Phosphors and Silicone Dispersions
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Presented at the Phosphor Global Summit, February 28 – March 2, 2005, San Diego, CA.
Abstract
From the perspective of a silicone material chemist, this paper will address the benefits of using silicone in phosphor dispersions for High Brightness LED (HBLED) packages. This investigation first provides an overview of how versatile a material silicone can be to the HB LED industry. An examination of the chemistry of silicone, the multiple material composition options and various cure chemistries demonstrates how silicone can be tailored to fit specific applications. A brief discussion of both physical and optical properties of two types of material compositions, Cured Gels and Thermosets, the most common types used in HB LED packaging. Then, a general investigation of the way a silicone interacts with a phosphor, in regards to compatibility, particle size and potential interactions. The paper will also review methods of dispersion, processing considerations and equipment.

Introduction
In a Lumileds patent filed in 2002, they discuss the problem of large particle size phosphor, 2-20 microns, embedded in lower refractive index, 1.50, ‘host’ material like silicone, causing light losses due to scattering. The more phosphor added the worse the problem becomes. Also, this problem continues when the refractive index of the phosphor is increased without increasing the refractive index of the ‘host’ material. Lumileds provided a statistic of 50% light power lost due to this scattering effect. They reference several ways to overcome this problem, decreasing particle size of the phosphor, increasing the refractive index of the ‘host’ material, and improving the dispersion of the phosphor into the ‘host’ material.

The chemistry behind silicone essentially equates to material versatility, and this versatility allows silicone materials to be custom designed to fit HB LED applications. The polymer chemistry that constitutes silicones allows various types of silicone polymers, which each provide varying properties beneficial to different applications. Silicone chemistry also makes a diverse set of material compositions available for a broad range of applications. Finally, silicone cure chemistry provides options to optimize how a silicone can be used when applied to specific applications.

Silicone Chemistry
The term “Silicone” is actually a misnomer. Normally the suffix ‘-one’ delineates a substance has a double bonded atom of oxygen in its backbone. Scientists initially believed that silicone materials contained double bonded oxygen, hence the use of ‘silicone.’ However, silicones are really inorganic polymers, having no carbon atoms in the backbone, and therefore should be named ‘Polysiloxanes.’ The diagram below shows their typical structure:

\[
\text{\begin{tabular}{cccccccc}
R & R & R & R & R & R & R \\
\cdots & \text{Si} & \text{O} & \text{Si} & \text{O} & \text{Si} & \text{O} & \text{Si} & \text{O} & \cdots \\
\text{R} & \text{R} & \text{R} & \text{R} & \text{R} & \text{R} & \text{R} & \text{R} \\
\end{tabular}}\]

[1]
R=CH₃, phenyl (aromatic carbon ring), F₃CCH₂CH₂, CHCH₂

This structure allows polysiloxanes to be used in a wide array of applications because this structure allows for different types of polysiloxanes. Different polysiloxanes can provide a variety of excellent elastomeric properties that can be chosen according to the specific application; temperature stability (-115 to 260°C), fuel resistance, optical clarity (with refractive indexes as high as 1.60), low shrinkage (2-%), and low shear stress (2). Different types of silicones, or polysiloxanes, and their property advantages include:

Dimethyl silicones, or dimethylpolysiloxanes, are the most common silicone polymers used industrially. These types of polymers are typically the most cost effective to produce and generally yield good physical properties in silicone elastomers and gels. The polymer pictured below contains vinyl endgroups that participate in a platinum catalyzed addition reaction (see section on Cure Chemistry for more information). All dimethylpolysiloxanes have a refractive index of 1.40, 25°C at 598nm.

Methyl phenyl silicone systems contain diphenyldimethylpolysiloxane copolymers. The steric hindrance of the large phenyl groups prohibits significantly high concentrations of diphenyl units on the polymer chain. The phenyl functionality boosts the refractive index of the polymers and silicone systems that use these polymers from 1.40 upwards to 1.60. Silicone polymers with diphenyl functionality are useful in biophotonic applications (e.g., intraocular lenses) where higher refractive index materials can be useful in creating a thin lens. The diagram below shows a typical structure for a methyl phenyl silicone:

