosphor binder.

WO 2007/126561 A1



Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

Q SILICONE-CONTAINING COMPOSITION, OPTOELECTRONIC ENCAPSULANT THEREOF AND DEVICE THEREOF

BACKGROUND OF THE INVENTION

[0001] This invention is generally related to a composition comprising a phosphor and a Q-containing silicone, an encapsulant formulation comprising a phosphor and a Q-containing silicone, and an optoelectronic device such as LED including an encapsulant that is made from the formulation comprising a phosphor and a Q-containing silicone.

[0002] How to strongly adhere phosphor into and/or onto a substrate remains a technical challenge. For example, current silicone materials used as phosphor binders pose problems in terms of adhesion and exposure to thermal shock conditions. To address this problem, commercial silicones that contain fillers or adhesive promoters have to be used.

[0003] Moreover, United States Patent Application 20030122477 has disclosed binders to hold powder phosphor particles together as well as to the glass screen of a field emission display device, and to prevent shedding of phosphor material. According to the publication, the binder material is selected from Group A including potassium silicate, ammonium silicate, tin(II) 2-ethylhexanoate, tin (IV) isopropoxide, tin (II) oxalate, titanium (IV) ethoxide, zinc 2,4-pentane dionate, zinc acetate, zinc oxalate indium oxalate, and cadmium oxalate; or from Group B including polyvinyl alcohol, poly(propylene carbonate), poly(propylene carbonate) and poly(ethylene Carbonate) etc.

[0004] United States Patent Application 20040173807 filed by Tian et al. has disclosed application of cerium-doped garnet phosphors to semiconductor LED

chips for manufacturing lighting devices. The phosphors are applied to the LED by forming a phosphor slurry with a polymerizable material such as polyvinyl alcohol in a solution, coating the exposed surface of the LED with the slurry, and polymerizing the polymerizable material thermally or photochemically.

[0005] United States Patent Application 20010048966 filed by Trumble et al. has taught a luminescent binder comprising SiO₂ nanoparticles doped with terbium or terbium and yttrium. The binder promotes adherence of phosphor coatings to lamp envelopes and emits visible light under UV and VUV excitation.

[0006] Advantageously, the present invention offers a composition comprising a phosphor and a Q-containing silicone; an encapsulant formulation comprising a phosphor and a Q-containing silicone; and a device including an optoelectronic device such as LED, a phosphor, and a Q-containing silicone. The Q-containing silicone passes thermal shock condition of up to 150°C, and has many suitable properties such as viscosity to function as a phosphor binder.

BRIEF DESCRIPTION OF THE INVENTION

[0007] One aspect of the invention provides a composition comprising a phosphor and a Q-containing silicone. The Q-containing silicone passes thermal shock condition of up to 150°C, and has many suitable properties such as viscosity to function as a phosphor binder.

[0008] Another aspect of the invention provides an encapsulant formulation comprising a phosphor and a Q-containing silicone.

[0009] Still another aspect of the invention provides a device including an optoelectronic device such as LED, a phosphor, and a Q-containing silicone.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] FIGURE 1 shows thermal aging profiles for three Q-containing silicone samples in an embodiment of the invention;

[0011] FIGURE 2 shows light transmission spectra of a Q-containing silicone at 0 hour and 17 hours after curing in an embodiment of the invention;

[0012] FIGURE 3 shows light transmission spectra of another Q-containing silicone at 0 hour and 17 hours after curing in an embodiment of the invention;

[0013] FIGURE 4 shows light transmission spectra of still another Q-containing silicone at 0 hour and 17 hours after curing in an embodiment of the invention;

[0014] FIGURE 5 shows a schematic diagram of a LED device according to an embodiment of the present invention;

[0015] FIGURE 6 shows a schematic diagram of a LED array on a substrate according to one embodiment of the present invention;

[0016] FIGURE 7 shows a schematic diagram of a LED device according to another embodiment of the present invention; and

[0017] FIGURE 8 shows a schematic diagram of a vertical cavity surface emitting laser device according to still another embodiment of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0018] It is to be understood herein, that if a "range" or "group" is mentioned with respect to a particular characteristic of the present invention, for example, Q% value, viscosity, substitute species, and temperature etc., it relates to and explicitly incorporates herein each and every specific member and combination of sub-ranges

or sub-groups therein whatsoever. Thus, any specified range or group is to be understood as a shorthand way of referring to each and every member of a range or group individually as well as each and every possible sub-range or sub-group encompassed therein; and similarly with respect to any sub-ranges or sub-groups therein.

[0019] The present invention provides a composition comprising a phosphor and a Q-containing silicone. In a variety of exemplary embodiments, the Q-containing silicone typically has a Q% value of from 1% to 20%, preferably from 2% to 10%, and more preferably from 5% to 6%. The Q-containing silicone functions as a phosphor binder for the phosphor and may be used to incorporate phosphor materials into various optoelectronic devices such as light emitting diode (LED).

