NuSil SILICONE TECHNOLOGY

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Characterization of Ultra Low Outgassing™ Silicone Materials for Aerospace Applications

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Presented at the 2007 SAMPE Conference, June 3-7, Baltimore, MD.

ABSTRACT

The Aerospace Industry has used silicone adhesives and coatings for over five decades[1]. Silicones ability to maintain its elasticity and low modulus over a broad temperature range, –130 to 260°C, provides excellent utility in space, where spacecraft are often exposed to these extreme temperatures. The National Aeronautics & Space Administration (NASA) and the European Space Agency (ESA) recommend testing low outgassing materials per ASTM E-595 prior to use in space. [2] These materials should meet the specifications outlined in NASA SP-R-0022A and ESA PSS-014-702, which require a maximum Total Mass Loss (TML) of 1% and Collected Volatile Condensable Material (CVCM) of 0.1%[3,4]. TML and CVCM levels higher than this specification can cause outgassing and subsequent contamination of expensive equipment. Although a standard for many years, many in the industry question whether these specifications are low enough.

Boeing Satellite suspects gaseous emission contamination has caused excessive power degradation on six 702 satellites.[5, 6] The large solar panel temperatures reach greater than 120°C and surface temperature strongly affects contamination buildup and can volatilize larger molecules.[7] The Aerospace Corporation performed a contamination analysis comparing two different temperature solar arrays. This comparison showed high temperature arrays can contaminate to a greater degree.[8] This paper will characterize newly developed *ultra low outgassing*™ materials with TML and CVCM one-tenth the previous specifications. Characterization will include physical, outgas, and optical testing and comparisons will be made to standard materials meeting the basic outgassing requirements.

KEY WORDS: Silicone Polymers, outgassing, adhesives/Adhesive Bonding

1. INTRODUCTION

Early NASA flights used silicones around the space capsule windows and other areas. Upon recovery from the flight, an oily residue was observed. Analysis of this residue showed it to be low molecular weight silicone polymers that had not cross-linked into the matrix. Therefore, NASA realized the importance of using low outgassing silicones and ASTM E-595 and the current standards were born.

NASA recommends all adhesives used in extraterrestrial environments be tested by ASTM E-595. This test method is primarily a screening technique and very useful in identifying materials with relatively low potential for contamination, verifying material quality, and aiding in material selection and qualification for the space, electronics, clean-room, or other high vacuum applications such as leak detectors and particle accelerators. The criteria used for acceptance or rejection of material is determined by the user and based upon specific component and system requirements. Historically a maximum TML of 1% and a maximum CVCM of 0.1% have been used as screening levels.

Silicone has come a long way since those early days. Advances in formulating, processing, and testing have created a generation of silicones that have excellent performance in low vacuum environments and the outgassing phenomena causing contamination has been greatly diminished. At the turn of the millennium, it was discovered that some of our low outgassed materials could and had been produced, achieving much better TML and CVCM values than required. Based on this discovery, manufacturing processes were examined and it was determined that tighter specifications could be held on a regular basis.

However, was this tighter specification relevant to the space community? Many satellite manufacturers both in the U.S. and Europe, including the ESA, were interviewed regarding this matter. Many questioned whether these levels were low enough and all expressed a great interest in materials that would have lower TMLs and CVCMs. They had three primary interests in lower outgassed materials:

1) With the existing levels of adhesive/sealants currently used on a spacecraft, manufacturers must closely monitor their cumulative contaminant levels. By having materials with lower outgas levels, manufacturers would have the ability to use more material when necessary for mechanical reasons, and have the ability to choose material from a broader material range.
2) Materials with lower TML and CVCM values could create more efficient solar cells. Lower outgassing would produce lower contamination and extend the life of a cell. The spacecraft would now last longer in space, therefore displacing the huge cost to build and transport spacecraft over a longer period of time.
3) Any optical application in spacecraft (e.g., optical telescope) is very sensitive to contamination of any kind. Optical engineers want the lowest possible outgassing material to limit the risk of creating any contamination.