Fluorosilicones are based on trifluoropropyl methyl polysiloxane polymers and used for applications that require fuel or hydrocarbon resistance. The trifluoropropyl group contributes a slight polarity to the polymer, resulting in swell resistance to gasoline and jet fuels. However, polar solvents such as methyl ethyl ketone and methyl isobutyl ketone may significantly affect fluorosilicones. While some fluorosilicones contain 100% trifluoropropylmethylpolysiloxane repeating units, other systems contain a
combination of the fluorosiloxane units and dimethyl units to form a co-polymer. Adjusting the amount of trifluoropropyl methyl siloxane units in the polymerization phase provides optimal performance in specific applications. For photonic applications, the refractive index is 1.38 at 25ºC at 598nm. The diagram below shows a typical structure for a fluorosilicone:

![Structure of Fluorosilicone](image)

**Material Composition**

While the polymer chemistry and structure of silicone provide the different types of silicones outlined above, they also allow those different types of silicones to appear in a wide variety of material compositions. This broad range of material compositions makes silicone a viable option to endless numbers of HB LED packaging applications such as die encapsulation, die attach adhesive and lens type material.

Silicone Fluids are non-reactive and reactive silicone polymers formulated with dimethyl, methylphenyl, diphenyl, or trifluoropropylmethyl constituent groups, with refractive index ranging from 1.38 to 1.60. These materials’ viscosity depends largely on molecular weight of the polymer and steric hindrance of functional groups on the polymer chain and can range from 100cP (a light oil) to an extremely thick gum polymer. Fluids are typically used to fill air gaps in high temperature lens assemblies in order to displace dust, permit cooling action or reduce interfacial reflections. Also to fill lenses or micro channel waveguides because of the large thermo-optic coefficient of 2 to 5 x 10^-4/ºC. Optical fluids can be used as the working medium in bubble-action optical switches or attenuators.

Silicone Thixotropic Gels are comprised of an optical fluid immobilized in a nanoparticle powder. These gels have no curing characteristics and by nature they are thixotropic and do not have well-defined viscosities. At rest they are mechanically stable and will not migrate. Due to the index matching limitations of the nanoparticle powder, these materials are available from 1.46 to 1.59 refractive indices only. Their primary use is for improving the return loss in a single mode mechanical fiber splice.

Silicone Curing Gels contain reactive silicone polymers and reactive silicone crosslinkers in a two-part system. When mixed together these materials are designed to have a very soft and compliant feel when cured and will stick to substrates without migrating. Viscosities can be adjusted with the molecular weight of the polymers from 200 – 10,000cP. Depending on the functionality of the polymer, optical index matching can be formulated from 1.38-1.57. For HBLED applications this allows for the optimal light to come out of the die while protecting it from dust, moisture, vibration and changes in temperature. The yield strength of the gel is low enough to permit wire bonds to slice
through during thermally induced micromotion without risking wire bond failure. Steps need to be taken to manufacture these materials with minimal outgassing and low ionic species. Other applications besides encapsulating HBLEDs include potting of packaged modules such as transponders, transceivers and detector arrays.

Silicone Thermosets fall into two categories, moldable elastomers and adhesives. Like the Gels, these two-part systems contain reactive polymers and crosslinkers that cure up to a rubbery type hardness. Most will cure at room temperature, however some need heat to cure. To impart increased physical properties, typically these materials have higher viscosities. The moldable materials can be casted or injection molded into HBLED lenses. They have inherently stronger physical properties than the gels and can work as excellent adhesives in optical applications. Special versions of these can be produced to have extremely low outgassing for electronic and aerospace applications. These also can have the broad refractive index range of 1.38 – 1.57.

Silicone resins can range in structure from a highly branched amorphous resin to a regular ordered silsesquioxane, T Cube. Resin viscosities range from pourable to millions of centipoises. The empirical formula is:

\[ \text{R - Si - O}_{1.5} \]

Both the Polysilsesquioxane and T-resin names can be derived from the empirical formula. The root “sesqui” indicates the one and a half stoichiometry of the oxygen bond to silicon. T-resin indicates the trisubstitution of silicon by oxygen. The organic, or “R,” group also names silicone resins. These materials when cured can give very hard durometers up to Type D. The phenyl content can be adjusted providing refractive index from 1.40-1.57. Sample Resin Structures:

