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NuSil SILICONE TECHNOLOGY

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A Characterization of Yellowing Caused by UV Radiation on Silicone Encapsulants, and Improvements in Future Materials

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Summary

This study evaluates twenty-one samples for their change in optical transmission due to a 680-6800J/cm^2 dose of UV radiation. Samples were made from UV curing acrylate, epoxy and silicone chemistries. All samples were prepared and exposed the same way so that comparisons between the samples would be meaningful. Given the same dosage of UV, silicones perform better than UV curing acrylates, which perform better than epoxies.

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 test results, 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.

Test set up

<u>Sample prep</u>:

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. Encapsulant materials tested

No.	Sample description
1	UV Curable Acrylate
2	Optical Epoxy 1
3	Optical Epoxy 2
4	LS-3252, Silicone Gel, 1.52 RI
5	Silicone Gel, 1ppm Pt Catalyst, 1.52 RI
6	Silicone Gel, 9ppm Pt Catalyst, 1.52 RI
7	Silicone Gel, 1ppm Pt Catalyst, 1.57 RI
8	Silicone Gel, 9ppm Pt Catalyst, 1.57 RI
9	Silicone Thermoset, 6ppm Pt Catalyst, 1.57 RI
10	Competitive Silicone Gel 1, 1.52 RI
11	Silicone Gel, 0.15ppm Pt Catalyst, 1.52 RI
12*	Competitive Silicone Gel 2, Super-Clean, 1.52 RI
13	LS-3440, Silicone Gel, 1.40 RI
14	LS-6941, Silicone Thermoset, 1.41 RI
15*	Competitive Silicone Gel, Super-Clean, 1.40 RI
16*	Competitive Silicone Gel, Super-Clean, 1.54 RI
17	LS-6140, Low Outgassing Silicone Thermoset, 1.40 RI
18	Silicone Fluid, 1.61 RI
19*	Silicone Fluid, Super-Clean, 1.51 RI
20*	Silicone Fluid, Super-Clean, 1.46 RI
21	GEL-9617-30, Silicone Gel, 1.54 RI

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

<u>UV exposure and radiation recording set up</u>:

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):

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 $190mW/cm^2$. All samples received an initial exposure to the UV for 60 +/- 1minutes. Temperature readings in the chamber during exposure are typically 75 to 90ºC. 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. An example of the power levels recorded from this procedure is shown in Appendix B.

Six selected samples subsequently received an additional 6.6 to10 hour exposure, which was given and monitored in 3.3 hr intervals over 2 to 3 days. The UV intensity incident on the sample was also monitored for 1 minute immediately before and after exposing the sample for 3.3 hours.

<u>Data Collection</u>:

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.

