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Evaluation of Phosphor Settling Rate in Silicone Encapsulant

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Summary

Working with LED manufacturers reveals a common problem: how to effectively add phosphor to the silicone encapsulant without having it settle or incur processing problems like curing too soon, deairing and bubbles. A study was done to evaluate two silicone encapsulation materials for their ability to maintain phosphor in solution for ease of manufacturing and production of white light emitting diodes. The phosphor dispersions were evaluated over a large temperature range, -40 to 150°C, to attempt to understand the material in the most broad and general way. This temperature range was subsequently divided into storage, -40°C to -20°C, dispensing, 15°C to 35°C, and curing, > 40°C, recognizing these portions of the range have unique requirements for production applications.

Background

White light can be made a variety of ways; by mixing red, green, and blue wavelengths, and by using a UV/blue-emitting diode to excite a yellow, green or red emitting phosphor placed within the light emitting path. The combination of emitted wavelengths gives the appearance of white light.

Many white LEDs in production today use a 405nm blue gallium nitride LED covered by a yellowish cerium doped yttrium aluminum garnet (YAG) phosphor coating. The phosphor coating is made from powdered phosphor suspended in a silicone encapsulation material. The phosphor coating may be located either directly on top of the LED die, or spaced away from the die by a transparent spacer – usually the silicone encapsulation gel.

Silicones have become the standard transparent LED encapsulation material. Usually a two-part addition cure silicone is used, which is initially flowable and then cures to form a soft gel or higher durometer final material. The required pot life can be optimized for long dispensing times but typically requires full cure to occur at elevated temperatures. Some silicones require the ability to cure at lower temperatures due to cure stresses or other problems associated with differences in Coefficients of Thermal Expansion (CTE). These types of silicones may have shorter pot lives so that they can cure at lower temperatures. Silicones can also be formulated to have a wide variety of initial viscosities. For purposes of dispensing phosphor into LEDs, the 5,000 to 15,000 cP range has been found to be the most workable.

Phosphors typically come in powder form and are dispersed into silicone during the assembly process. The typical phosphor particle diameter is 2-20 microns, and their specific gravity is about 4.5 (relatively heavy compared to silicone). Depending on the application, it is desirable for the phosphor to remain in suspension during the entire time of dispensing. The ability of the silicone to keep the phosphor in suspension has been determined to depend at least in part on the viscosity of the silicone. Whether or not the phosphor settles can be selected for by choosing a high or low viscosity silicone for

dispersing the phosphor. As such the silicone dispersion serves as the delivery system for the phosphor onto the LED die. When the silicone cures it becomes the adhesive to hold the phosphor in place.

A common practice for HPLED is mixing the phosphors into a two part, addition cure silicones encapsulants. This can be referred to as a phosphor coating that will be used to dispense the phosphor onto the die. The same silicone encapsulant is typically used to encapsulate the area between the phosphor coated die and the lens. In this situation, the silicone must be able to crosslink at low temperatures due to the problems seen with differences in CTE (bubbles). These types of silicones may have a relatively short pot life to be able to cure at lower temperatures.

The purpose of this study is to investigate and characterize phosphors dispersed in two different silicone polymers used as silicone encapsulants (LS3-3354 and LS-3351). The phosphor dispersions were evaluated over a large temperature range, -40°C to 150°C , to attempt to understand the material in the most broad and general way. This temperature range was subsequently divided into storage, -40°C to -20°C , dispensing, 15°C to 35°C , and curing, $> 40^{\circ}\text{C}$, recognizing these portions of the range have unique requirements for production applications.

Viscosity of Silicones

The viscosity of silicones is strongly a function of temperature. Figure 1a shows the viscosity (measured in centipoises, cP) for the two silicone polymers tested in this study, between 5 and 40°C . Over this relatively small temperature range simple models suggest that when this data is plotted as the log (viscosity (cP)) vs $1/T$, where T is expressed in degrees Kelvin, it will be nearly linear. This translation of the data in Figure 1a to this form is shown in Figure 1b, and shows it does produce mostly linear curves.