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**Amorphous**

**T, Cube**
Cure Chemistry

When a manufacturer in the HB LED industry chooses a material for a specific application, material properties aren’t the only deciding factor. That manufacturer also has to examine how the material is used. Inconvenience in production or material by-products can make a chosen material ineffective for a specific application. Silicones, however, can be designed around various cure chemistries to accommodate different production needs. Silicone systems can cure by platinum catalyzed addition cured systems, tin condensation cure systems, peroxide cure systems, or oxime cure systems. Some of the oldest cure chemistry used with silicones utilizes an acetoxy tin condensation cure system, such as used in household bathroom caulk. These systems yield a vinegar-like smell (acetic acid), a byproduct of the reaction. For various reasons as described below, platinum systems are the most appropriate for HBLED applications.

Platinum catalyzed silicones utilize a platinum complex to participate in a reaction between a hydride functional siloxane polymer and a vinyl functional siloxane polymer. The result is an ethyl bridge between the two polymers. The reaction mechanism is pictured below:

Platinum systems are often cured quickly with heat, but can be formulated to cure at low temperatures or room temperature if necessary. The advantages of these systems include a flexible cure schedule and no volatile byproducts. The possibility of inhibiting the cure is the main disadvantage of platinum systems. Inhibition is defined as either temporarily or permanently preventing the system from curing. Some types of inhibitors are purposefully added to these systems to control the rate of cure. However, contact with tin, sulfur, and some amine containing compounds may permanently inhibit the cure. Compounds that inhibit the cure can be identified easily by attempting to cure a platinum catalyzed system in contact with the compound, as inhibition results in uncatalyzed regions of elastomer systems or inconsistency in cure over time.

Tin condensation systems involve hydroxyl functional polymers and alkoxy-functional crosslinking compounds. The alkoxy functional crosslinker first undergoes a hydrolysis step and is left with a hydroxyl group. This hydroxyl group then participates in a condensation reaction with another hydroxyl group attached to the polymer. The reaction can proceed without the assistance of the tin catalyst, but the presence of the catalyst boosts the rate of reaction. The reaction mechanism is pictured below:
The main disadvantages of condensation systems are the leaving group, shrinkage and long cure time, as several days are often required for to completely cure an elastomer.

Peroxide catalyzed systems, have a reaction mechanism that involves a peroxide catalyst and either methyl groups or vinyl functional groups. The peroxide catalysts create free radical species of the methyl and vinyl that can then form covalent bonds. Pictured below is the reaction mechanism involving a peroxide catalysis of two methyl groups:

\[
\begin{align*}
    \text{OR} \quad \text{RO-Si-OR} + 4\text{OH} & \xrightarrow{\text{Moisture}} \text{Si-O-Si} + 4\text{ROH} \\
    \text{OR} & \\
\end{align*}
\]

Disadvantages include a lengthy post-curing step at high temperatures in order to remove the reaction’s byproducts. Other disadvantages include the possibility of the catalyst interacting with active agents.

**Physical Properties**

We will focus on two of the material types, Curing Gels and Thermosets, and describe various physical properties attainable. Durometer is the hardness of the cured material tested as penetration, Type “OO”, Type “A”, and Type “D”. Curing Gels, designed to be loosely crosslinking materials, will have either a penetration or a Type “OO” value. Penetration, the softest durometer, is tested on a penetrometer. The penetrometer allows a defined foot, or probe, to push into the cured sample at a defined force producing a measurement.

Referencing ASTM D 2240, Type “OO” durometer is measured by curing a sample at least 0.25” thick and placing it on a test stand with Type “OO” indenter. The indenter is forced down into the material at a constant force and a measurement is obtained. Thermosets will have durometers in the Type “A” and Type “D” range, which is harder than Type “OO”. These are tested just like the “OO” except using a Type “A” or Type “D” indenter. As an example, a pencil eraser has a Type “A” durometer of 60 and a hardwood desktop a Type “D” durometer of 90. Cured gels and thermosets can be formulated to within ±10% of practically any hardness, from a penetration of 25mm to Type “D” of 30. The hardness for the HB LED packager depends on the application and
what is being achieved. For wire bond stress and die protection, a soft Type “OO” 10, may be used. To eliminate the need for a lens and provide more durability, a harder Type “A” 40 may be used.

