APPLICATION NOTE

Considerations for Encapsulant Material Selection for Phosphor-Converted LEDs

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Introduction: White light from Light Emitting Diodes (LEDs) is generated by combining blue photons from LED chips with photons of other colors from phosphor material(s). In a direct contact layout, blue LED chips are coated with phosphors. However, since phosphors are produced as powders, most LED manufacturers use an encapsulant material to suspend the phosphor powder and allow for easy deposition onto the blue LED chip. In this application note, we describe the different encapsulant requirements for various phosphor materials applications, the technical tradeoffs between encapsulant materials, and a number of case studies illustrating how to overcome challenges for some of the most common design goals.

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OVERVIEW: COMMON ENCAPSULANTS AND THEIR PROPERTIES

Many potential encapsulating materials, typically polymeric in nature, are commercially available with a wide variety of physical and performance characteristics. An LED package designer will evaluate the performance of materials along optical, mechanical, chemical and thermal metrics, with some figures of merit bearing more importance to the overall system performance than others. The consideration of these technical parameters is necessary for all successful designs. The material specific information contained in this application note represents the current state of the art, though the field is changing rapidly as LED package manufacturers become more and more sophisticated and demand higher performance from encapsulant vendors.

	Lifetime	Refractive Index	Viscosity (Pa-s)	Hardness	Working Time, RT
Dimethyl silicone	150°C, 1000 hr (98%)	1.41	0.5-5	35-70 JIS A	Varies
Phenyl silicone	150°C, 1000 hr (95%)	1.54	2-5	30-70 Shore D 25-60 JIS A	Varies
Epoxy	150°C, 500 hr	1.55	0.35-2	~90 Shore D	4-8 hr
Acrylic (PMMA)	>2000 hr weathering test	1.5	N/A	30-105 Rockwell	n/a
Polycarbonate	1500 hr weathering test	1.58	N/A	50-120 Rockwell	n/a

Table 1. Common encapsulants and their properties. Representative data. Specific grades may vary.

OPTICAL PARAMETERS

The first design consideration is often the set of optical parameters, which include measures such as the refractive index (RI), transparency, and retention of transparency over time.

Refractive Index (RI)

Snell's Law tells us that as light travels through a medium, changes in the refractive index will alter the light beam's path, leading, often, to lower light extraction out of the LED package as photons become trapped reflecting around the package rather than escaping as useable light. Therefore, the ideal condition is a perfect match of the index of refraction between all optical components in the system, in order to prevent unintended reflections during both the absorption and emission steps of the phosphor down conversion process. Typically, though, the refractive index of the blue LED material is generally around 2.4[1], while most phosphor materials have indices of refraction in the 1.8-2.0[2] range and most encapsulants have RI values from 1.4 to

1.6[3]. Clearly, such a perfect three-way match is impossible; nevertheless a RI of the encapsulant on the higher end of their range does result in better light extraction, and is therefore desirable. Further, the interface at the chip is much less important than the interface between the phosphor and the encapsulant, since photons will scatter with much greater frequency between these two integrated optical components and any ability to reduce that scattering will significantly increase the photon extraction. On the other hand, most photons that reflect back to the chip are lost to heat after a single reflection, with no chance of recovery regardless of the index of refraction difference.

Transparency

Another optical parameter, the transparency of a material, is simply a metric measuring the amount of photons that are lost, typically to absorption, as they travel through the material. As one might imagine, the higher the transparency of an encapsulant, the less it gets in the way of useable light escaping from the LED package. In the ideal case, an encapsulant material is 100% transparent to visible light.