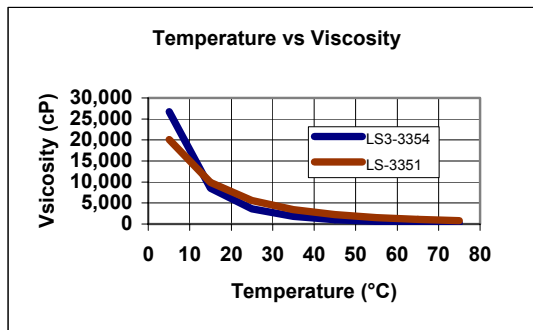


Fig. 1a. Temperature vs Viscosity for Two Silicone Polymers

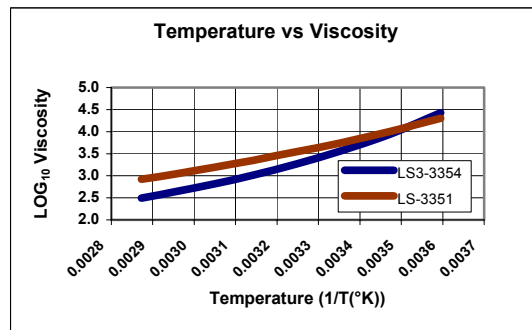


Fig. 1b. The same data as Fig. 1a Plotted as $1/T(^{\circ}\text{K})$ vs Log (Viscosity(cP))

This has uses in estimating the viscosity of silicone polymers at other temperatures that might be of interest. This type of model is restricted to roughly 0 to 80°C , and it is

important to note that the further the model is extrapolated the less accurate it is likely to be.

Temperature and Cure Rate

Silicone polymer systems are typically made up of two parts which when mixed together initiate a crosslinking reaction. Crosslinking, another name for curing, is the conversion of many discrete polymer molecules into one highly interconnected molecule. Most optical silicone systems utilize a curing mechanism called 'addition cure'. Addition cure has the advantages of producing no curing by-products, has minimal shrinkage when cured, and is a reaction that can be manipulated for various cure schedules and physical properties.

The two parts of a silicone polymer system contain 1) vinyl functional siloxane polymers (CH=CH₂ groups), and 2) hydride functional crosslinker (H). Mixing the two parts together allows these functional groups to react as shown in Fig. 2 below. For this reaction to proceed, there must be some platinum catalyst present. The platinum, being a catalyst, does not participate in the reaction; it only accelerates the rate of the reaction.

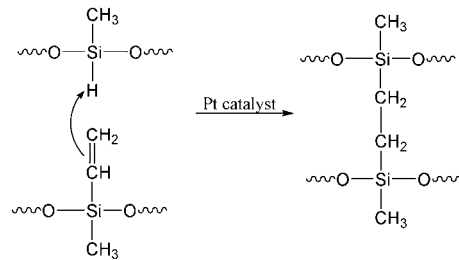


Fig. 2 – Addition Cure reaction.

Temperature will also accelerate the rate of this reaction. Like many chemical reactions, the cure rate of silicones fits the Arrhenius formula, $e^{-\Phi/kT}$, which describes the dependence of a chemical reaction rate on temperature. Based on empirical data obtained for LS3-3354 and LS-3351 every 10°C between 5 and 75°C, the unknown coefficients Φ and k were solved for, and the data extrapolated to -40°C and +150°C. The obtained cure rate versus temperature curves for the silicones used in this study are shown in Figure 3. These data show that LS3-3354 cures considerably faster than LS-3351.

