



Creative Partners in a Material World



**A Characterization of UV Effects on Optical Silicones used in
Opto-electronic Devices and New Developments in Resistant
Materials**

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ABSTRACT

Opto-electronic devices such as LEDs, optical sensors, LCDs and color filters have the need for optically transparent encapsulants or adhesives. Maintaining the highest transmission possible of the encapsulant/adhesive throughout the life of the device is a critical criteria for the device designer. Silicones as encapsulants/adhesives in opto-electronic devices have been used throughout the last decade^{1,2}. The high light flux and associated heat proved too much for the traditional epoxies. Data confirms silicone encapsulants/adhesives provide longer optical transmission life than epoxy encapsulants³.

Almost all optical devices have some interaction with UV wavelengths. Manufacturers of Blue LEDs with wavelengths near 405nm, and other LEDs that emit wavelengths deeper into the UV (365-399nm), have concerns about the effects of this radiation on the light transmission of the encapsulant over time. LCD and sensor devices may have UV radiation from the sun to contend with. This paper looks at many different encapsulants/adhesives, silicone, epoxy and acrylate, for their change in optical transmission due to a 680-68000J/cm² dose of radiation with the following spectral output: 34% in the UVA (320-399nm), 17% in the UVB (280-319nm), and 49% concentrated at 405nm and 450nm. All samples were prepped and exposed the same way so that comparisons between the samples would be meaningful. Results show that silicones perform better than acrylates, which perform better than epoxies, and not all silicones perform equally. Data will be provided of the best performing materials and a discussion of future work given the understanding of the chemistry.

Key Words: Silicone encapsulants, silicone adhesives, UV radiation

1. INTRODUCTION

This study evaluates twenty-two samples for their change in optical transmission due to a 680-68000J/cm² dose of UV radiation. Among the silicone samples were those designed to test the following suspected sources for yellowing:

- 1) Amount of Pt catalyst
- 2) Amount of Phenyl – related to the refractive index
- 3) Impurities

The results conflict with previous observations, and possible reasons for this are discussed in the report. However, the results show that yellowing is not caused by the amount of platinum, amount of phenyl, nor impurities.

2. TEST SET UP

2.1. Sample prep

All samples were prepared by curing the candidate material between two standard microscope slides spaced a distance of 2mm apart with a silicone gasket around three sides of the slides. Care was taken to deair all the samples and ensure proper curing according to each materials requirement. A list of the materials used in this test is shown in Table 1.

Table 1. Test samples

Number	Chemistry	Refractive Index	Comments
1	Acrylate		UV curable
2	Epoxy		Optical grade
3	Epoxy		Optical grade
4	Silicone	1.52	LS-3252
5	Silicone	1.52	Low catalyst containing gel
6	Silicone	1.52	Medium catalyst gel
7	Silicone	1.57	Low catalyst containing gel
8	Silicone	1.57	Medium catalyst gel

9	Silicone	1.57	Medium catalyst elastomer
10	Silicone	1.52	Competitive gel
11	Silicone	1.52	Very low Catalyst gel
12*	Silicone	1.52	Competitive 'Super clean' Gel
13	Silicone	1.40	LS-3440
14*	Silicone	1.40	Competitive 'Super clean' Gel
15*	Silicone	1.54	Competitive 'Super clean' Gel
16	Silicone	1.40	LS-6140
17	Silicone	1.61	Fluid
18*	Silicone	1.51	Fluid 'Super clean'
19*	Silicone	1.46	Fluid 'Super clean'
20	Silicone	1.54	GEL-9617-30
21	Silicone	1.54	GEL3-9617-30
22	Silicone	1.57	LS-6257

*Note: Samples denoted as 'super-clean' either received extra steps to ensure cleanliness during synthesis, or were sent out for supercritical extraction.

2.2 UV exposure and radiation recording

The test set up used to expose the samples to UV radiation is a Dymax UV Flood Light Curing System utilizing a Visible ("V" Spectrum) Bulb, (PN 36658). The spectral output for this bulb is described below in Table 2 (See Appendix A for graph)⁴:

Table 2. Distribution of UV Bulb Spectral Energy

Spectral Band	% of total radiation	mW/cm ²
Visible (400 – 750 nm)	49%	93
UVA (320 – 400 nm)	34%	64
UVB (280 to 320 nm)	17%	32
UVC (<280 nm)	0%	0

All samples tested are placed 6 inches from the bulb, where the total radiation exposure incident on the sample is approximately 190mW/cm². All samples received an initial exposure to the UV for 60 +/- 1minutes. Temperature readings in the chamber during exposure are typically 75 to 90°C. The UV intensity incident on the sample is monitored by placing an EIT UV Power Puck in the same location as the sample for 1 minute immediately before and after exposing the sample for one hour.