Retention of Transparency over Time

Retention of transparency over time is often far more important than the initial transparency of a material. This requirement is particularly acute for many LED manufacturers that seek to achieve at least 70% of their light output for a minimum of 25,000 hours of operation, due to Energy Star or other industry standards requirements.[4] Generally, the transparency over time parameter is the one given the most weight in encapsulant selection, and it is the one reason that dimethyl silicones have found widespread adoption despite having a refractive index closer to 1.4. Phenylmethyl silicones have a higher RI, around 1.5, but often show yellowing during aging, which both reduces the light output and shifts the color point of the white light. The tradeoff of higher RI for yellowing with age may be acceptable in certain high performance packages, which are closely monitored and replaced before the performance degrades, or, separately, in packages that are not expected to have a long operating life, or where initial package brightness is a high priority.

MECHANICAL PROPERTIES

The mechanical properties of encapsulants serve a key function – to protect the LED assembly from the outside environment. This is generally a balancing act between rigidity and elasticity, where weak wire connections and the rest of the assembly need protection from external forces while the system needs to have the ability to flex with thermal expansions and contractions without generating cracks where light is lost to scattering. Epoxy encapsulants were widely used in low power LEDs during the infancy of the LED lighting industry, but they have not shown high resiliency as today's high power (high brightness) LEDs have generated more and more heat. For this reason, epoxy encapsulants have generally been replaced by the more forgiving elastic silicones.

Other mechanical properties of encapsulants that are important to consider include properties of the encapsulant before curing, as well as the cure parameters. The requirements for these curing related properties will vary greatly depending on the LED packaging process, though the uncured mechanical property of greatest interest (uncured chemical properties will be addressed later in this note) is the viscosity. Typical LED phosphors vary in particle size from 4 microns to 30 microns in diameter and in density from 3.0 g/cm^3 to 6 g/cm^3. It is necessary for the phosphor to maintain a uniform mixture within the encapsulant from the time of mixing through deposition and final cure. For example, if phosphor particles settle during the deposition process, it is likely that there will be a wide distribution of color points formed, typically by spreading out the color point of the final product from the center point of the white color bin towards the upper right and lower left corners of the bin (see Chart 1). In fact, excessive settling could even shift the color point of the LED package away from pure white, resulting in greenish or pinkish tints in portions of the lot.

Another consideration is differential settling in phosphor blends formed for warm white or high CRI products. Phosphors in the red nitride family tend towards the lower end of the density range, while the yellow and green phosphors with which they are blended tend towards the higher end of the density range. Differential settling can result in shifting of the color point of the products from the upper left to the lower right within the bin – or even out of the bin (see Chart 2).