Cure Rate vs Temperature

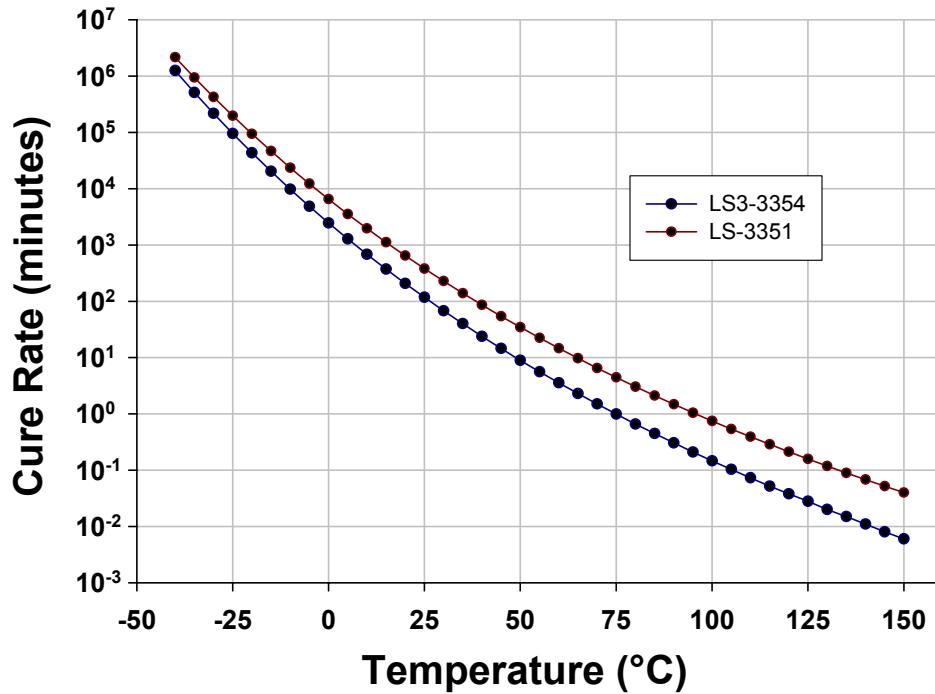
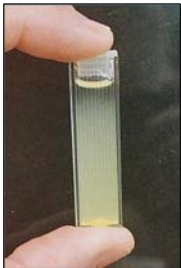


Fig. 3. Cure Rate vs Temperature for LS3-3354 and LS3-3351.

Phosphor Precipitation Rate

For LED applications the typical weight percent of phosphor used in a silicone dispersion is between 10 to 30%. A concentration of 10% phosphor creates a dispersion too opaque to see into, obscuring the view if any of the phosphor is precipitating. Several ideas were investigated for measuring phosphor precipitation, and for this study a 1% phosphor dispersion was used. While 1% phosphor still turns the polymer yellow, it is transparent enough to see into, see Figure 4 (i.e. in a glass cuvette) to observe any precipitation of the phosphor.



Phosphor was dispersed in non-curing versions of the silicone (easily made by omitting the platinum catalyst) so the precipitation time was not complicated by the usual crosslinking of the silicone. The precipitation rate was defined as the time it took starting when the phosphor was thoroughly stirred into the silicone to the time any visual precipitate could be seen in the bottom of a cuvette. The photo at left shows a cuvette of silicone with the first visible precipitated phosphor. Although there was a visible precipitate in the bottom of the cuvette, there was still a lot of phosphor suspended in the polymer. This view was just the first sign of non-uniformity of the phosphor suspension. The results of this testing is shown in Figure 4a.

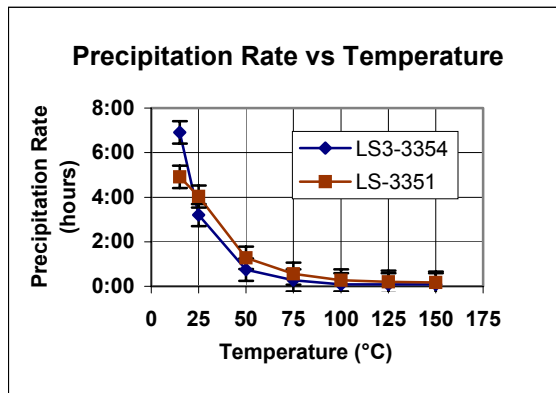


Fig. 4a. Comparative Precipitation Rate of Phosphor vs Temperature in Un-catalyzed versions of LS3-3354 and LS-3351.