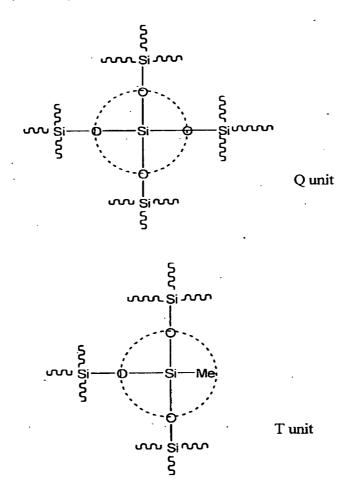
[0020] In a variety of exemplary embodiments, not only the viscosity of the phosphor binder mixture varies, when cured, from a lower level that is suitable for phosphor inclusion to a higher level that is suitable for robustly binding the phosphor into an optoelectronic device, but also the interpenetrating network generated from the Q resin strengths the integration of the phosphor in the cured composition, enabling endurance against harsh conditions such as thermal shock, temperatures exceeding 125°C, and UV exposure etc.

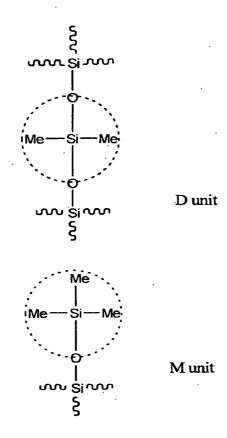
[0021] In an embodiment of the invention, the Q-containing silicone can be cured to contain sufficient viscosity for phosphor inclusion. When exposed to, for example, thermal shock conditions of up to 150°C, the Q-containing silicone formulation can maintain structural integrity, and show a stable and prolonged transmission capability for a wide spectrum of light, such as 350nm -750nm.

[0022] Various advantages of the Q-containing silicone include, for example, availability, ease in handling, sufficient viscosity, and passing thermal shock.

Without being bond by any theory, it is believed that interpenetrating network of the Q-containing silicone resin is at least partially responsible for the advantages of the Q-containing silicone.

[0023] According to the present invention, Q% value of the Q-containing silicone is defined based on the "MDTQ" shorthand nomenclature system for silicone materials and silicone resins. The four units under the nomenclature, Q, T, D, and M, are defined respectively as shown below.





[0024] A prime on the unit symbols, for example, M', D', T', and Q', denote substituents other than the methyl group (Me) as shown above. For example, M^{vi} and D^{Ph} denote that the methyl groups in the above M and D units have been replaced by vinyl (Vi) or phenyl (Ph) group.

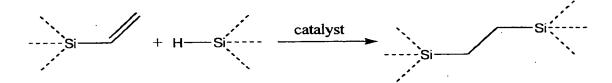
[0025] According to the present invention, the percentage of Q units, Q%, in a given silicone sample is calculated by the following equation:

$$Q\% = N_Q/(N_M + N_D + N_T + N_Q) \times 100\%$$

in which N_M , N_D , N_T , and N_Q are respectively the total moles or number of M and any M'; D and any D'; T and any T'; and Q and any Q' units in the silicone sample.

[0026] In a variety of exemplary embodiments, the Q-containing silicone is an aliphatic silicone, and contains minimal or no aromatic groups such as phenyl group.

[0027] An ethylene bond (-CH₂CH₂-) between two silicone atoms may be formed by a hydrosilylation reaction as shown below.



In a variety of exemplary embodiments, the hydrosilylation reaction may [0028] be carried out to prepare the Q-containing silicone of the invention, in the presence of a hydrosilylation catalyst selected from the group of ruthenium, osmium, rhodium, iridium, palladium and platinum hydrosilylation catalysts. Exemplary of such catalysts are those described in U.S. Pat. Nos. 2,823,218; 3,159,601; 3,159,662; and 3,775,452. Preferably, the catalysts are platinum catalysts such as platinum black, platinum chloride, chloroplatinic acid, the reaction products of chloroplatinic acid with monohydric alcohols, complexes of chloroplatinic acid with olefins. platinum bisacetoacetate, and other solubilized platinum compounds. A skilled person in the art may consult numerous prior patents and references on the usage of platinum catalyst. For example, platinum compounds having the formula (PtCl₂Olefin) and H(PtCl₃Olefin) are described in U.S. Pat. No. 3,159,601; cyclopropane complex of platinum chloride is described in U.S. Pat. No. 3,159,662; a complex formed from chloroplatinic acid with up to 2 moles per gram of platinum of a member selected from the class consisting of alcohols, ethers, aldehydes and mixtures of the above is described in U.S. Pat. No. 3,220,972. Other catalysts are described in U.S. Pat. Nos. 3,715,334; 3,775,452; and 3,814,730 to Karstedt. Additional background concerning the art may be found at J. L. Spier, "Homogeneous Catalysis of Hydrosilation by Transition Metals, in Advances in

Organometallic Chemistry, volume 17, pages 407 through 447, F. G. A. Stone and R. West editors, published by the Academic Press (New York, 1979).

[0029] In preferred embodiments of the invention, the platinum catalysts are those platinum compound catalysts that are well soluble in the reaction mixture, and optical clarity of the cured composition can be obtained, for example, reaction product of H₂PtCl₆ in n-octanol.

[0030] In a variety of exemplary embodiments, the hydrosilylation reaction uses Pt catalyst. The Pt catalyst concentration in the silicone may range from 5 to 20 ppm, preferably from 10 to 15 ppm.

[0031]

ensure cure control.

In preferred embodiments of the invention, the preparation of the Q-

containing silicone may be accomplished by using various commercially available ingredients. As a merit of the embodiment, the preparation is easy and convenient.