Some samples subsequently received an additional 6.6 to 10 hour exposure, which was given and monitored in 3.3 hr intervals over 2 to 3 days. One of the best performing materials was exposed for 100 hours.

3. DATA COLLECTION

Degradation caused by the UV radiation was measured by comparing the transmission spectra curves before and after exposure to the UV flood light set up. An example of this is shown in Figure 1. The initial unexposed curve is shown with the solid black line and the curve obtained after one hour of exposure is shown in the dashed red line. For reference and comparison purposes, the visible part of the spectrum, 400 to 750nm, is denoted with vertical dotted lines.

Optical Transmission vs. Wavelength

LS-3252, Silicone Gel, 1.52 RI
before and after 1 hr exposures to uv

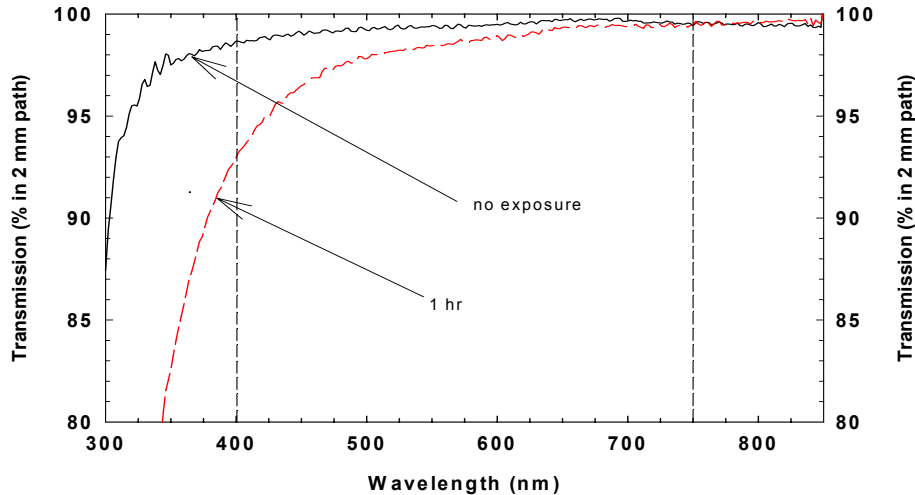


Figure 1. Example of data collected before and after exposure for 1 hour.

The result of the UV exposure is always to shift the transmission spectra of the sample down and to the right, or in other words, to cause the roll off, or the knee of the curve, to move further into the visible part of the spectrum. The amount of this shift is equal to the amount of ‘yellowing’ of the sample as seen by the naked eye. The data collected in this test are shown in Appendices B-F.

3. 1. One-hour exposures, non-silicones and varying amounts of Pt

The results of Data Set 1, the first set of 1 hour exposures are shown in Appendix B. The data are organized as follows:

- 1) Column 1 shows the non-silicone materials, Samples 1, 2 and 3 above.
- 2) Column 2 shows three concentrations of Pt, in a 1.52 gel, samples 5, 6 and 11.
- 3) Column 3 shows three concentrations of Pt for a 1.57 refractive index gel and a 1.57 thermoset, samples 7, 8 and 9.

3.2. 1 hour exposures, varying amounts of phenyl

Data Set 2 is shown in Appendix C. In general arrangement of the data is by increasing phenyl concentration from top to bottom, specifically:

- 1) Row 1 shows materials with refractive indices of 1.40, Samples 13, 14 and 16.
- 2) Row 2 shows materials with refractive index 1.52, Samples 6, 10 and 12.
- 3) Row 3 shows three 1.54 refractive index materials, Samples 15, 20 and 21.
- 4) Row 4 shows one material with a refractive index of 1.57, Sample 22.

3.3. Data Set 3, 1-hour exposures, fluids

The third set of materials tested is all fluids. The results are shown in Appendix D. The Samples are 20, 19 and 18, arranged in this order from top to bottom, which is also the order of increasing refractive index.