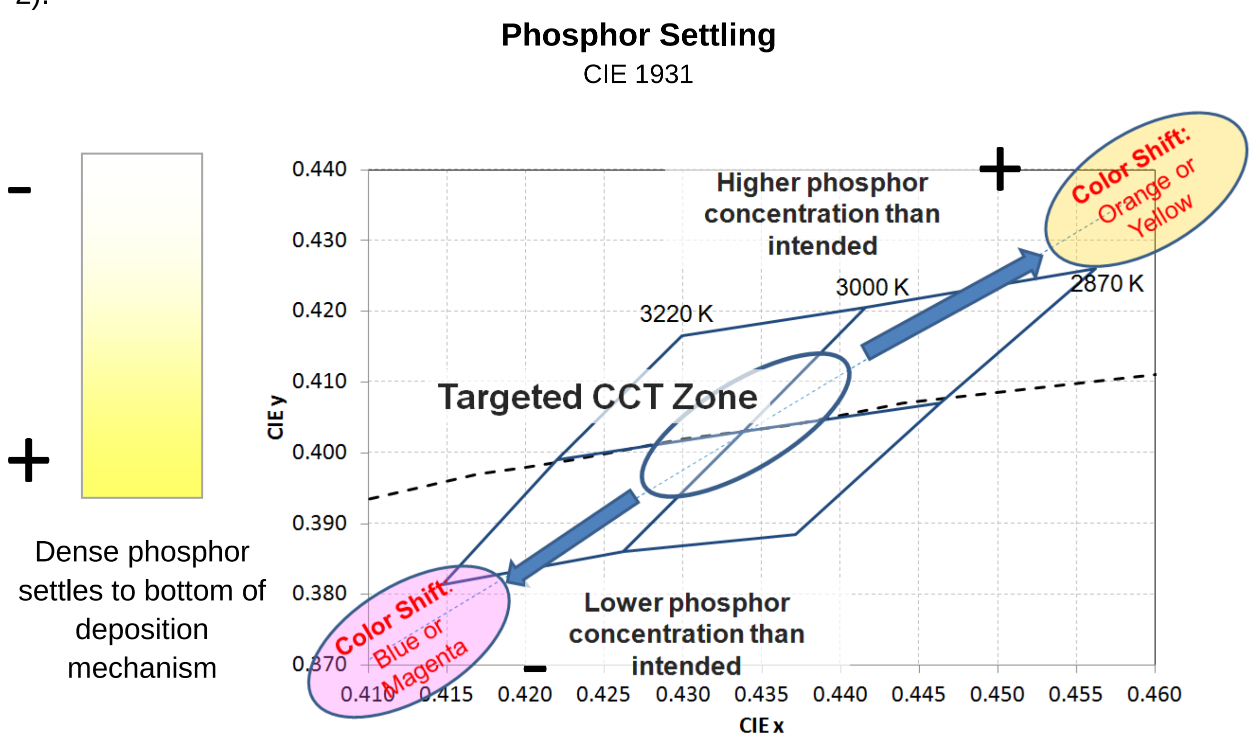

Chart 1. If phosphor particles settle during the deposition process, a wide distribution of color points is formed from the upper right to the lower left corners of the bin