2. SILICONE CHEMISTRY

Silicone adhesives, or more appropriately named 'Polyorganosiloxanes', are over sixty years old. [9] The diagram below shows their typical structure (FIGURE 1):

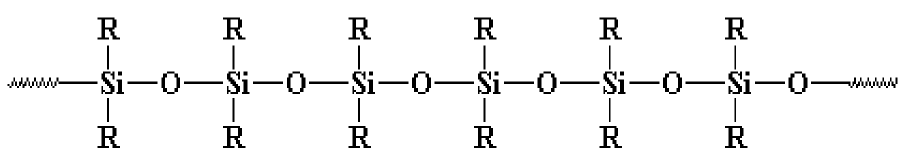


Figure 1 –Structure of polyorganosiloxane; R=CH_3, phenyl, $Fl_3CCH_2CH_2$

Silicones have very unique properties compared to organic based rubbers. Their ability to remain elastic at low temperatures and resistance to molecular break down at high temperatures make its use necessary in harsh environments. The typical Glass Transition point (Tg) of many silicones is < - 115ºC. Other properties silicone offers are low modulus, moisture resistance (< 0.4 %), dielectric strength of 500 V/mil, low shrinkage

(< 1%), low ionic content (< 20 ppm) and formulation flexibility. Silicones are used in a wide array of applications due to these property advantages.[10]

Addition cure adhesives, based on a two-part platinum catalyst system, do not require moisture to cure. Both parts A and B generally contain a vinyl functional silicone polymer with the platinum catalyst added to Part A and a hydride functional crosslinker and inhibitor added to Part B.   Often the silicone can also contain reinforcing fillers, pigments and special additives such as barium sulfate for radio-opacity or boron nitride for thermal conductivity. The cure involves the direct addition of the hydride functional crosslinker to the vinyl functional polymer forming an ethylene bridge crosslink (See Figure 2).

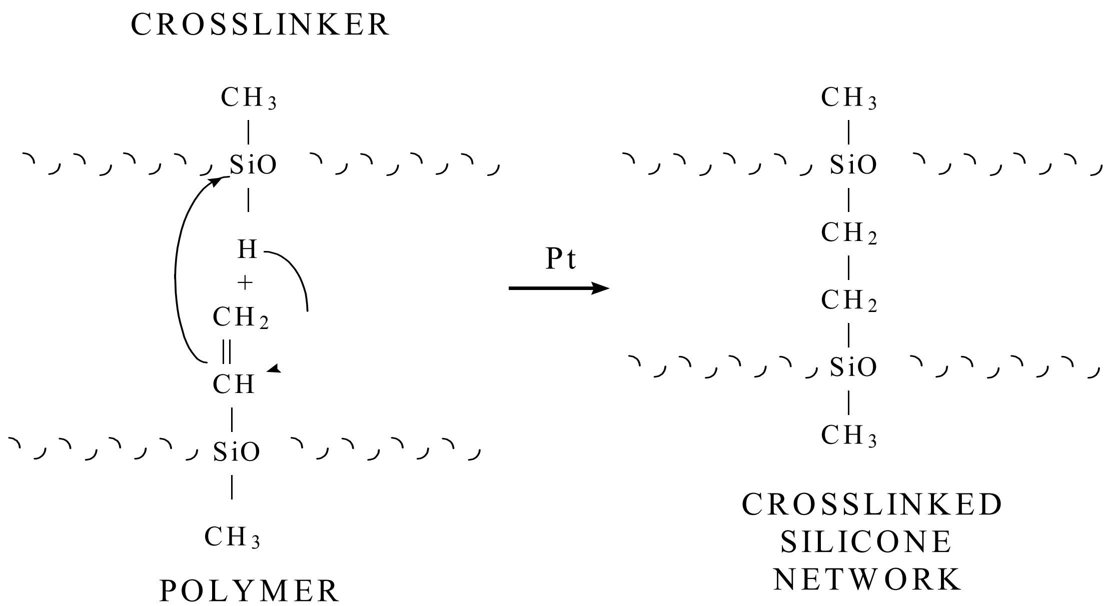
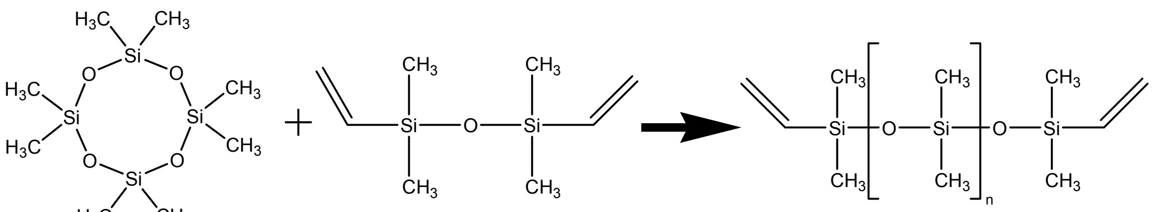


Figure 2-Additon cure mechanism.