3.4. Data Set 4, 6 to 10 hour exposures

The results of the longer exposure times for selected samples are shown in Appendix E. The data are arranged in increasing refractive index from top to bottom. Of particular interest are:

- 1) Samples 13 (top left), 20 and 21 (third row), and 22 (very bottom) show little degradation from the extended exposure.
- 2) Most samples show the greatest spectral degradation in the first 3.3 hours of exposure, which was equal to what would be expected based on the 1 hour exposure data.
- 3) The subsequent second and third 3.3 hour exposures result in little further degradation of the transmission for all materials except Sample 12 (middle right), which continues to degrade.

3.5. Data Set 5, 100 hour exposure

This much longer exposure is shown in Appendix F. Notice, little degradation from this extended exposure.

4. DISCUSSION

The data collected in this study shows the initial shape and shift in spectral transmission between 300 and 850nm before and after UV exposure. This translates into a level of transmission over a range of wavelengths that makes comparisons between samples difficult to quantify in any simple terms. Mostly our interpretations of the data have been made by subjectively comparing the overall spectral shapes between samples of interest. Careful juxtaposition of samples is more responsible for yielding results than any technique used in this experiment.

4.1. Differences in UV curing acrylates, epoxies and silicones

The results for the UV curing acrylates and epoxies are shown in Data Set 1, Column 1. Using the 400nm wavelength as a reference, and the shape of the post exposure curves, the data for these non-silicone chemistries shows these materials yellowed more than any of the other samples in the test, which are all silicones: the epoxies yellowed the most, then the UV curable acrylate, then the silicones.

4.2. Amount of Platinum

In Data Set 1, Columns 2 and 3, containing samples with 1ppm, 9ppm, 6ppm and 0.15ppm platinum catalyst, show no obvious differences in the level or shape of the transmission curves. This indicates the amount of platinum catalyst does not matter. This is contrary to results previously observed, however the levels of platinum were 30ppm, higher than those tested here.

4.3. Amount of Phenyl

Data Set 1, Columns 2 and 3, and Data Set 2 show samples that have many different levels of phenylation, resulting in a range of refractive indices from 1.40 to 1.57. The data do not suggest that lower phenyl content results in a smaller shift in transmission due to UV exposure, and higher phenyl content causes a larger shift in transmission due to UV exposure.

Further exoneration of phenyl as a source of yellowing comes from Data Set 3, Position 3, Sample 17, which is the sample containing the highest phenyl content of any in the entire test. This sample showed hardly any degradation at all with UV exposure. We feel this provides good evidence that phenyl by itself, is not a contributor to yellowing.

4.4. Impurities

Through out the four sets of data collected for this study are five samples:

- Sample 12-Data Set 2, Row 1, Position 2
- Sample 14-Data Set 2, Row 2, Position 3
- Sample 15-Data Set 2, Row 3, Position 1
- Sample 18-Data Set 3, Position 1
- Sample 19-Data Set 3, Position 2

where either special processes were used during synthesis to ensure a very low degree of contamination, or treatments such as supercritical extraction were used. We find no evidence that super-cleaning alone

improves the transmission degradation from UV exposure. Even in Data Set 3, where the super-clean materials perform very well, so does the other member of that set, Sample 17, the 1.61 refractive index fluid, which received none of these treatments. Though cleanliness and low contamination are desirable for many intuitive reasons, we conclude that contaminants that might be prevented by careful synthesis or extraction are not the source of yellowing in this test.

Having eliminated the three hypotheses responsible for yellowing in silicones, namely platinum concentration, phenyl concentration and impurities, our test does not seem to lead to a direct solution for the yellowing problem. It appears that yellowing cannot be attributed to any one of these elements individually, suggesting the cause is something else or a combination. However, in the course of this data collection there were materials that did well with UV exposure. Our investigation turned to these materials to find the reasons for their good performance. This has led to insights about the cause of yellowing, and has so far resulted in the synthesis of two new materials, Samples 20 and 21, GEL-9617-30 and GEL3-9617-30, whose performance you can see in Data Set 4 and 5. GEL3-9617-30 is an improved adhesion version.