[0032] In an embodiment of the present invention, the Q-containing silicone is prepared from room temperature vulcanizing (RTV) silicone systems. RTV silicones usually come as uncured rubbers with liquid or paste-like consistencies, and are used for sealants, mould making, encapsulation and potting. RTV curing is based on chemical reactions that provide cross-linking and increase molecular weights, e.g. hydrosilylation as described above, preferably in the presence of catalysts to

[0033] In preferred embodiments, the Q-containing silicone of the present invention is prepared from a RTV-2 silicone system. The curing of RTV-2 silicones may be triggered by mixing together two separate components (part A and part B), preferably one of which contains a catalyst such as a hydrosilylation catalyst, e.g. Pt catalyst.

In a variety of exemplary embodiments, Part A and part B components of [0034] the RTV-2 may be mixed according to desired mix ratio. With clean tools, one may thoroughly mix the ingredients together, scraping the sides and bottom of the container carefully to produce a homogeneous mixture. When using power mixers, an operator should avoid excessive speeds which could entrap large amounts of air, or cause overheating of the mixture, resulting in shorter pot life. Air entrapped during mixing should be removed to eliminate voids in the cured product. The mixed material may be exposed to a vacuum of about 25 mm (29 in.) of mercury. The material will typically expand, crest, and recede to approximately the original level as the bubbles break. Degassing is usually complete approximately two minutes after frothing ceases. For potting, a deaeration step may be necessary after pouring to avoid capturing air in complex assemblies. In some embodiments, automatic equipment designed to meter, mix, deaerate, and dispense the composition of the present invention will add convenience to continuous or large volume operations. In an embodiment, cure temperature for the RTV silicone is in the range of [0035] about 50°C to about 160°C, preferably in the range of about 80°C to about 155°C. Cure through time or cure time may be in the range of about 0.1 hours to about 4 hours, preferably in the range of about 0.5 hours to about 3 hours and most preferably in the range of about 1 hour to about 2 hours.

[0036] The viscosity of a fluid is its resistance to shear or flow and is a measure of the fluids adhesive/cohesive or frictional properties. The resistance is caused by intermolecular friction exerted when layers of fluids attempts to slide by another. There are many ways to measure viscosity and consequently many ways to express it, for example, CentiStokes (cSt), CentiPoises (cP), Saybolt Universal Seconds (SSU) and degree Engler. A skilled person knows how to convert one viscosity unit

to another, for example, CentiPoises (cp) = CentiStokes (cSt) x Density. In typical embodiments of the invention, the RTV silicone may have a viscosity (@ 25°C, uncured and mixed) in the range of about 3500 to about 4500 cps.

[0037] Other properties of the cured RTV silicone may include, for example, a thermal expansion in the range of about $20-35 \times 10^{-5}$ (°C)⁻¹; a thermal conductivity in the range of about 0.18 to about 0.2 W/m · °K; and any other suitable properties such as brittle point, hardness, tensile strength, elongation, volume resistivity, dielectric strength, and dielectric constant etc.

[0038] In a variety of exemplary embodiments, the RTV-2 Q-containing silicone system will normally cure in contact with most clean, dry surfaces such as phosphor particles, LED, and other encapsulating materials such as epoxy resin. However, it should be noted that certain materials, such as butyl and chlorinated rubber, sulfur-containing materials, amines, and certain metal soap-cured RTV silicone rubber compounds, can cause cure inhibition. Cure inhibition is characterized by a gummy appearance of the RTV silicone rubber compound at the interface between it and the substrate.

[0039] Preferred specific examples of RTV-2 silicone materials include, but are not limited to, those are known and readily available commercially such as RTV 615 and RTV 656 or 655 from General Electric Silicones.

[0040] GE RTV 615 per se is clear and dispensed easily and may be used as silicone rubber compound for electronic potting with optical clarity allowing maximum light transmission, and also protecting electronic components against shock, moisture, and other environmental hazards. RTV 615 comprises polydimethylsiloxane bearing vinyl groups and a platinum catalyst (Part A) and a cross-linker containing silicon hydride (Si-H) groups (Part B) which form a covalent

bond with vinyl groups. RTV 615 normally comprises Part A and Part B in a weight ratio of 10:1 (Part A: Part B). More information on GE RTV 615 is available in the following Table 1.

Table 1

RTV615	silicone Protects	vo part, high strength, probber compound for estemption entropies electronic components mental hazards. Allows	lectronic potting for against shock, n	or optical clarity. noisture, and other
Property		Value	Test	Method and Condition
Appearance		Clear -		Uncured, Mixed
CHEMISTRY		Addition	-	-
CURE		Room Temperature or Heat	-	-
Coefficient of Expansion		0.00027°C cm/cm	Cured 1 hr. @ 100°C (212°F)	-
Consistency/l Form	Physical	Flowable	-	Uncured, Mixed
Density		1.02 g/cm^3	-	catalyzed 10:1
Dielectric Co	nstant	2.89	Cured 1hr. @ 100°C (212°F)	-
Dielectric Stre	ength	19.7 kV/mm	Cured 1hr. @ 100°C (212°F)	-
Dissipation F	actor	0.0004	Cured 1hr. @ 100°C (212°F)	-
Durometer Ha	ardness	44 Shore A	Cured 1hr. @ 100°C (212°F)	-
Elongation		160%	Cured 1hr. @ 100°C (212°F)	-
Mix Ratio		10:1	-	-
Refractive Index		1.406	Cured 1hr. @ 100°C (212°F)	-
Shrinkage		0.2%	Cured 1hr. @ 100°C (212°F)	-
Specific Heat		1.25 J/g.K	Cured 1hr. @ 100°C (212°F)	-
Tensile Stren	igth	6.37 MPa	Cured 1hr. @	_