Lap Shear, following ASTM D1002, this test demonstrates the adhesive strength of a material to stainless steel or other substrates that one would want. Each substrate of choice is cut into a lap shear configuration, 1 inch wide by 4 inches long. Six strips of each substrate are prepared to make 3 test panels. Panels are cleaned with isopropanol to remove dirt, grease or particulates. To improve adhesion a primer is sometimes added to one square inch area on one end of each lap panel as described above and let to sit for at least 30 minutes. A bond thickness target of 5ml(0.005in) is used for applying the Curing Gel or Thermoset to the primed area of the panels. The two panels are pressed together forming a sandwich (See Figure 1). The sandwiched panels are then cured as required.

Because of their weak crosslinking, most cured gels cannot be tested in this way. Current data shows 1.46 refractive index, silica filled thermoset materials to have the best adhesion to aluminum at over 500psi. NuSil technology is currently involved in more extensive adhesion studies, looking at higher refractive index materials and many of the common substrates used in HB LEDs; silver, gold, ceramic and polyphthalamide (PPA).

Figure 1. Lap joint.

Tear Strength referencing ASTM D 624, is a standard test to determine the tear properties of a cured material test sample to which a specific “cut” has been made to initiate the “tear”. These figures typically given in pounds per inch (ppi), or their metric equivalent kN/m, describe the internal integrity of the material. Tear is a good descriptor of how well the material might wear under physical demands. Again, because of the low crosslinking, cured gels exhibit very low tear strength. The thermosets with refractive index up to 1.46 can reach 75ppi. Developmental materials have been produced with higher refractive indices, that exhibit 30ppi. The limitation to higher refractive index materials is due to the inability to add reinforcing fillers.

Tensile Strength based on ASTM D 412, is a standard test to determine the strength of a material given a determined amount of strain. These figures typically corresponding to units of pounds per square inch or their metric equivalent mega Pascals, MPas. The higher the number the stronger the material. For Curing Gels, like tear, tensile values are too low to test. Also, similarly, 1.46 thermosets can get as high as 1200psi, while developmental materials >1.46 report 600psi.

Coefficient of Thermal Expansion (CTE) is the measured expansion of a cured material under heat measured per 1°C rise or fall of temperature. Tested per ASTM D-3386-00, CTE reports above and below the glass transition temperature range as parts per million (PPM), i.e. LS-XXXX has a CTE value of 260 ppm per °C. Silicone materials typically have higher CTE values than other adhesive systems like epoxy, urethane, and acrylics, and in combination with their low modulus, allows them to be great bridge
materials between two substrates with dissimilar CTE values. If a low CTE material were used as a bridge it would probably stress the substrates it is attached to and cause cracking.

Volatile Content and Low Outgassing, based on ASTM D 2288 and E-595, determines the amount of material that does not get cured in a Cured Gel or Thermoset. This material does have the possibility of being outgassed under heat and pressure. Volatile content, ASTM D 2288, is determined by weighing a cured sample before and after being exposed to 150°C in a forced air oven for 3 hours. Most cured silicone gels and thermosets can be formulated to have 0 volatile content and match the E-595 requirements for low outgassing. Most materials used in HBLEDs should have at least <0.5 volatiles.

Ionic Content, or Elemental Analysis of Trace Metals, is a water-extract test to determine the level of ionic contamination in a material. It commonly follows the requirements set out by MIL-STD-883E; <200ppm Chloride, < 50ppm Sodium, < 50ppm Potassium and < 50ppm Fluoride. The test involves placing 3 grams of the cured material into a cleaned flask. The weight of the material is recorded to the nearest milligram and 150 grams of deionized water with low measured conductance is added. The flask is refluxed at 150°C for 20 hours. Several of the silicone cured gels and thermosets have been tested and fall under the MIL-STD-883E requirements.

Thermal Gravimetric Analysis (TGA) is a method for determining the thermal degradation of a material by measuring the weight loss of a material as the material is heated. Results are plotted as material weight percent vs. temperature. Testing of several silicone cured gels and thermosets show TGA at 1% weightloss to be 300-360°C.

Viscosity, a standard test to determine how thin or thick a liquid is. Used as a comparative figure, units are typically in centipoise, cps, or centistokes, cst, both essentially the same until comparing thicker liquids, or their metric equivalent milli Pascal seconds, mPas. Water is essentially 1cP, Pancake syrup 2500cP, honey 10,000cP, and peanut butter is around 250,000cP. For cured gels and thermosets, viscosity is measured prior to cure, often in the mixed form for a two-part system. Although there are limitations based on the overall properties, viscosity can be formulated to within ± 10% of any thickness desired. Current materials exist from 200 to 250,000cP.