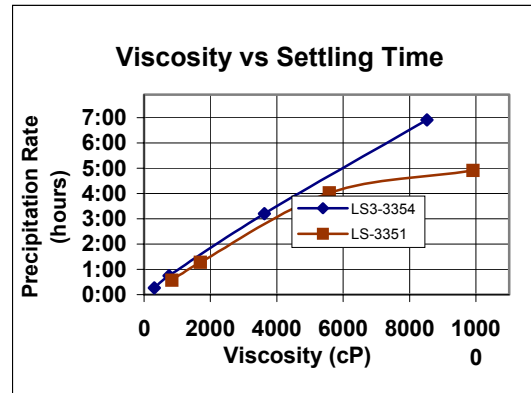


Fig. 4b. Viscosity vs Precipitation Rate of Phosphor in Un-catalyzed versions of LS3-3354 and LS-3351. (Variations in viscosity achieved by varying the temperature)

To test the hypothesis that a higher viscosity material helps keep the phosphor suspended, precipitation rate was plotted as a function of viscosity. This is shown in Fig. 4b. The varying viscosities shown on the X-axis of Fig. 4b were achieved by variations in temperature. While there are not a lot of data points, Fig. 4b shows the viscosity/precipitation rate relationship is linear up to about 6000cP, which for the silicones in this study correspond to temperatures of room temp and higher. Beyond 6000cP viscosity alone may not explain why the phosphor stays in or falls out of suspension. Above 6000cP there is only one data point, and this part of the graph corresponds to room temperatures and colder where it is difficult to obtain data with visual precipitate criteria precipitation happens so gradually. However, this part of the graph suggests that other differences between LS-3351 and LS3-3354 besides viscosity may be needed to explain this difference in retention of phosphor at colder temperatures. This may have important implications for settling of the phosphor during storage, which may not behave the same from one material to the next when maintained at -40°C (see Storage below). It should be mentioned that just the addition of 10 to 30% phosphor increases the viscosity of the silicone by about 15 to 20%. This effect has not been taken into account in trying to understand how the phosphor might come out of suspension.

Combining the Results

To relate the above data to the potential use of a one-part phosphor dispersion in a production setting, the properties of a one-part were considered from three points of view: storage, dispensing and curing.

Storage

From the storage aspect, it is essential that the one-part be kept at -40°C . This is apparent from Fig. 3. Visually averaging through the cure curves, a minimum of -25°C corresponds to a pot life (defined as 2x initial viscosity) of about 100,000 minutes,

equaling 70 days. At -40°C the pot life is 1,000,000 minutes, which equals about 1.9 years. To guarantee a shelf life of months, cold storage of these materials needs to be -40°C . This is just to prevent the material from curing. This does not address the phosphor settling issue. Based on Fig. 4b, there may be other considerations besides viscosity that help keep the phosphor suspended, i.e. affinity of the phosphor for some part of the silicone polymer, another additive acting as an emulsifier, etc. At this time Fig. 4b simply suggests that LS3-3354 is likely to be better at keeping the phosphor in suspension at colder temperatures.

Dispensing

Dispensing is an operation normally done at room temperature, about 15 to 25°C . Assuming the differences in phosphor precipitation rate between the two polymers tested are insignificant at these temperatures, Fig. 4a shows a precipitation rate of about 3 to 4 hours at 25°C . While different applications may vary in the desire for uniformity of the phosphor in the final product, within the dispensing reservoir it seems essential the phosphor remain uniformly suspended. The 3 to 4 hour precipitation rate suggests a minimum dispensing time for roughly 1 hour.

While dispensing, it is also desirable for the initial mixed viscosity to remain unchanged. Once the one-part material is removed from -40°C storage, curing starts at a rate commensurate with the ambient temperature, and the viscosity starts increasing. This is when the dispensing equipment's ability to handle a change in viscosity and maintain a specified shot size becomes important. Based on the data in Fig. 3, and assuming a doubling in initial viscosity is acceptable, the pot life of these materials at 25°C is hundreds of minutes, or a few hours. This coincides with the precipitation rate of the phosphor and suggests a minimum of 1 hour where the viscosity is relatively unchanged and the dispersion of the phosphor is largely uniform.