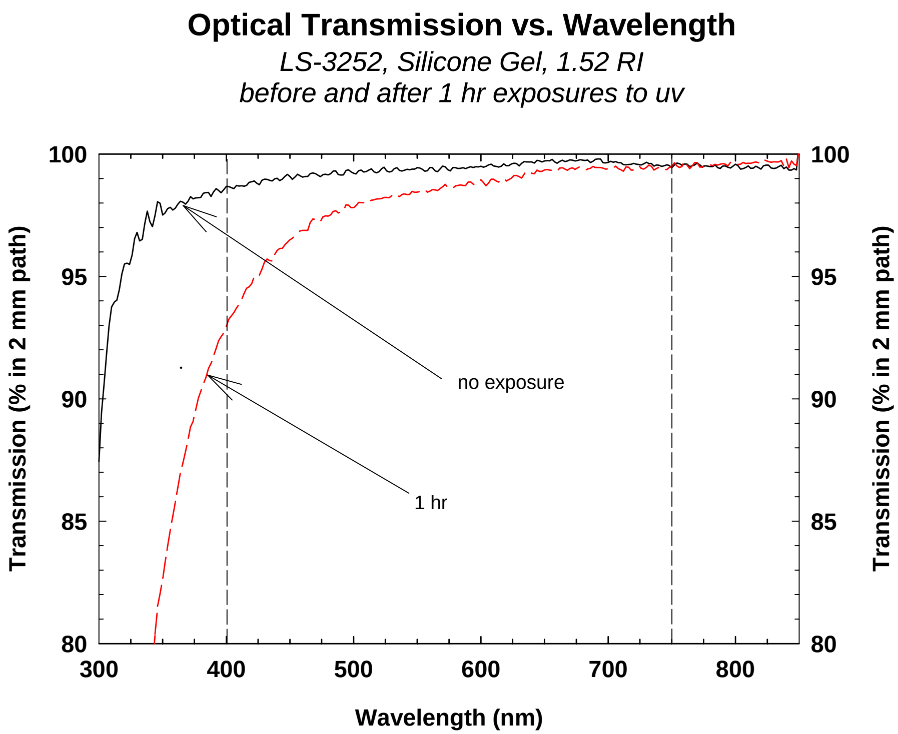


Figure 1. Example of data collected before and after 1 Hour UV exposure

Results

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 C-F.

<u>Data Set 1, 1 hour exposures, non-silicones and varying amounts of Pt</u>:

The results of Data Set 1, the first set of 1hour exposures are shown in Appendix C. 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.
4) Column 4 shows two competitive silicones with 1.52 refractive index and unknown Pt concentration.

<u>Data Set 2, 1 hour exposures, varying amounts of phenyl</u>:

Data Set 2 is shown in Appendix D. In general arrangement of the data is by increasing phenyl concentration from left to right, specifically:

1) Columns 1 and 2 show materials with refractive indices of 1.40 and 1.41, Samples 13, 14, 15 and 17.
2) Column 3 shows materials with refractive index 1.52, Samples 6, 10 and 12.
3) Column 4 shows two 1.54 refractive index materials, Samples 16 and 21.

<u>Data Set 3, 1 hour exposures, fluids:</u>

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

<u>Data Set 4, 6.6 to 10 hour exposures</u>:

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

1) Samples 13 (top left) and 21(bottom right) 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 (top right), which continues to degrade.

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.

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.

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 obtained, however the levels of platinum previously tested were 9 and 30ppm, which is higher than those tested here.

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, Column 3, Sample 18, 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 is not a contributor to yellowing.

Impurities

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

Sample 12-Data Set 1, Column 4, Position 2 and Data Set 4, Column 3, Position 1
Sample 15-Data Set 2, Column 1, Position 2
Sample 16-Data Set 2, Column 4, Position 2
Sample 19-Data Set 3, Column 2, Position 1
Sample 20-Data Set 3, Column 1, Position 1

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 18, 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 solution for the yellowing problem. 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 lead to insights about the cause of yellowing, and has so far resulted in the synthesis of one new material, Sample 21, GEL–9617-30, whose performance you can see in Data Set 2, Column 1, Position 1 and Data Set 4, Column 3, Position 2.