5. Conclusion

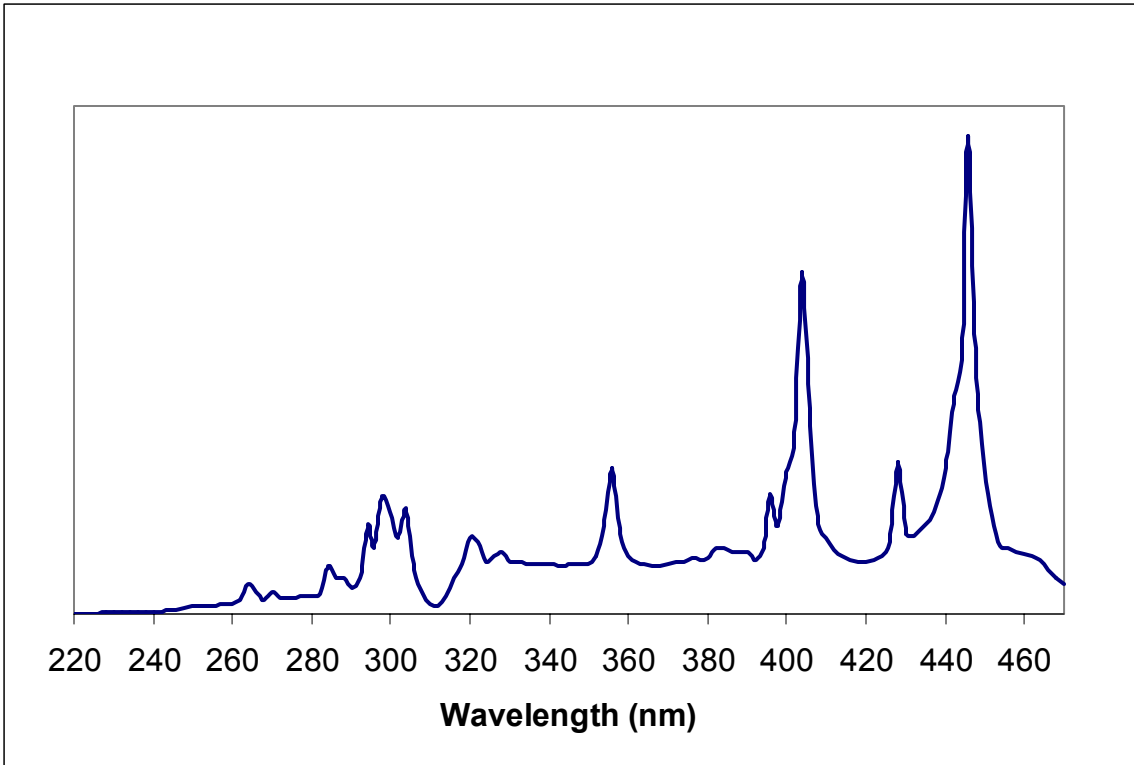
When it comes to non-yellowing behavior of encapsulation materials, silicones perform better than UV curable acrylates, which perform better than epoxies. Based on the results obtained during this study we have been able to eliminate the amount of platinum catalyst used, the amount of phenyl used, and the presence/absence of impurities that would result from routine, and not extra-clean synthesis procedures, as causes for yellowing under UV exposure.

Having eliminated all the hypotheses intended for this test, the data itself provided new evidence enabling the synthesis of a new formulation that ultimately became part of this test, Samples 20 and 21. Further material developments using the information learned from this test are ongoing at NuSil. This test represents a best effort to replicate the degradation in transmission due to UV exposure that might be encountered in the LED application. This test identified several materials that comparatively perform well under this harsh UV condition. They are LS-3440, LS-6257, GEL-9617-30 and GEL3-9617-30.

REFERENCES

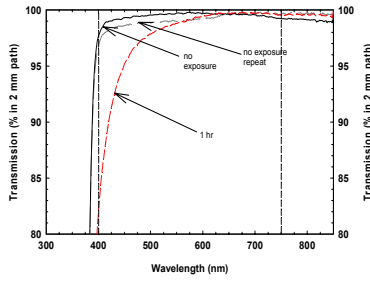
1. Mueller, Gerd et al, Lumileds Lighting LLC, U.S. Pat.Application 20030227249 (December 2003)
2. Shimizu, Yoshinori et al, Nichia, U.S. Patent Application 20040222435 (November 2004)
3. G.Harbers, S. Paolini, M. Keuper, Performance of High-Power LED Illuminations in Projection Displays, Lumileds Lighting, San Jose
4. Dymax Visible ("V" Spectrum) Bulb, (PN 36658) specification sheet