		100°C (212°F)	
Thermal Conductivity	0.19 W/m deg K	Cured 1hr. @ 100°C (212°F)	-
Viscosity	4000 cps	-	Uncured, Mixed
Volume Resistivity	1.8E15 ohm-cm	Cured 1hr. @ 100°C (212°F)	-
Work Time	4 hours	-	Uncured, Mixed

on a non-silicone substrate. For example, SS4120 primer (RTV 615-1P) may be used with RTV 615, and SS4155 primer may be used with RTV 656. Non-silicone surface may be thoroughly cleaned with a non-oily solvent such as naphtha or methyl ethyl ketone and allow to dry. Then apply a uniform thin film of silicone primer and allow the primer to air dry for one hour or more. Finally, apply freshly catalyzed mixture of RTV-2 to the primed surface and cure as desired.

[0042] The following examples are included to provide additional guidance to those skilled in the art in practicing the claimed invention. The examples provided are merely representative of the work that contributes to the teaching of the present application. Accordingly, these examples are not intended to limit the invention, as defined in the appended claims, in any manner.

Examples

Example 1

[0043] GE RTV 615 Q-containing silicone was prepared. The conditions were mix ratio 1:10, 3 x 12 s in mixer; 17.5 g, 60 mm mold, degas, cure; cure at 85°C for 1

hour and at 150° for 1 hour. Advance thermal age at 150°C. Formation of clean elastic disks has been observed.

Example 2

[0044] GE RTV 615 Q-containing silicone was prepared. The conditions were mix ratio 1:10, 3 x 12 s in mixer; 17.5 g, 60 mm mold, degas, cure; Cure at 150° for 1 hour; and advance thermal age at 150°C. Formation of clean elastic disks has been observed.

Example 3

[0045] GE RTV 615 Q-containing silicone was prepared. The conditions were mix ratio 1:10, 3 x 12 s in mixer; 17.5 g, 60 mm mold, degas, cure; Cure at 150° for 2 hour; and advance thermal age at 150°C. Formation of clean elastic disks has been observed.

[0046] Figure 1 shows thermal aging profiles for the Q-containing silicones from Examples 1, 2 and 3. The transmission percentage (T%) was measured at 400nm. Figure 2 shows light transmission spectra of the Q-containing silicone from Example 1 at 0 hour and 17 hours after curing. Figure 3 shows light transmission spectra of the Q-containing silicone from Example 2 at 0 hour and 17 hours after curing. Figure 4 shows light transmission spectra of the Q-containing silicone from Example 3 at 0 hour and 17 hours after curing. As shown in the figures, at the first 17 hours of aging, a slight possible photobleaching in all the Q-containing silicone samples has been observed, after which the transmission leveled off.

[0047] In an embodiment, the composition of the invention passes accelerated thermal aging greater than or equal to 150°C and simultaneous UV exposure greater than or equal to 300 milliwatts at 400nm.

[0048] The present invention provides a composition comprising a phosphor and a Q-containing silicone. There is no specific limitation imposed on the selection of the phosphor. For example, if a LED white light device is to be made, one can use a UV light emitting LED combined with blue, green and red-emitting phosphors; or use a blue LED with a yellow phosphor; or use a blue LED with combined red and green emitting phosphors.

[0049] An exemplary phosphor is the cerium-doped yittrium aluminum oxide Y₃Al₅O₁₂ garnet ("YAG:Ce"). Other suitable phosphor examples are based on YAG doped with more than one type of rare earth ions, such as (Y_{1-x-y}Gd_xCe_y)₃Al₅O₁₂ ("YAG:Gd,Ce"), $(Y_{1-x}Ce_x)_3(Al_{5-y}Ga_y)O_{12}$ ("YAG:Ga,Ce"), $(Y_{1-x-y}Gd_xCe_y)(Al_{5-z}Ga_z)O_{12}$ ("YAG:Gd,Ga,Ce"), and (Gd_{1-x}Ce_x)Sc₂Al₃O₁₂ ("GSAG"), where $0 \le x \le 1$, $0 \le y \le 1$, $0 \le z \le 5$, and x+y≤1. For example, the YAG:Gd,Ce phosphor shows an absorption of light in the wavelength range from about 390 nm to about 530 nm (i.e., the blue-green spectral region) and an emission of light in the wavelength range from about 490 nm to about 700 nm (i.e., the green-to-red spectral region). Related phosphors include Lu₃Al₅O₁₂ and Tb₂Al₅O₁₂, both doped with cerium. In addition, these cerium-doped garnet phosphors may also be additionally doped with small amounts of Pr (such as about 0.1-2 mole percent) to produce an additional enhancement of red emission. Non-limiting examples of phosphors that are efficiently excited by radiation of 300 nm include green-emitting phosphors about 500 $Ca_8Mg(SiO_4)_4Cl_2:Eu^{2+}, Mn^{2+}; GdBO_3:Ce^{3+}, Tb^{3+}; CeMgAl_{11}O_{19}:Tb^{3+}; Y_2SiO_5:Ce^{3+}, Tb^{3+}; Y_2SiO_5:Ce^{3+}; Y$ Tb3+; and BaMg2Al16O27:Eu2+, Mn2+ etc.; red-emitting phosphors such as