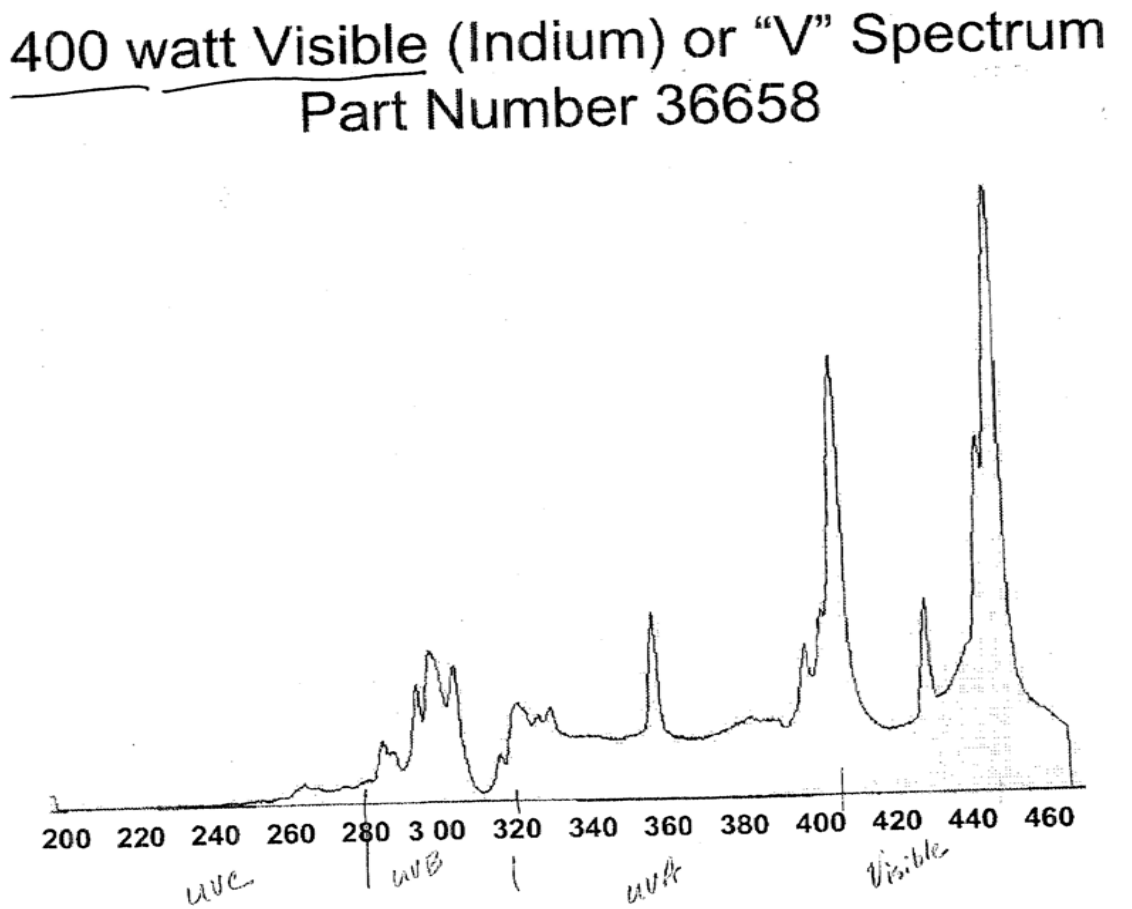
Conclusion

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, Sample 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 two gel materials that perform well under this harsh UV condition. They are LS-3440 and GEL-9617-30.



Appendix A. UV Flood Light Bulb Spectrum

Data Sheet for UV exposure

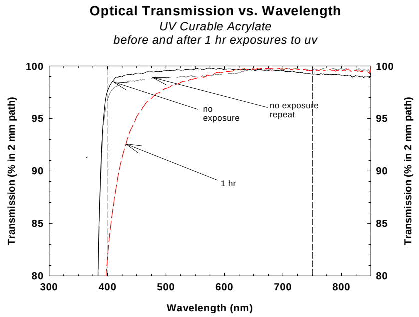
Date: 3/1/2005
Sample Name: **LS-3252-standard**
Notes: 1st exposure

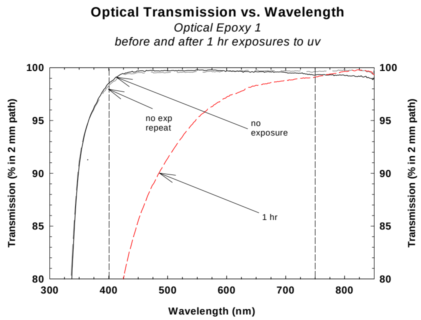
	1 min Intensity/Dosage check before exposure:			1 Hr	1 min Intensity (W/cm^2) check after exposure:		
UVA	Intensity:	0.064	W/cm^2	**U**	Intensity:	0.064	W/cm^2
	Dosage:	3.62	J/cm^2	**V**	Dosage:	3.828	J/cm^2
UVB	Intensity:	0.032	W/cm^2	**e**	Intensity:	0.031	W/cm^2
	Dosage:	1.585	J/cm^2	**x**	Dosage:	1.718	J/cm^2
				p			
UVC	Intensity:	0	W/cm^2	**o**	Intensity:	0	W/cm^2
	Dosage:	0	J/cm^2	**s**	Dosage:	0	J/cm^2
				u			
UVV	Intensity:	0.093	W/cm^2	**r**	Intensity:	0.093	W/cm^2
	Dosage:	5.486	J/cm^2	**e**	Dosage:	5.734	J/cm^2