APPENDIX A. UV Flood Light Bulb Spectrum

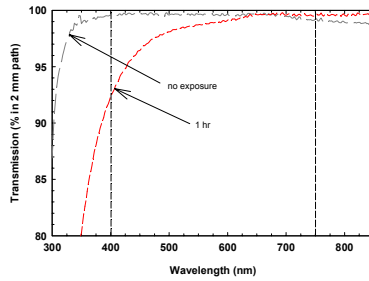


APPENDIX B. DATA SET 1 Non Silicones and catalyst content

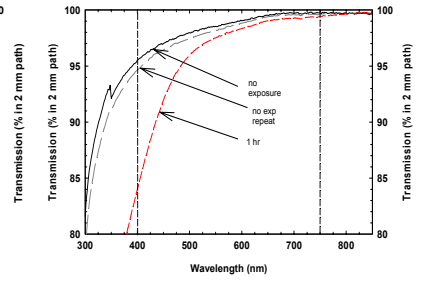
Optical Transmission vs. Wavelength
UV Curable Acrylate
before and after 1 hr exposures to uv



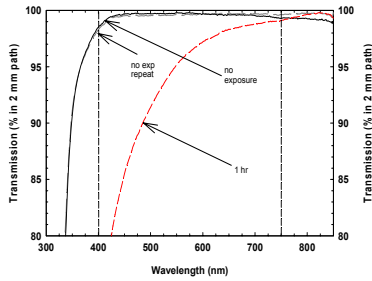
Optical Transmission vs. Wavelength
Silicone Gel, 1ppm Pt Catalyst, 1.52 RI
before and after 1 hr exposures to uv



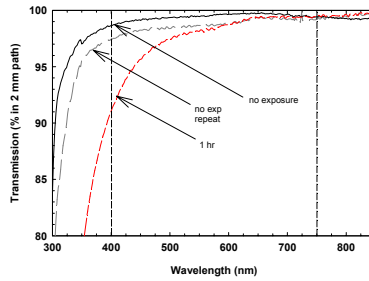
Optical Transmission vs. Wavelength
Silicone Gel, 1ppm Pt Catalyst, 1.57 RI
before and after 1 hr exposures to uv



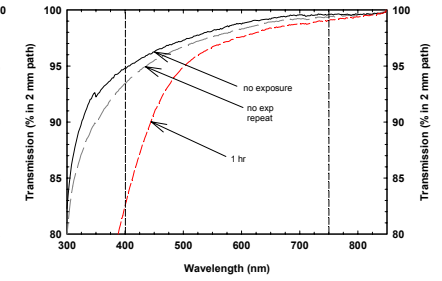
Optical Transmission vs. Wavelength
Optical Epoxy 1
before and after 1 hr exposures to uv



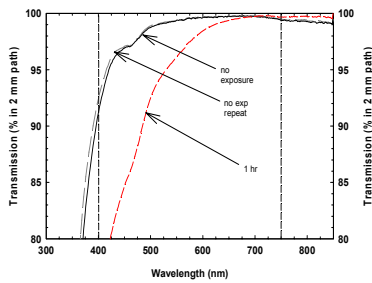
Optical Transmission vs. Wavelength
Silicone Gel, 9ppm Pt Catalyst, 1.52 RI
before and after 1 hr exposures to uv



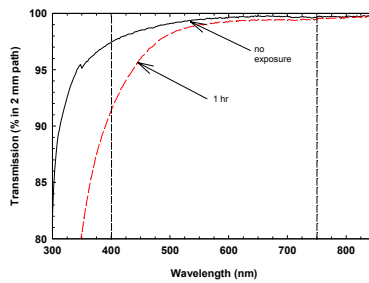
Optical Transmission vs. Wavelength
Silicone Thermoset, 6ppm Pt Catalyst, 1.57 RI
before and after 1 hr exposures to uv



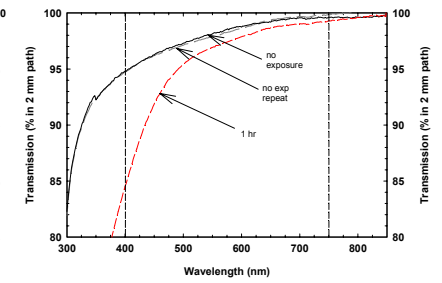
Optical Transmission vs. Wavelength
Optical Epoxy 2
before and after 1 hr exposures to uv



Optical Transmission vs. Wavelength
Silicone Gel, 0.15ppm Pt Catalyst, 1.52 RI
before and after 1 hr exposures to uv



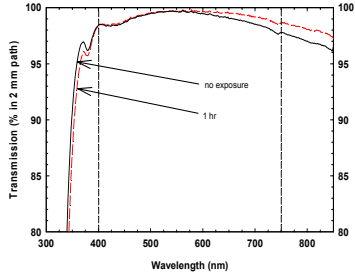
Optical Transmission vs. Wavelength
Silicone Gel, 9ppm Pt Catalyst, 1.57 RI
before and after 1 hr exposures to uv