Optical Properties

Refractive Index, the measurement of the speed of light traveling through a transparent material. It is measured at 589 nanometer (nm) wavelength (a.k.a. “the Sodium D line”, or “nD”) with a refractometer using the method of ASTM D-1218 at a fixed temperature of 25.0°C. As previously mentioned, silicones have a refractive index range of 1.38-1.60. Figure 2, provides a chart of various substrates and their refractive index.
Refractive Index of Common Substances

<table>
<thead>
<tr>
<th>Material</th>
<th>Acronym</th>
<th>Tradenames</th>
<th>nD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td></td>
<td></td>
<td>1.34</td>
</tr>
<tr>
<td>Polytetrafluoroethylene</td>
<td>PTFE</td>
<td>Teflon®</td>
<td>1.34</td>
</tr>
<tr>
<td>Magnesium Fluoride</td>
<td>MgF2</td>
<td></td>
<td>1.38</td>
</tr>
<tr>
<td>Fused quartz</td>
<td></td>
<td></td>
<td>1.46</td>
</tr>
<tr>
<td>Acrylate</td>
<td>PMMA</td>
<td>PLEXIGLASS®</td>
<td>1.49</td>
</tr>
<tr>
<td>Cyclic Olefin</td>
<td>COC</td>
<td>Topas®</td>
<td>1.53</td>
</tr>
<tr>
<td>Diphenyldimethylsiloxanes</td>
<td>PVMQ</td>
<td>Up to 1.60</td>
<td></td>
</tr>
<tr>
<td>Polycarbonate</td>
<td>PC</td>
<td>Lexan®</td>
<td>1.59</td>
</tr>
<tr>
<td>Aluminum Oxide</td>
<td>Sapphire</td>
<td></td>
<td>1.76</td>
</tr>
<tr>
<td>Yttrium Aluminum Garnet</td>
<td>YAG</td>
<td></td>
<td>1.80</td>
</tr>
<tr>
<td>Gallium Nitride</td>
<td>GaN</td>
<td></td>
<td>2.5 to 2.7</td>
</tr>
<tr>
<td>AlGaInP</td>
<td></td>
<td></td>
<td>3.25</td>
</tr>
</tbody>
</table>

Figure 2. Refractive Index of common substrates

Refractive index versus change in temperature is conducted at 25°C to 50°C in 5-degree steps. Typical data are reported as shown in Figure 3, and the least squares linear regression fit to the data for the thermo-optic coefficient (in units of dn/dT) is also calculated and provided on the chart.

**Refractive Index vs. Temperature, 5 λ's**

*Lightspan Encapsulation Gel*

*LS-3252, Lot# 20423-0417*

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**Linear Regression Fit for Thermo-optic Coefficient (dn/dT):**

- $\lambda = 411$ nm: $dn/dT = -3.92 \times 10^{-4}$ °C
- $\lambda = 589$ nm: $dn/dT = -4.07 \times 10^{-4}$ °C
- $\lambda = 833$ nm: $dn/dT = -3.58 \times 10^{-4}$ °C
- $\lambda = 1306$ nm: $dn/dT = -3.65 \times 10^{-4}$ °C
- $\lambda = 1550$ nm: $dn/dT = -3.11 \times 10^{-4}$ °C

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Figure 3

Refractive Index versus change in Wavelength data are measured at 411nm, 589nm, 833nm, 1306nm and 1550nm at 25.0°C and presented as shown in Figure 4.
Coefficients are also printed on the plot for a Sellmeier dispersion curve fit.