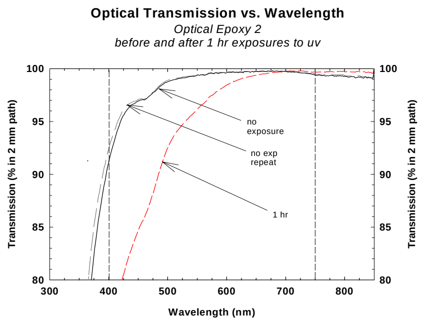
Notes: Masked 3/4 of sample with tin foil. Temp in UV chamber, 70C

Appendix B. Sample of power levels recorded before and after 1 hour exposure of sample to UV.

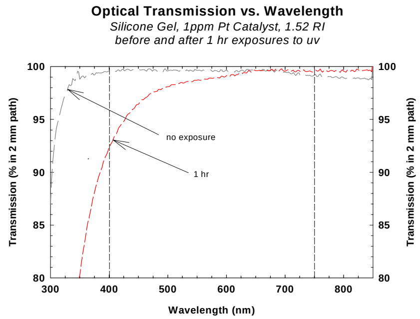
UV Cure/Epoxies

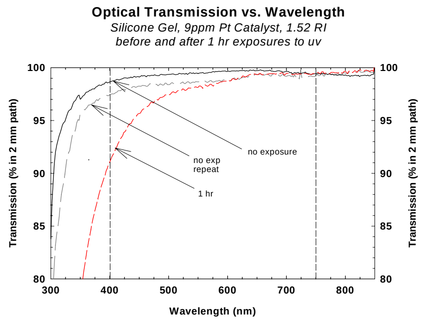


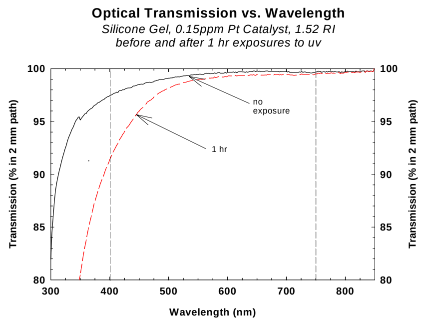




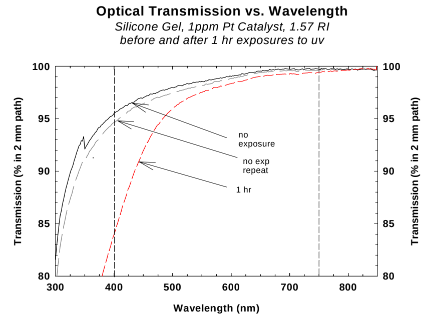
1.52 - 0.1, 1 & 9ppm Pt

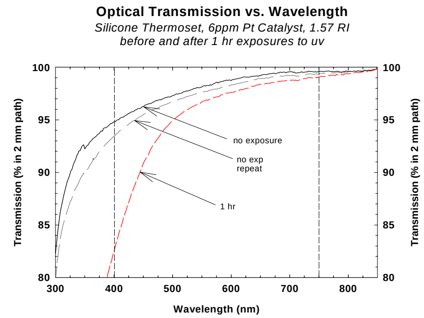