APPENDIX C. DATA SET 2 Phenyl content

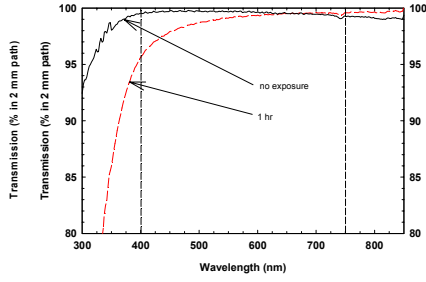
Optical Transmission vs. Wavelength

LS-3440, Silicone Gel, 1.40 RI
before and after 1 hr exposures to uv



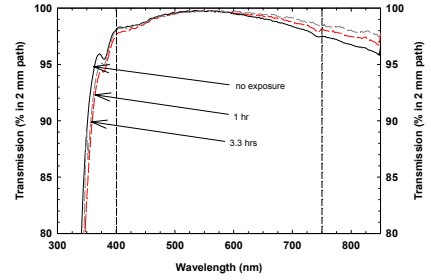
Optical Transmission vs. Wavelength

Competitive Silicone Gel, Super-Clean, 1.40 RI
before and after 1 hr exposures to uv



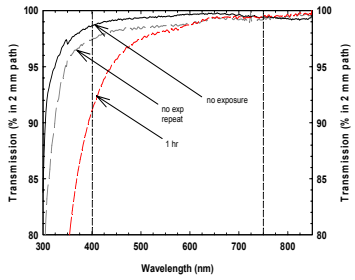
Optical Transmission vs. Wavelength

LS-6140, Low Outgassing Silicone Thermoset, 1.40 RI
before and after 1 hr and 3.3 hrs exposure to uv



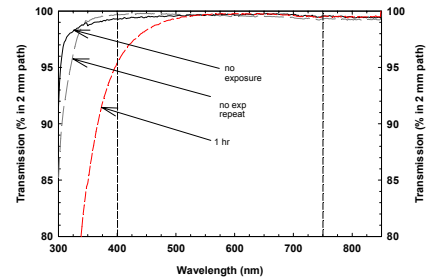
Optical Transmission vs. Wavelength

Silicone Gel, 9ppm Pt Catalyst, 1.52 RI
before and after 1 hr exposures to uv



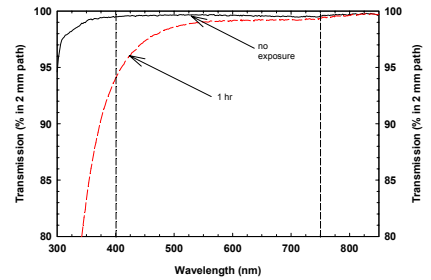
Optical Transmission vs. Wavelength

Competitive Silicone Gel 1, 1.52 RI
before and after 1 hr exposures to uv



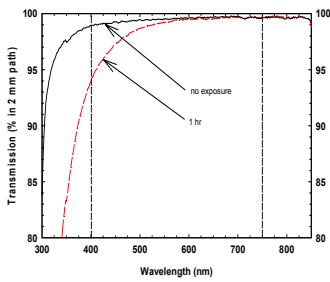
Optical Transmission vs. Wavelength

Competitive Silicone Gel, Super-Clean, 1.52 RI
before and after 1 hr exposures to uv



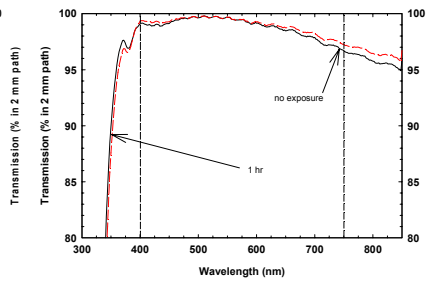
Optical Transmission vs. Wavelength

Competitive Silicone Gel, Super-Clean, 1.54 RI
before and after 1 hr exposures to uv