Refractive Index vs. Wavelength (25°C)
Lightspan Encapsulation Gel
LS-3252, Lot# 11031-0313

\[ n = 1.495 + (1.096 \times 10^4) \lambda^{-2} + (-1.660 \times 10^9) \lambda^{-4} + (2.072 \times 10^{14}) \lambda^{-6} \]

Measured Data:

<table>
<thead>
<tr>
<th>( \lambda ) (nm)</th>
<th>( n )</th>
</tr>
</thead>
<tbody>
<tr>
<td>411</td>
<td>1.5443</td>
</tr>
<tr>
<td>589</td>
<td>1.5174</td>
</tr>
<tr>
<td>833</td>
<td>1.5075</td>
</tr>
<tr>
<td>1306</td>
<td>1.5008</td>
</tr>
<tr>
<td>1550</td>
<td>1.4987</td>
</tr>
</tbody>
</table>

Figure 4

Optical Absorption versus change in Wavelength is measured across the wavelength range of 300nm to 1700nm, with 2nm resolution, using a spectrophotometer with the sample temperature at 25°C. Spectrophotometers come in many styles, though a typical spectrophotometer measures radiation transmission over a range of wavelengths starting in the ultra violet portion of the spectrum, passing through the visible, and extending into the infrared spectrum. The discrete wavelengths of the spectrum used for the testing are generated by splitting a white beam of light with a diffraction grating (prism like device). Rotation of the diffraction grating selects the portion of the spectrum illuminating the sample. In a double beam spectrophotometer the beam illuminating the sample is split into a reference beam and a sample beam. The reference beam is directed to a photodetector without passing through the sample. The reference beam is a measure of the incident radiation on the sample. The material being tested is placed in the path of the sample light beam, and only the light that passes through the material is detected at the photodetector. This is the transmitted radiation. Transmittance is defined as the incident radiation (Io) divided by the transmitted radiation (I):

\[ T = \frac{I}{Io}, \text{ and } \%T = 100 \times \frac{I}{Io} \]

The Beer-Lambert Law defines Absorbance, A, as

\[ A = \log \left( \frac{I}{Io} \right) \text{ and } \%
A = 100 \times \%T \]

Absorbance is often more useful than transmittance since samples with low concentrations of absorbing species show a linear relationship between absorbance and the concentration of the absorbing species. Absorption is a function of distance so the path length of the sample is standardized to 1 cm. Absorption is correctly expressed as a certain percent per unit length. An example of an absorption vs wavelength graph is
shown in Figure 5, demonstrating that a high refractive index silicone thermoset has less than 1% absorption in the visible spectrum, the common spectrum for HB LEDs.

![Optical Absorption vs. Wavelength](image)

**Figure 5**

**Phosphors**

In general terms, a phosphor can be defined as a material, which absorbs the light from one type of wavelength and emits the light at a different wavelength. For example the white HB LEDs have a blue gallium nitride (GaN) semiconductor die, exciting a yellow phosphor coating, made from cerium doped yttrium aluminium garnet (YAG:Ce) powder dispersed in a gel or adhesive like silicone. The result is the yellow light mixing with the unabsorbed blue light to produce white light. Typical phosphor particle size is 2-20 microns in diameter with a specific gravity of 4.5. These conventional phosphors have a refractive index of 1.7-2.3 for visible light. A dispersant may be used with the phosphor such as barium titanate, titanium oxide or aluminum oxide.

Phosphors typically come in powder form and are dispersed into a silicone system, typically the same material that is used to encapsulate the die, at a 30% level by weight. As discussed above, there are numerous possibilities in choosing a silicone system; all factors should be taken into consideration. To avoid confusion we will call the mixture of silicone with phosphor the ‘silicone dispersion’.

Some factors to consider; given that all phosphors have a higher refractive index than any silicones available, choose the highest refractive index silicone system available, 1.57. As mentioned earlier, a 2-part platinum cure system will most likely be chosen.
Cure inhibitors such as sulphur, amines, and tins should be recognized in the HB LED package. Often fluxes and die attach adhesives contain such materials. If these materials cannot be altered, custom silicone dispersion formulations may need to be developed to compensate for this inhibition.

The package design and stress at the die level, will be the primary factors in choosing the hardness and adhesion strength of the silicone dispersion when cured. Multiple materials may have to be experimented with to find just the right fit to the particular package. Durometer, lap shear, and tear strength will need to be examined of potential materials. By adding phosphor, most of the physical properties including adhesion will decrease.

The silicone dispersion will see the highest temperature in the HB LED package, situated directly on top of the die. This temperature may have an effect on the dispersion of the phosphor in the silicone. Most high refractive index silicone systems will have the best thermal stability of any available silicones. The addition of the phenyl functions not only increases refractive index but also decreases the effects of temperature on the chemical structure of the silicone polymer due to steric hydrance.