 Y_2O_3 :Bi³⁺,Eu³⁺; Sr₂P₂O₇:Eu²⁺,Mn²⁺; SrMgP₂O₇:Eu²⁺,Mn²⁺; (Y,Gd)(V,B)O₄:Eu³⁺; and 3.5MgO-0.5MgF₂·GeO₂:Mn⁴⁺ (magnesium fluorogermanate) etc.; blue-emitting BaMg₂Al₁₆O₂₇:Eu²⁺; $Sr_5(PO_4)_{10}Cl_2:Eu^{2+}$; phosphors such as $(Ba.Ca.Sr)(PO_4)_{10}(Cl,F)_2:Eu^{2+}$; and $(Ca,Ba,Sr)(Al,Ga)_2S_4:Eu^{2+}$ etc.; and yellowemitting phosphors such as (Ba,Ca,Sr)(PO₄)₁₀(Cl,F)₂:Eu²⁺,Mn²⁺ etc. Still other ions may be incorporated into the phosphor to transfer energy from the emitted light to other activator ions in the phosphor host lattice as a way to increase the energy utilization. For example, when Sb³⁺ and Mn²⁺ ions exist in the same phosphor lattice. Sb³⁺ efficiently absorbs light in the blue region, which is not absorbed very efficiently by Mn²⁺, and transfers the energy to Mn²⁺ ion. Thus, a larger total amount of light from light emitting diode is absorbed by both ions, resulting in higher quantum efficiency.

[0050] The phosphor used in the invention may take the form of powder or particles. Phosphor particles may be prepared from larger pieces of phosphor material by any grinding or pulverization method, such as ball milling using zirconiatoughened balls or jet milling. They also may be prepared by crystal growth from solution, and their size may be controlled by terminating the crystal growth at an appropriate time. Typically, the phosphor particles have a size in the range of from 1 to 5 μ m in diameter.

[0051] Optional components may be added to the composition of the invention, for example, fire resistant properties can be improved by the addition flame retardant additives such as platinum compounds, carbon black, aluminium trihydrate, zinc or ceric compounds. It should be noted that carbon black addition also increases electrical conductivity. Ferric oxide may also be added to improve heat stability, titanium dioxide and other organometallic compounds as pigments.

[0052] The present invention further provides an encapsulant formulation for optoelectronic device such as LED, which comprises a phosphor and a Q-containing silicone. The Q-containing silicone typically has a Q% value of from 1% to 20%, preferably from 2% to 10%, and more preferably from 5% to 6%. The encapsulant formulation may optionally comprise other ingredients such as epoxy resin, silicone, stabilizer such as thermal stabilizer and UV-stabilizer, cure modifier, refractive index modifier, flame retardant, mold releasing additives, anti-oxidant, and plasticizing additive etc.

[0053] An encapsulant made from the formulation of the invention may be used as part of a so-called "LED package", which is the optical, electrical and/or mechanical support apparatus associated with a LED. Typically, such a package includes systems to provide thermal stability, mechanical stability, photon frequency conversion, optical focusing, electrical connection, thermal management, and so on.

[0054] The encapsulant of the present invention can be prepared by combining the various formulation components, and optional components if desired, in any convenient order. In various embodiments, all the components may be mixed together. In other embodiments, two or more components may be premixed and then subsequently combined with other components.

[0055] The encapsulant formulation of the present invention may be by hand mixed but also can be mixed by standard mixing equipment such as dough mixers, chain can mixers, planetary mixers, and the like. The blending can be performed in batch, continuous, or semi-continuous mode.

[0056] The present invention also provides a device including an optoelectronic device, a phosphor, and a Q-containing silicone. The Q-containing silicone typically

has a Q% value of from 1% to 20%, preferably from 2% to 10%, and more preferably from 5% to 6%.

[0057] As a skilled person in the art knows, optoelectronics is the branch of electronics that deals with solid-state and other electronic device for generating, modulating, transmitting, and sensing electromagnetic radiation in the ultraviolet, visible, and infrared portions of the spectrum. Optoelectronic device, sometimes referred to as semiconductor device or solid state device includes, but are not limited to, light emitting diodes (LEDs), charge coupled devices (CCDs), photodiodes, vertical cavity surface emitting lasers (VCSELs), phototransistors, photocouplers, opto-electronic couplers, and the like.

[0058] Encapsulation techniques for optoelectronic devices comprise casting, resin transfer molding and the like. After the device is enveloped in the uncured encapsulant formulation, typically performed in a mold, the formulation is cured. The curing may be conducted in one or more stages using methods such as thermal, UV, electron beam techniques, or combinations thereof.

[0059] With reference to Figure 5, the figure schematically illustrates a device according to one embodiment of the present invention. The device contains a LED chip 104, which is electrically connected to a lead frame 105. For example, the LED chip 104 may be directly electrically connected to an anode or cathode electrode of the lead frame 105 and connected by a lead 107 to the opposite cathode or anode electrode of the lead frame 105, as illustrated in FIG. 5. In a particular embodiment illustrated in FIG. 5, the lead frame 105 supports the LED chip 104. However, the lead 107 may be omitted, and the LED chip 104 may straddle both electrodes of the lead frame 105 with the bottom of the LED chip 104 containing the contact layers, which contact both the anode and cathode electrode of the lead frame 105. The

lead frame 105 connects to a power supply, such as a current or voltage source or to another circuit (not shown).