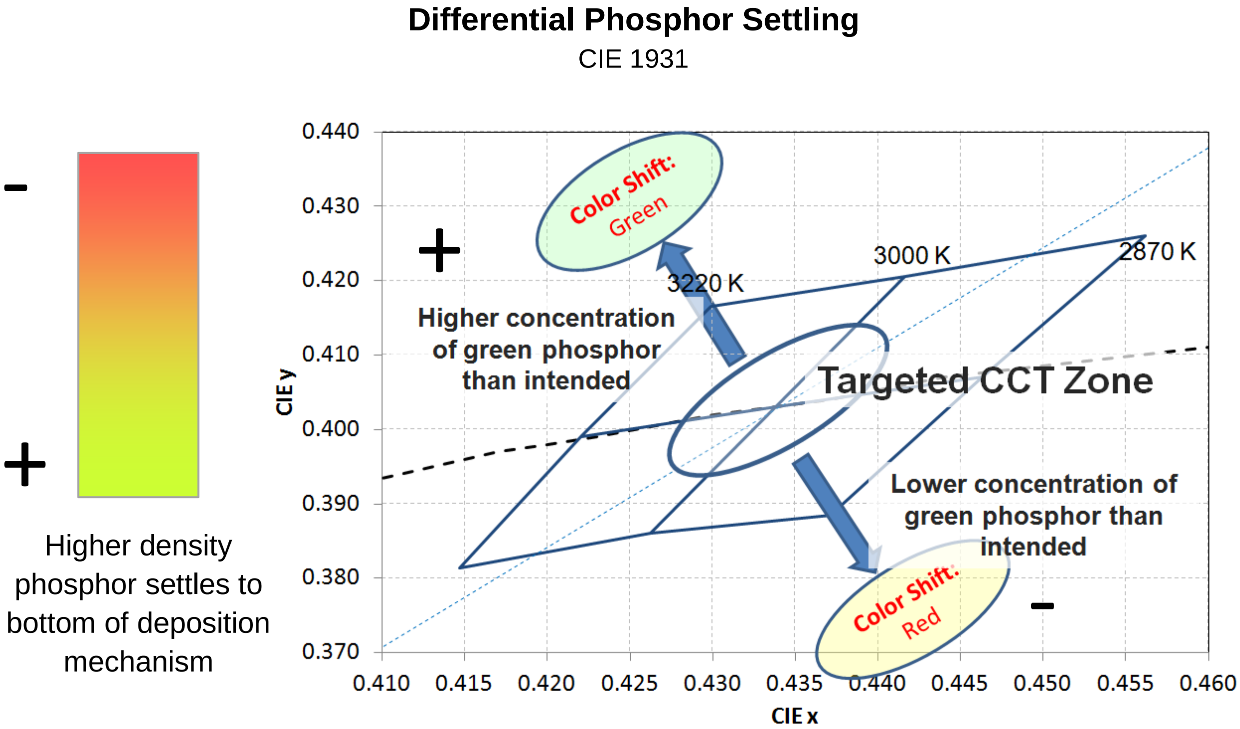

Chart 2. Differential settling can result in shifting of the color point of the products from the upper left to the lower right within the bin – or even out of the bin

While a high viscosity encapsulant would seem to be desired to prevent settling, it turns out a higher viscosity typically implies longer preprocessing times with slower depositions, so these two requirements must be balanced. The cure time (or pot time) is also important, as a change in viscosity during the packaging/deposition can change the amount of phosphor and encapsulant deposited, mimicking the product distribution/spread outlined in the case of single particle settling outlined above. Architecture will also factor in; for example, higher viscosity is necessary for wide area chip-on-board applications compared to traditional chip in cup packages.

CHEMICAL COMPATIBILITY

Another important consideration is the chemical compatibility of the encapsulant with the system. All phosphors exhibit some susceptibility to moisture, acids and oxidizers, though the extent of susceptibility depends on the family of phosphor. Phosphors are susceptible to degradation through failures either in the host material, such as a Silicate or a Nitride, or in the chromophore, which is to say, typically the rare earth element responsible for the electronic structure that makes down conversion possible. Silicates, due to the higher porosity of the orthosilicate structure and the stability of the active, divalent europium state relative to the inactive trivalent state, are the most susceptible. Nitrides and oxynitrides have a more robust crystal host, but still are susceptible to europium oxidation. Garnets and aluminates have robust crystal hosts and the trivalent cerium chromophore is less susceptible to further oxidation making them the least susceptible to the environment. For these reasons, it is desirable for the encapsulant to be hydrophobic and to form a good barrier against vapor phase intrusions. Silicones tend to perform well when mapped against the properties shown in Table 2.

↑ Chromophore Stability Increases	Sulfides:Ce^{3+}	YAG, GAL
	Orthosilicates, Sulfides:Eu^{2+}	Nitrides, Oxynitrides
	Host Stability Increases →	

Table 2. Silicone performance as related to chromaphore and host stability

Another important chemical parameter often neglected in considerations is the off-gassing product of the cure. Some silicone resins, typically those used specifically to create water tight seals, cure by elimination of acetic acid. These types of materials should be avoided not just for encapsulation, but anywhere in the LED module or luminaire due to the potentially corrosive effect of the acetic acid. Further, off-gassing may result in a mechanical change in the encapsulant, which could alter the ability of the material to meet the structural requirements discussed earlier.

Other chemical compatibility concerns focus on the potential surface chemistry interactions of the phosphor with the encapsulants. Dimethyl silicones, in general show no interactions. However, with other encapsulant systems, the very basic (i.e. high pH) surface chemistry of the orthosilicates can be a factor. Additionally, the rare earth ions used as chromophores in the phosphors can catalyze reactions, such as polymerization and depolymerization of the encapsulants. Such reactions can result in clouding of otherwise transparent systems or unexpected changes in viscosity of the encapsulant during processing. In general, it is best to work with materials already qualified as LED phosphor encapsulants; however, if non-qualified materials must be used, both the phosphor and encapsulant manufacturer should be consulted for potential drawbacks and alternate solutions.