**Silicone Dispersion**

The bond angles of the silicon-oxygen bonds create large amounts of free volume in silicone elastomers. This free volume associated with the high compressibility found in silicones, boards well for dispersions made with silicone. The more free space, the more filler that can be added and the more uniform the dispersion.

Many powder fillers are currently added to silicone systems to achieve different properties, see Figure 6.

<table>
<thead>
<tr>
<th>PROPERTIES</th>
<th>FILLER</th>
<th>PARTICLE SIZE (micron)</th>
<th>DENSITY (lbs/ft^3)</th>
<th>Surface Area (m^2/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Increase strength</td>
<td>Fumed Silica</td>
<td>0.011-0.014</td>
<td>2-5</td>
<td>200-255</td>
</tr>
<tr>
<td>Reduce density</td>
<td>Microballoons</td>
<td>35-135</td>
<td>0.16g/cc</td>
<td></td>
</tr>
<tr>
<td>Color</td>
<td>Ferro Black, TiO2</td>
<td>1 , 0.3</td>
<td>5g/cc, 5g/cc</td>
<td></td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td>Boron Nitride</td>
<td>7-10</td>
<td>0.4g/cc</td>
<td>13</td>
</tr>
<tr>
<td>Thermal stability</td>
<td>Iron oxide red</td>
<td>3</td>
<td>4.1</td>
<td></td>
</tr>
<tr>
<td>Increase hardness</td>
<td>Diatomaceous Earth</td>
<td>7</td>
<td>352g/l</td>
<td></td>
</tr>
<tr>
<td>Electrically</td>
<td>Carbon, Silver</td>
<td>30nanometers, 30-40</td>
<td>6, 2.7g/cm3</td>
<td>254, 10</td>
</tr>
<tr>
<td>Conductivity</td>
<td>YAG</td>
<td>2-20</td>
<td>4.5</td>
<td></td>
</tr>
</tbody>
</table>

Figure 6. Various Silicone fillers properties.

The following example demonstrates how variations in similar fillers can greatly alter the properties desired. Fumed silica for increased strength is the most common filler added to silicone systems. This is the main ingredient that produces the many silicone rubbers used in multiple industries today. In the early development of silica added silicone rubbers it was found that the basic precipitated version of silica was not as effective in producing the best rubber. Precipitated silica, SiO₂, is produced by reacting
Sodium silicate solution with an acid and/or metal salt solution, filtered to remove the salt, dried to remove water and milled.

\[
\text{Si(O Na)}_4 + 4\text{HCl} \rightarrow \text{SiO}_2 + 4\text{NaCl} + 2\text{H}_2\text{O}
\]

The result is a low cost, porous particle (see Figure 7). Conversely, fumed silica is a more costly process that burns Silicon tetrachloride in a flame of hydrogen and oxygen to produce primary spherical particles. While still semi-molten, the primary particles fuse irreversibly into second groupings called aggregates. During further cooling, collecting and bagging the aggregates become physically entangled to form agglomerates (see Figure 7). These particles are nonporous and allow a better interaction with the silicone they are dispersed into. To improve the solubility and wet-out of the silica even more into the silicone, the fumed silica is often treated with a chemical to reduce the attractive forces called hydrogen bonding.

\[
\text{SiCl}_4 + 2\text{H}_2 + \text{O}_2 \xrightarrow{\Delta} \text{SiO}_2 + \text{HCl}\uparrow
\]

Consistency is the key in making a dispersion of any powder. The objective is to uniformly mix, disperse the powder particles throughout the entire liquid. The ideal dispersion would be to have the phosphor particles all broken down into primary particles of uniform size and separated from each other uniformly with each particle covered by a uniform layer of silicone. Non-uniform mixing will cause clumping, settling and not provide the desired effects required from the dispersion, in our case, optimum light output. Consistency is dependent on the shearing capacity of the dispersion equipment, the length of shearing time, the viscosity of the liquid, and the particle size and density of the powder.
Typically, the maximum shear time is determined when the viscosity has plateaued or slightly decreased. The higher the surface area of the particle, the more difficult the powder is to disperse. More energy is needed to wet-out the surface areas. Another key property affecting dispersions is the powder particle structure. The more highly structured the particle means that it is harder to get into the space around the particles and more difficult to disperse (see Figure 8).