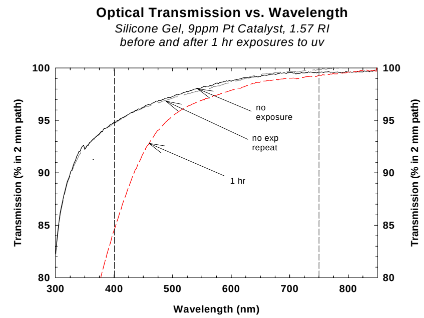




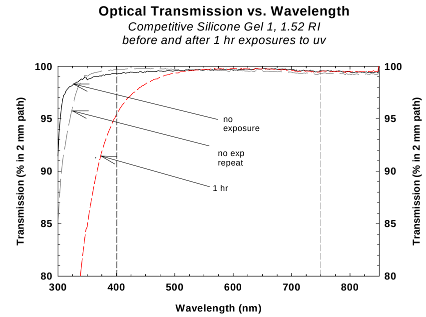
1.57 - 1, 6 & 9ppm Pt

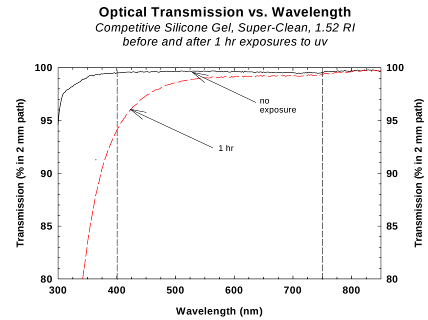






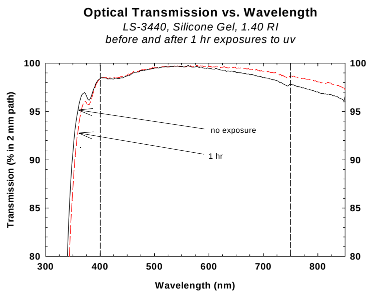
1.52 - Competitive Silicones

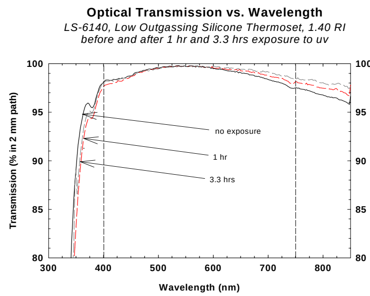


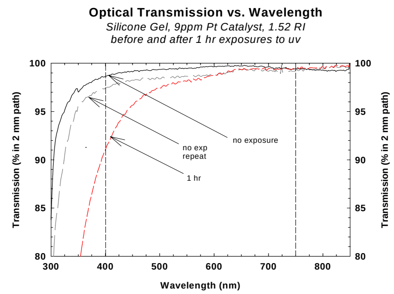


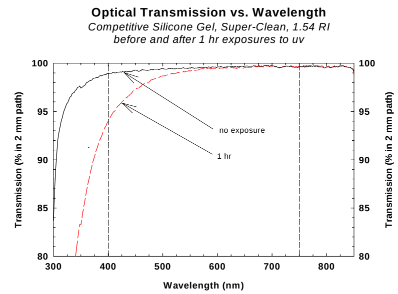
Appendix C. Data Set 1. Non-silicones, 1.52 and 1.57 materials with varying amounts of Pt catalyst.