[0060] The LED chip 104 emits radiation from the radiation emitting surface 109. The LED may emit visible, ultraviolet or infrared radiation. The LED chip 104 may comprise any LED chip 104 containing a p-n junction of any semiconductor layers capable of emitting the desired radiation. For example, the LED chip 104 may contain any desired Group III-V compound semiconductor layers, such as GaAs, GaAlAs, GaN, InGaN, GaP, etc., or Group II-VI compound semiconductor layers such as ZnSe, ZnSSe, CdTe, etc., or Group IV-IV semiconductor layers, such as SiC. The LED chip 104 may also contain other layers, such as cladding layers, waveguide layers and contact layers.

present invention. In one embodiment, the LED packaging includes encapsulant 111 located in a package, such as a shell 114. The shell 114 may be any plastic or other material, such as polycarbonate, which is transparent to the LED radiation. However, the shell 114 may be omitted to simplify processing if encapsulant 111 has sufficient toughness and rigidity to be used without a shell 114. Thus, the outer surface of encapsulant 111 would act in some embodiments as a shell 114 or package. The shell 114 contains a light or radiation emitting surface 115 above the LED chip 104 and a non-emitting surface 116 adjacent to the lead frame 105. The radiation emitting surface 115 may be curved to act as a lens and/or may be colored to act as a filter. In various embodiments the non-emitting surface 116 may be opaque to the LED radiation, and may be made of opaque materials such as metal. The shell 114 may also contain a reflector around the LED chip 104, or other components, such as resistors, etc., if desired.

[0062] According to the present invention, a phosphor may be interspersed or mixed as a phosphor powder with encapsulant 111 or coated as a thin film on the LED chip 104 or coated on the inner surface of the shell 114. As described *supra*, any phosphor material may be used with the LED chip. For example, a yellow emitting cerium doped yttrium aluminum garnet phosphor (YAG:Ce³⁺) may be used with a blue emitting InGaN active layer LED chip to produce a visible yellow and blue light output which appears white to a human observer. Other combinations of LED chips and phosphors may be used as desired. A detailed disclosure of a UV/blue LED-Phosphor Device with efficient conversion of UV/blue Light to visible light may be found in U.S. Pat. No. 5,813,752 (Singer) and U.S. Pat. No. 5,813,753 (Vriens).

[0063] While the packaged LED chip 104 is supported by the lead frame 105 according to one embodiment as illustrated in FIG. 5, the LED can have various other structures. For example, the LED chip 104 may be supported by the bottom surface 116 of the shell 114 or by a pedestal (not shown) located on the bottom of the shell 114 instead of by the lead frame 105.

[0064] A device including a LED array fabricated on a plastic substrate is illustrated in Figure 6. With reference to Figure 6, the LED chips or die 204 are physically and electrically mounted on cathode leads 206. The top surfaces of the LED chips 204 are electrically connected to anode leads 205 with lead wires 207. The lead wires may be attached by known wire bonding techniques to a conductive chip pad. The leads 206, 205 comprise a lead frame and may be made of a metal, such as silver plated copper. The lead frame and LED chip array are contained in a plastic package 209, such as, for example, a polycarbonate package, a polyvinyl chloride package or a polyetherimide package. In some embodiments the

polycarbonate comprises a bisphenol A polycarbonate. The plastic package 209 is filled with an encapsulant 201 of formulation according to the present invention. The package 209 contains tapered interior sidewalls 208, which enclose the LED chips 204, and form a light spreading cavity 202, which ensures cross fluxing of LED light. Figure 7 shows a device in which the LED chip 304 is supported by a [0065] carrier substrate 307. With reference to Figure 7, the carrier substrate 307 comprises a lower portion of the LED package, and may comprise any material, such as plastic, metal or ceramic. Preferably, the carrier substrate is made out of plastic and contains a groove 303 in which the LED chip 304 is located. The sides of the groove 303 may be coated with a reflective metal 302, such as aluminum, which acts as a reflector. However, the LED chip 304 may be formed over a flat surface of the substrate 307. The substrate 307 contains electrodes 306 that electrically contact the contact layers of the LED chip 304. Alternatively, the electrodes 306 may be electrically connected to the LED chip 304 with one or two leads as illustrated in FIG. 7. If desired, the shell 308 or a glass plate may be formed over the encapsulant 301 to act as a lens or protective material.

[0066] A vertical cavity surface emitting laser (VCSEL) is illustrated in Figure 8. With reference to Figure 8, the VCSEL 400 may be embedded inside a pocket 402 of a printed circuit board assembly 403. A heat sink 404 maybe placed in the pocket 402 of the printed circuit board 403 and the VCSEL 400 may rest on the heat sink 404. The encapsulant 406 of the present inventive formulation may be injected into the cavity 405 of the pocket 402 in the printed circuit board 403 and may flow around the VCSEL and encapsulate it on all sides and also form a coating top film 406 on the surface of the VCSEL 400. The top coating film 406 protects the VCSEL 400 from damage and degradation and at the same time is inert to moisture and is

transparent and polishable. The laser beams 407 emitting from the VCSEL may strike the mirrors 408 to be reflected out of the pocket 402 of the printed circuit board 403.

[0067] It should be understood that the Q-containing silicone can also be used with non-light emitting chips and electronic components, for example, logic and memory devices, such as microprocessors, ASICs, DRAMs and SRAMs, as well as electronic components, such as capacitors, inductors and resistors.