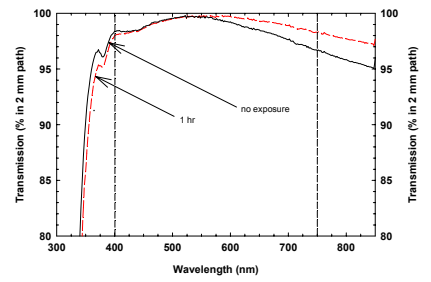
Optical Transmission vs. Wavelength

GEL-9617-30, Silicone Gel, 1.54 RI
before and after 1 hour exposures to uv



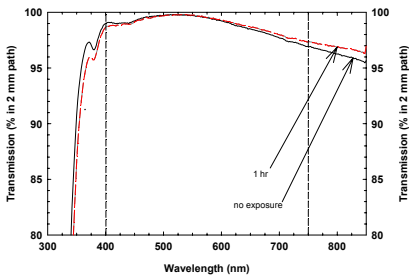
Optical Transmission vs. Wavelength

GEL3-9617-30, Silicone Gel, 1.54 RI
before and after 1 hr exposure to uv



Optical Transmission vs. Wavelength

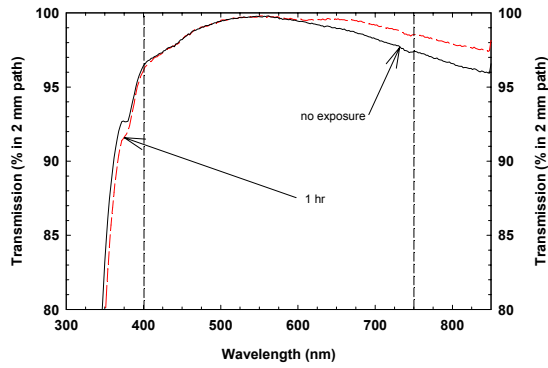
LS-6257, Silicone Thermoset, 1.57 RI
before and after 1 hr exposure to uv