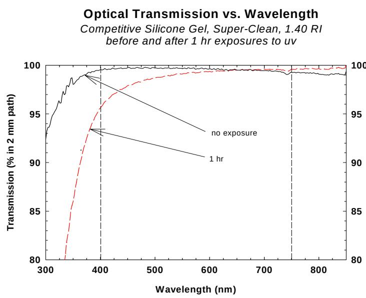
1.40	1.40 & 1.41	1.52	1.54

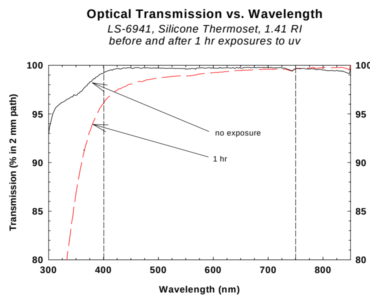


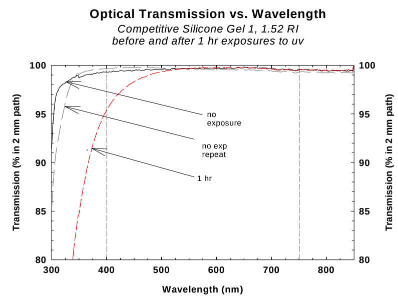


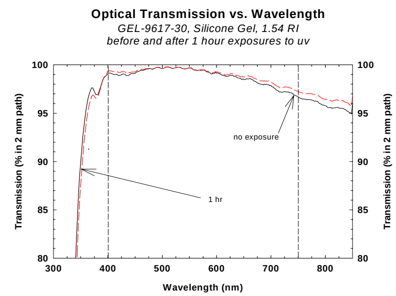


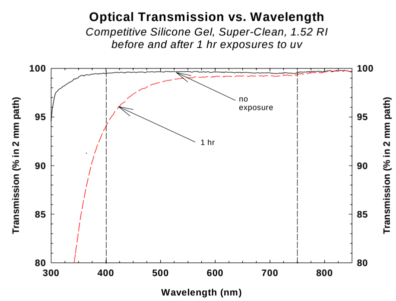






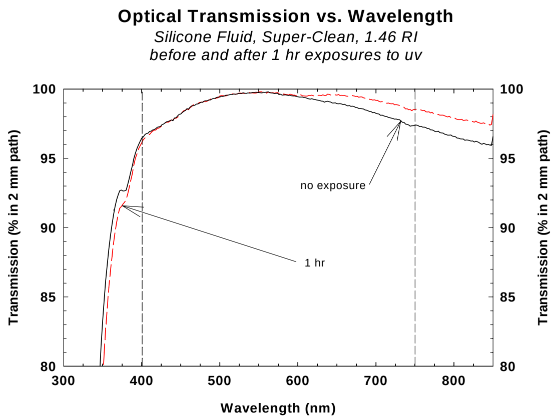




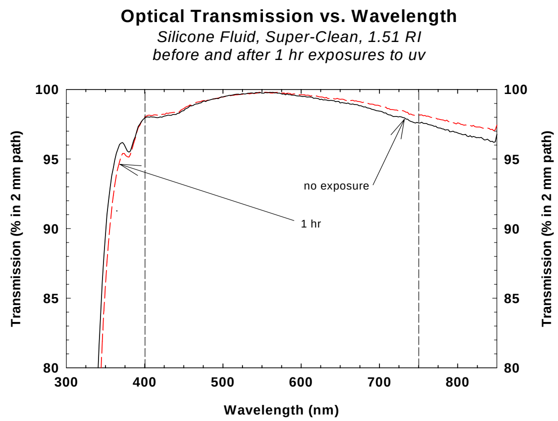


Appendix D. Data Set 2. Materials with varying amounts of phenyl (RI from 1.40 to 1.54).

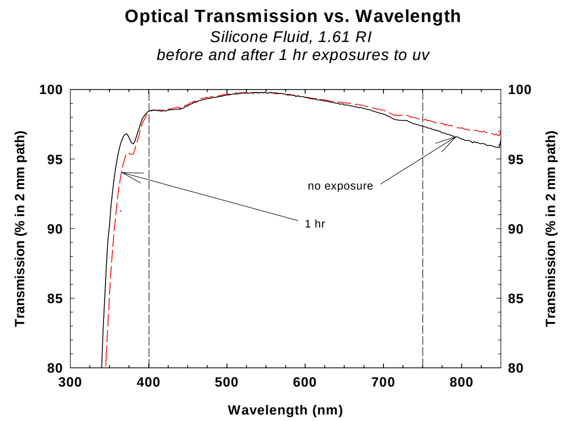
1.46 Fluid, Super-Clean



1.51 Fluid, Super-Clean



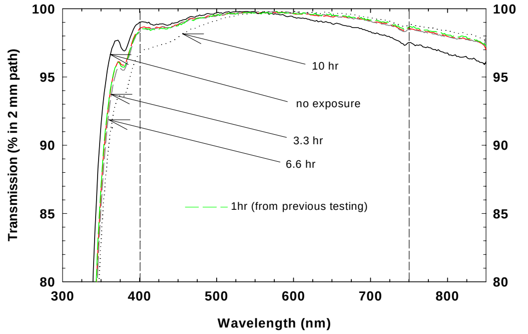
1.61 Fluid



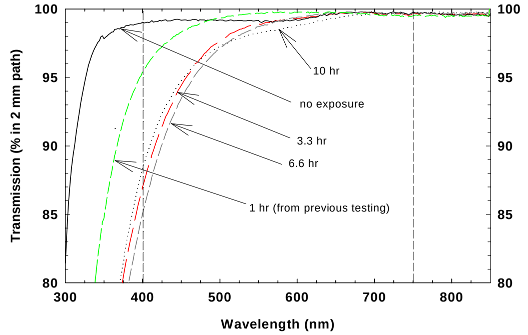
Appendix E. Data Set 3. Silicone Fluids: Super-Clean and High Phenyl Content