Curing

The final stage of working with a silicone is curing, which frequently involves temperatures above room temperature. If it is desirable for the phosphor to remain uniformly dispersed in the silicone, it is assumed that the phosphor not precipitate faster than the material cures. To evaluate this it was first decided that the precipitation rates for the two materials tested were essentially the same for temperatures above room temperature (refer to Figs 4a and 4b). Thus a nominal precipitation rate curve was developed by averaging the data for the two materials. To emphasize the approximate nature of this data, the data points were given substantial size to encompass room for variation and error. This data was plotted on top of the cure rate data of Fig. 3 and is presented in Fig. 5 below. Fig. 5 shows at temperatures of 75°C and above, the cure rates of both materials are much faster than the precipitation rate of the phosphor.

Cure Rate & Average Phosphor Precipitation Rate vs Temperature

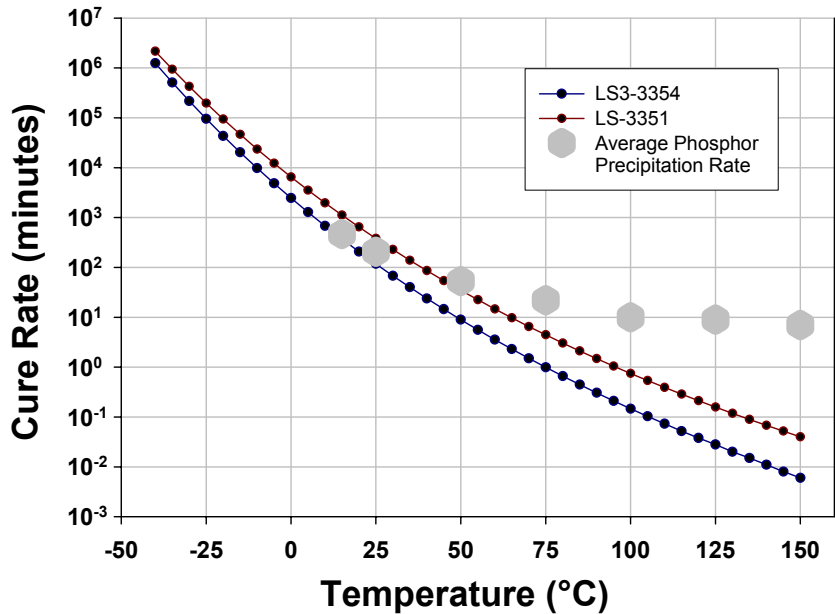


Fig. 5. Cure Rate vs Temperature with Phosphor Precipitation Rate superimposed.

Developmental Phosphor Dispersions

Based on the above study, LS3-3354 was chosen as the silicone encapsulant to disperse Intematix Y-4156 phosphor. Two concentrations of phosphors were dispersed:

Experimental Gel #1: LS3-3354 with 29% by weight Y4156

Experimental Gel #2: LS3-3354 with 11% by weight.

Both materials were produced and stored in a -30°C freezer. Table 1 shows the initial properties of Gel #2 and after 3 months cold storage. Other than the 10% increase in initial viscosity, most likely due to not using a -40°C freezer, all other properties are the same within testing specifications.

Table 1. Gel #2 properties before and after cold storage.

Property	Initial	3 months
Initial Viscosity 25°C (cP)	4098	4496
Time to 2x Initial Viscosity (minutes)	143	143
Durometer (OOO) Cured 1hr@ 70°C	68	73

Reliability Testing

Samples of Gel #1 and Gel #2 were used in the assembly of a 20mA LED and run in a humidity chamber at 85°C/85% RH for 1000 hours. These samples were evaluated for maintenance of color intensity and brightness over the 1000 hour interval. While no materials are known that show no deterioration in these parameters over 1000 hours, the Gel #1 showed performance comparable to any of the leading contenders in this capacity (see reference presentation below for 2007). These results support the concept of a one-part phosphor dispersion that is an assembly aid for the production of LEDs.

Conclusion

Two silicone encapsulation materials were evaluated for their ability to maintain phosphor in solution. These phosphor dispersions were evaluated over a large temperature range, -40 to 150°C, for settling of the phosphor and its implications for use in an LED production setting. One silicone was found to be better suited to maintaining the phosphor in suspension. NuSil Technology is continuing our efforts in evaluating the effects of storage conditions at -40 °C on phosphor suspension in catalyzed silicone encapsulants.

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Viscosity vs Temperature Application Notes, www.nusil.com

Acknowledgements

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