APPENDIX D. DATA SET 3 Fluids

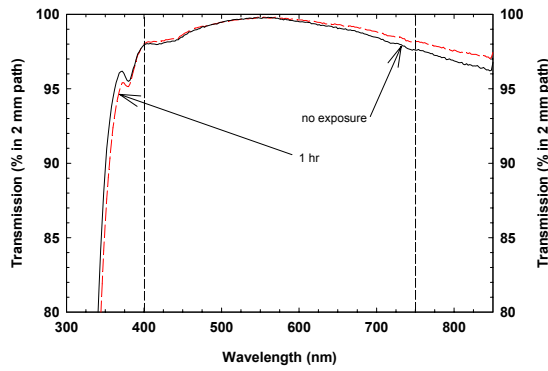
Optical Transmission vs. Wavelength

Silicone Fluid, Super-Clean, 1.46 RI
before and after 1 hr exposures to uv



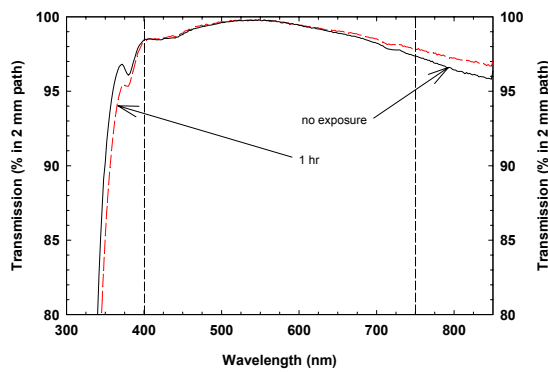
Optical Transmission vs. Wavelength

Silicone Fluid, Super-Clean, 1.51 RI
before and after 1 hr exposures to uv



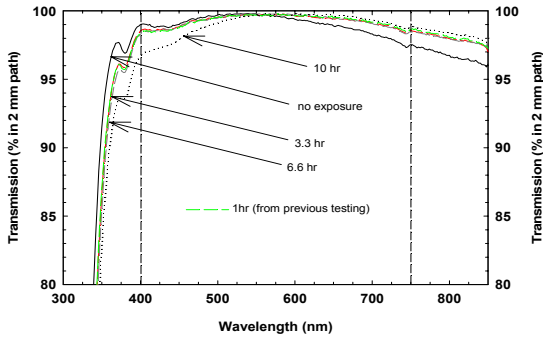
Optical Transmission vs. Wavelength

Silicone Fluid, 1.61 RI
before and after 1 hr exposures to uv

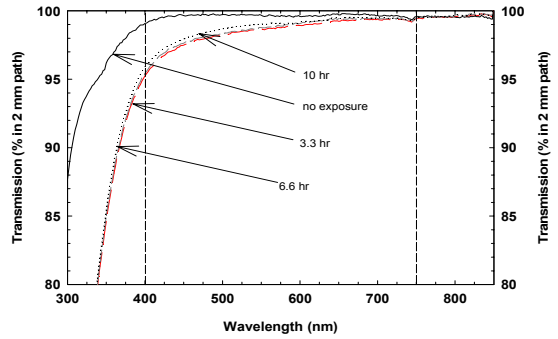


APPENDIX E. DATA SET 4 6-10 hour exposure

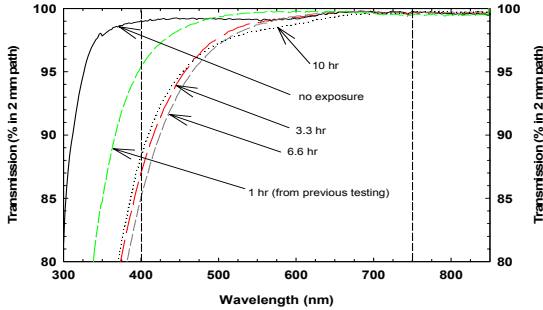
Optical Transmission vs. Wavelength
 LS-3440, Silicone Gel, 1.40 RI
 10 hr exposure to uv



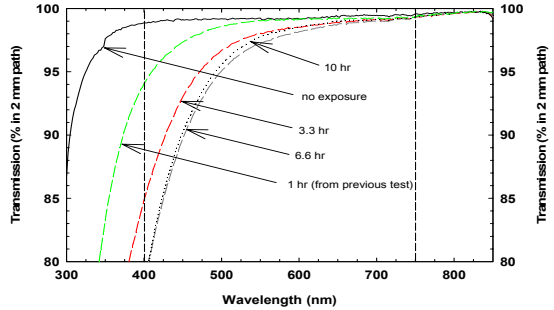
Optical Transmission vs. Wavelength
 LS-6941, Silicone Thermoset, 1.41 RI
 10 hr exposure to uv



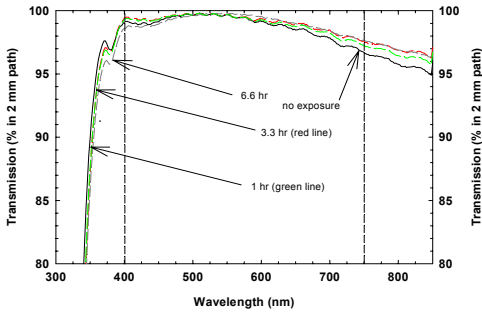
Optical Transmission vs. Wavelength
 Competitive Silicone Gel 1, 1.52 RI
 10 hr exposure to uv



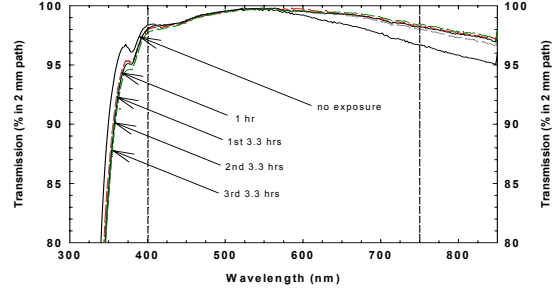
Optical Transmission vs. Wavelength
 Competitive Silicone Gel 2, Super-Clean, 1.52 RI
 10 hr exposure to uv



Optical Transmission vs. Wavelength
 GEL-9617-30, Silicone Gel, 1.54 RI
 6.6 hr exposure to uv

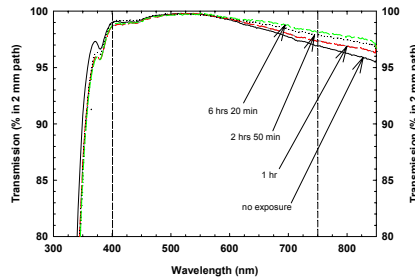


Optical Transmission vs. Wavelength
 GEL3-9617-30, Silicone Gel, 1.54 RI
 before and after 10 hrs exposures to uv



Optical Transmission vs. Wavelength

LS-6257, Silicone Thermoset, 1.57 RI
 before and after 1 hr, 2 hrs 50 min, and 6 hrs 20 min exposure to uv



Randall Elgin is a Senior Engineer for NuSil Technology LLC, the eight largest silicone manufacturer in the world. She heads up the Lightspan Application laboratory in Wareham, MA. Lightspan is the brand name for materials sold into the Photonics market. Formerly an Electrical Engineer for 17years at Sippican, now a Lockheed Martin company. She received her Masters in Electrical Engineering from Boston University.

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