6.6 to 10 hour testing - 3.3 hour intervals

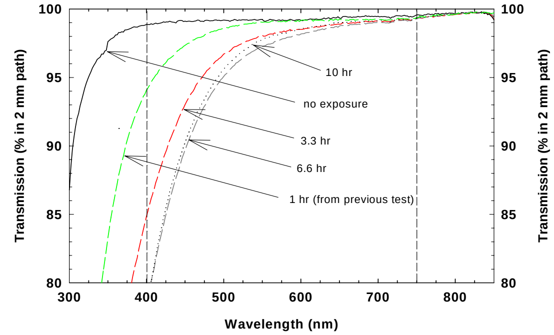
Optical Transmission vs. Wavelength
LS-3440, Silicone Gel, 1.40 RI
10 hr exposure to uv



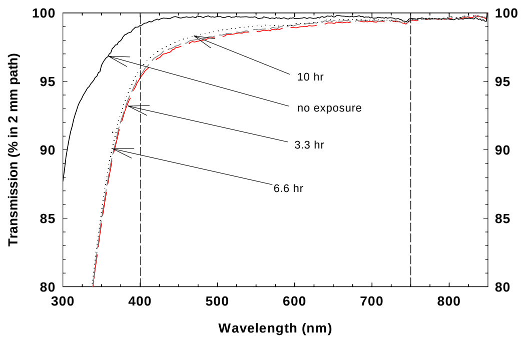
Optical Transmission vs. Wavelength
Competitive Silicone Gel 1, 1.52 RI
10 hr exposure to uv



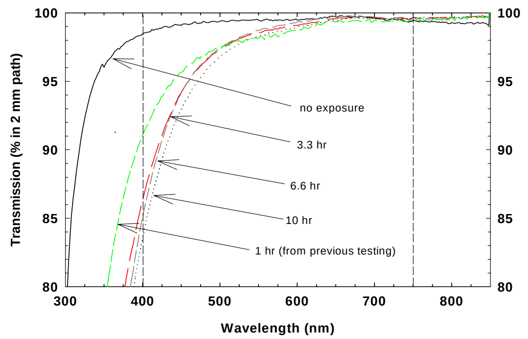
Optical Transmission vs. Wavelength
Competitive Silicone Gel 2, Super-Clean, 1.52 RI
10 hr exposure to uv



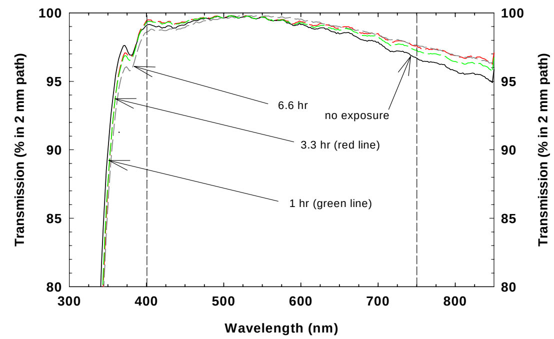
Optical Transmission vs. Wavelength
LS-6941, Silicone Thermoset, 1.41 RI
10 hr exposure to uv



Optical Transmission vs. Wavelength
LS-3252, Silicone Gel, 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



Appendix F. Data Set 4. 6.6 to 10 Hour Exposures

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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Rob Thomaier is a Research Director at NuSil Technology LLC. He has been in the silicone industry for over fifteen years, working in the R&D lab at NuSil Technology. Rob has a BS in Chemistry from UCLA.