[0068] While the invention has been illustrated and described in typical embodiments, it is not intended to be limited to the details shown, since various modifications and substitutions can be made without departing in any way from the spirit of the present invention. As such, further modifications and equivalents of the invention herein disclosed may occur to persons skilled in the art using no more than routine experimentation, and all such modifications and equivalents are believed to be within the spirit and scope of the invention as defined by the following claims. All patents and publications cited herein are incorporated herein by reference.

CLAIMS:

1. A composition, which comprises a phosphor and a Q-containing silicone.

- 2. The composition according to Claim 1, in which the Q-containing silicone has a Q% value of from 1% to 20%.
- 3. The composition according to Claim 1, in which the Q-containing silicone has a Q% value of from 2% to 10%.
- 4. The composition according to Claim 1, in which the Q-containing silicone has a Q% value of from 5% to 6%.
- 5. The composition according to Claim 1, in which the Q-containing silicone is an aliphatic silicone.
- 6. The composition according to Claim 1, in which the Q-containing silicone is prepared from hydrosilylation reaction.
- 7. The composition according to Claim 6, in which the hydrosilylation reaction uses Pt catalyst.
- 8. The composition according to Claim 7, in which the Pt catalyst concentration is from 5 to 20 ppm.

9. The composition according to Claim 7, in which the Pt catalyst concentration is from 10 to 15 ppm.

- 10. The composition according to Claim 1, in which the Q-containing silicone comprises a room temperature vulcanizing (RTV) silicone.
- 11. The composition according to Claim 10, in which the RTV silicone is a RTV-2 silicone.
- 12. The composition according to Claim 11, in which the RTV-2 silicone is selected from the group consisting of GE RTV 615, GE RTV 656, and GE RTV 655.
- 13. The composition according to Claim 1, which passes accelerated thermal aging greater than or equal to 150°C and simultaneous UV exposure greater than or equal to 300 milliwatts at 400nm.
- 14. An encapsulant formulation, which comprises a phosphor and a Q-containing silicone.
- 15. The encapsulant formulation according to Claim 14, in which the Q-containing silicone has a Q% value of from 1% to 20%.

16. The encapsulant formulation according to Claim 14, in which the Q-containing silicone has a Q% value of from 5% to 6%.

- 17. The encapsulant formulation according to Claim 14, further comprising other ingredient selected from the group consisting of epoxy resin, silicone, stabilizer such as thermal stabilizer and UV-stabilizer, cure modifier, refractive index modifier, flame retardant, mold releasing additives, anti-oxidant, and plasticizing additive.
- 18. A device, which includes an optoelectronic device, a phosphor, and a Q-containing silicone.
- 19. The device according to Claim 18, in which the optoelectronic device is selected from the group consisting light emitting diode (LED), charge coupled device (CCD), photodiode, vertical cavity surface emitting laser (VCSEL), phototransistor, photocoupler, and optoelectronic coupler.
- 20. The device according to Claim 18, in which the optoelectronic device is LED.