![Figure 8. A highly structured carbon black particle.](image)

**Dispersing Equipment**

The best way to obtain the desired consistency mentioned above is proper mixing. Hand mixing is impractical at a production level so dispersing equipment is needed in this process. Mixing a powder into a liquid has several challenges. The addition of any powder too quickly may result in slow dispersion times and agglomerates well beyond the desired particle size. Basic dispersion equipment is comprised of a motorized shaft with an impeller or blade, see Figure 9.

At dispersion speeds of 4,000-6,000 fpm (feet per minute), the impeller imparts high velocity to the material. The feet per minute measurement is mixing equipment-industry specific terminology allowing manufacturers to more quickly assess customer needs.

\[
\text{RPM (revolutions per minute) } \times 0.262 \times \text{Blade Diameter (in inches)} = \text{fpm}
\]

The high velocity creates a turbulent zone of intense flow (see Figure 10). The turbulent zone accomplishes rapid hydraulic utilizing shear and impact energy. This turbulent zone is normally within 1-2” of the blade diameter, and 75% of the kinetic energy is applied within this zone (see Figure 11).
Figure 9. A single Shaft LG Series Disperser from Morehouse-COWLES.

Figure 10: Creates intense “turbulent zone”.

Figure 11, Kinetic Energy versus distance to the blade.
Beyond the turbulent zone, the movement becomes laminar. This flow divides at the vessel wall, assuring complete circulation of the entire batch. Turbulence does not interrupt flow pattern. The laminar flow is what causes the vortex seen in the process (see figure 12). The vortex should end where the shaft meets the blade.

![Figure 12: Causes laminar flow for “total motion”](image)

The addition of powders too quickly can result in a choked vortex, which may irreversibly lead to agglomerates of powder particles (see Figure 13). Outside of the rotating shaft and impeller, the mixing vessel may also play a positive role in mixing powders into liquids. Low viscosity materials, i.e., <1000 cps, may require the use of vessels with baffles or structures mounted to the vessel wall. Some liquids can gather around the impeller and shaft, resulting in the whole mixture moving uniformly about the shaft. Protruding baffles can introduce counter-flow dynamics that prevent this from occurring.

![Figure 13, Pictures of a good (A) and choked (B) vortex.](image)

Lastly, equipment should be properly sized and powered for the application. Generally speaking, liquid silicone systems with viscosities under 20,000 cps should use 10 horsepower per 100 gallons of product.

**Testing of Dispersion Quality**

The most effective way to measure a dispersion quality is microscopically. However, this technique is costly, time consuming, and often impractical in a production process. A more common method used in the paint and ink industries is the Hegman Grind (see Figure 14). The dispersion to be tested is poured onto the top of a Grind gauge. The dispersion is then drawn down using a knife blade. The measurement of the largest particles can be made where the coarse particles have been screened out. The coating can also be visually looked at for clumping and non-uniformity and even compared to a reference standard.
Conclusion

The theme of this paper demonstrates the many choices the HB LED package designer has with regards to silicone systems and phosphor dispersions. Modifying the polymer chemistry can produce a fluorosilicone with a refractive index of 1.38 or a methyl phenyl silicone with an index up to 1.60. Different forms of the same material can be produced, fluid, thixotropic gel, cured gel, thermoset and resin. Different cure systems can be designed, however for HB LEDs, the platinum systems offer the most advantages, therefore concerns for materials that inhibit the cure need to be examined. Physical properties can also be custom formulated to specific requirements, adjusting the durometer, tear and tensile strength, viscosity and volatile content. The optical properties of these silicone materials can be characterized and favor use in HB LEDs. The best plan for a HB LED package designer is to involve the siliconew material provider early in the development process, so that the best material for the package can be found.

Future Studies

NuSil Technology is committed to remain in the forefront of HB LED packaging materials. We have ongoing tests with improving adhesion, UV effects on yellowing, both from sunlight and specific UV wavelengths, physical property improvements in the area of toughness with > 1.50 refractive index and finally a range of Type “D” hard materials for possible lens use.

Acknowledgements

We would like to thank our staff at our Lightspan Application Lab in Wareham, MA. for all the optical testing performed. MorehouseCowles, the mixing equipment division of NuSil Technology, provided their expertise in the Equipment and Dispersion sections of the paper.
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