THERMAL CONDUCTIVITY

Expansion and contraction of encapsulants with temperature was discussed earlier, but thermal conductivity of the encapsulant is another parameter to consider, especially in the high brightness (and thus high temperature) applications which are increasingly seen as the de facto standard operating conditions in major applications. Phosphors, however, tend to operate better when kept at lower temperatures. Since the LED die is the major source of heat in an LED package, it is desirable that the encapsulant insulate the phosphor from the heat produced by the die. However, in certain applications, such as those where the phosphor is spatially separated from the die, it is necessary to consider that the phosphor is itself a heat source. Energy lost in the down conversion process and energy lost to quantum efficiency losses are manifested as heat, and the ability to remove that heat from the phosphor could be a desirable requirement. At the current time, no commercial solutions offer the high transparency, long life, and high thermal conductivity to excel in this type of application, but be sure to check with encapsulant providers, as new products are released frequently.

CURING

There are two common methods of encapsulant cure – temperature and ultraviolet exposure. The prime consideration with temperature cure systems is the robustness of the package components, as most phosphor is able to withstand, without permanently degrading, processing temperatures of 200°C (400°F), which is above normal cure temperatures. UV cure systems are generally compatible with phosphors, but consideration must be given to the ability of the phosphor to absorb some of the UV energy and convert it into visible light energy, resulting in the need for longer exposure/cure times, or higher exposure intensities.

CASE STUDIES

Case Study 1: Reduced Light Output

A customer had prototyped a medium power, high brightness lighting system utilizing orthosilicate phosphor encapsulated in polyurethane. For production, the customer needed to change over to polymethylmethacrylate (PMMA), but in the pilot run samples, the light output dropped significantly compared to the prototypes. Analysis of the failed samples showed no evidence of phosphor degradation, but it did show evidence of foaming in the polymer. This foaming was acting as a diffuser and reducing the light output. Ultimately, the foaming was attributed to a chemical reaction between the phosphor and the polymer. Because the customer was locked into using PMMA, the customer changed to a GAL series green phosphor, and encountered no further chemical compatibility issues.

Case Study 2: Color Shift

A customer was developing a high power, high brightness chip-on-board lighting system. The system was utilizing a mixture of a green aluminate (GAL) phosphor and a red nitride phosphor to deliver a high CRI warm white solution. During pilot studies, the customer noticed that delivered CCT shifted during the course of the run. Analysis of the color shift was determined to be caused not by a shift in the amount of phosphor, but by a shift in the phosphor blend ratio. This shift in blend ratio during the course of the run was attributed to differential settling of the phosphors due to the wide differences in the materials' densities and the low viscosity of the silicone encapsulant being used. The recommendation was for the customer to reduce pot time of the phosphor/silicone slurry, shift to a higher viscosity encapsulant, or potentially both. The customer shifted to a higher viscosity encapsulant and noted significantly less color variation.

Case Study 3: Maximizing Brightness

A customer was developing a high brightness, high color rendering lighting system for an entertainment industry application. The customer was looking to maximize brightness, and was not as concerned with lifetime due to the niche application. The customer was able to switch from the dimethyl silicone they had been using to a phenyl silicone system and increase their brightness by several percent.

SUMMARY

There are many parameters to examine with respect to choosing the correct encapsulant for phosphor in an LED system. Generally speaking, the LED industry today leans towards dimethylsilicones as the first choice primarily due to their long transparency lifetime, and ease of processability. Other solutions are currently under development by encapsulant manufacturers, and may offer higher RI and longer lifetime.

For more information, visit www.intematix.com
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[1] http://www.lrc.rpi.edu/programs/solidstate/cr_impact.asp, accessed on September 30, 2011.
[2] http://www.lrc.rpi.edu/programs/solidstate/cr_impact.asp, accessed on September 30, 2011; US **7547888**; CRC handbook of optical materials.
[3] http://www.lrc.rpi.edu/programs/solidstate/cr_impact.asp, accessed on September 30, 2011.
[4] ENERGY STAR® Program Requirements Product Specification for Luminaires (Light Fixtures) Eligibility Criteria Version 1.1, ENERGY STAR® Program Requirements for SSL Luminaires – Version 1.3, and ENERGY STAR® Program Requirements for Integral LED Lamps Eligibility Criteria - Version 1.4.