1 of 8

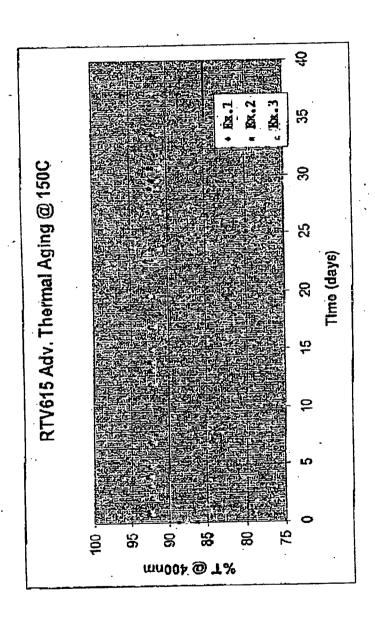


Figure 1

Figure 1

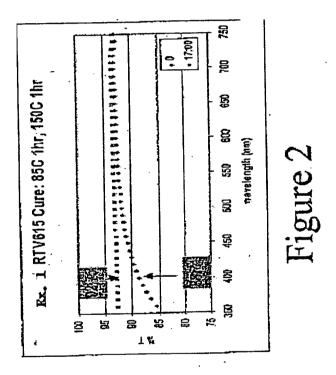


Figure 2

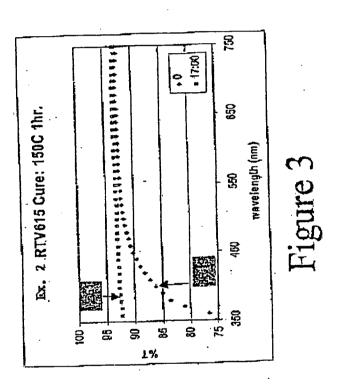


Figure 3

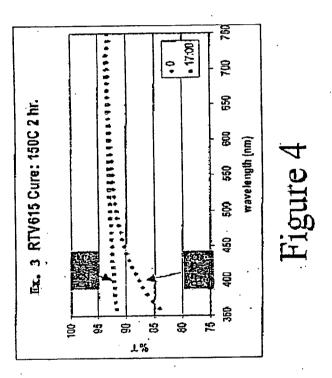


Figure 4

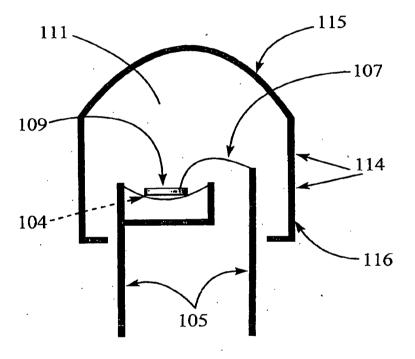


Figure 5

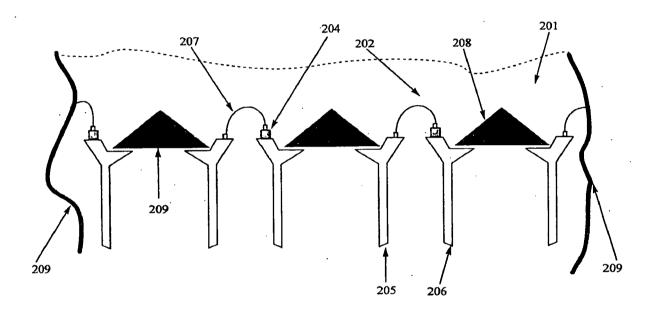


Figure 6

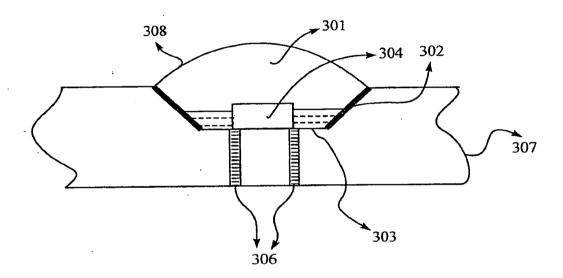


Figure 7

8 of 8

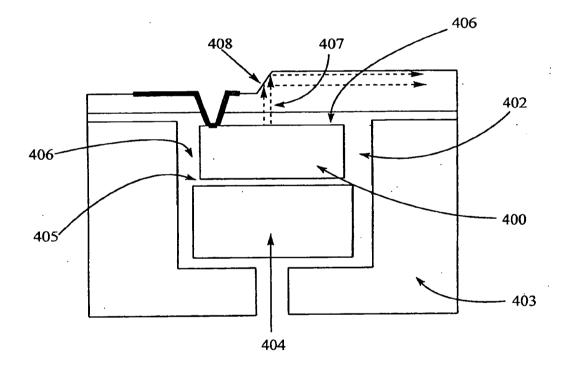


Figure 8

INTERNATIONAL SEARCH REPORT

International application No PCT/US2007/006076

A. CLASSIFICATION OF SUBJECT MATTER INV. C09K11/08 H01L H01L33/00 H05B33/04 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) CO9K HO1L HO5B 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 practical, search terms used) EPO-Internal, WPI Data C. DOCUMENTS CONSIDERED TO BE RELEVANT Citation of document, with indication, where appropriate, of the relevant passages Relevant to claim No. χ US 2002/185965 A1 (COLLINS WILLIAM DAVID 1-20 [US] ET AL COLLINS III WILLIAM DAVID [US] ET AL) 12 December 2002 (2002-12-12) * page 3, paragraphs [0027] to [0032], Figures, claims * WO 2005/098977 A (CREE INC [US]; ANDREWS PETER S [US]; COLEMAN THOMAS G [US]; χ 1-20 IBBETSON J) 20 October 2005 (2005-10-20) * page 3, line 33 through page 8, line 22, Figures 3A-3C, claims * χ WO 2005/101447 A (GELCORE LLC [US]) 1 - 2027 October 2005 (2005-10-27) * page 4, paragraph [0017] to page 7, paragraph [0031], Figures 1-3, claims \ast χ Further documents are listed in the continuation of Box C. See patent family annex. Special categories of cited documents: "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 "A" document defining the general state of the art which is not considered to be of particular relevance invention "E" earlier document but published on or after the international "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 filing date document which may throw doubts on pricrity claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "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. O' document referring to an oral disclosure, use, exhibition or *P* document published prior to the International filing date but later than the priority date claimed "&" document member of the same patent family Date of the actual completion of the international search Date of mailing of the international search report 24 August 2007 03/09/2007 Name and mailing address of the ISA/ Authorized officer European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016 Nemes, Csaba A.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2007/006076

		PCT/US2007/006076
C(Continua	tion). DOCUMENTS CONSIDERED TO BE RELEVANT	
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2004/124429 A1 (STOKES EDWARD [US] ET AL STOKES EDWARD [US] ET AL) 1 July 2004 (2004-07-01) * page 2, paragraph [0018] to page 3, paragraph [0036], Figures, claims *	1-20
X	EP 1 081 771 A (HEWLETT PACKARD CO [US]) 7 March 2001 (2001-03-07) * page 4, paragraph [0032] to page 6, paragraph [0045], Figures, claims *	1-20

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2007/006076

Patent document cited in search report		Publication date		Patent family member(s)		Publication date
US 2002185965	A1	12-12-2002	DE JP TW	10225778 2003110153 552724	A	03-04-2003 11-04-2003 11-09-2003
WO 2005098977	Α	20-10-2005	EP US	1730794 2005221518		13-12-2006 06-10-2005
WO 2005101447	Α	27-10-2005	US	2005227388	A1	13-10-2005
US 2004124429	A1	01-07-2004	NON			
EP 1081771	Α	07-03-2001	JP US	2001111117 6504301	. •	20-04-2001 07-01-2003