Unlike one-part silicone adhesives, this mechanism involves no leaving group allowing these systems to cure in closed environments. Most platinum systems can fully cure at room temperature in twenty-four hours, or the cure can be accelerated with heat

3. ADHESIVE CHEMISTRY

An adhesive is manufactured in several steps. Initially a silicone polymer is produced to meet the standard outgassing specification (< 1.0% TML and <0.1% CVCM). Ring Opening Polymerization (ROP) is commonly used for commercial production of these silicone polymers. The process begins with polyorganosiloxane cyclics reacting with a chain terminating species, or “end blockers,” in the presence of an acid or base initiator (See Figure 3).



octamethyltetracyclosiloxane divinyltertamethylsiloxane vinyl endblocked polydimethylsiloxane

Figure 3: Basic Ring Opening Polymerization (ROP) reaction for a vinyl terminated polydimethylsiloxane.

Octamethylcyclotetrasiloxane (D4) is a ring structure and commonly used to provide the backbone of the polydimethylsiloxanes (PDMS). Siloxane (Si – O) bonds easily react in the presence of anionic or cationic compounds. Siloxane bonds will break and reform when the anionic or cationic compounds are active in the mixture. [11] The divinyltetramethyldisiloxane end blockers are responsible for controlling the ultimate molecular weight distribution, also known as Degree of Polymerization (DP), of the polymer when ROP is complete. The ROP reaction is thermodynamically controlled and allowed to reach equilibrium. When a polymerization is allowed to reach equilibrium conditions, the populations of total cyclics and linear polymers in the reaction mixture remain constant over time.

The product of this polymerization reaction is a mixture of various molecular weights of cyclics, short chained linear molecules and higher molecular weight polymers where the concentrations of each species is based on its thermodynamic equilibrium (Figure 4).

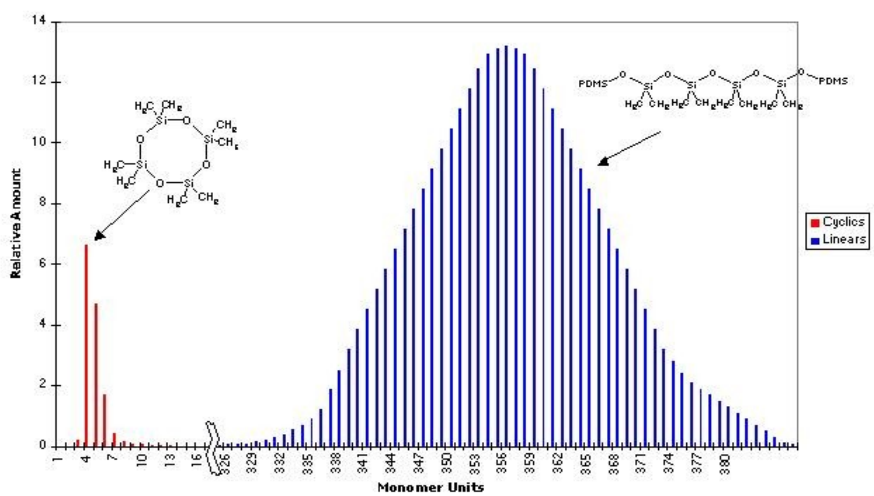


Figure 4: Molecular weight distribution of final ROP reaction products of PDMS.

The oily substance and fogging associated with silicones are primarily caused by the low molecular weight species represented in the smaller peak to the left and the lower molecular weight portion of the larger peak. These species are eliminated in low outgassing materials to prevent contamination.

A distillation process can remove these low molecular weight linears and cyclics from the polymer. The apparatus is typically an evacuated chamber with heated walls and a central cooling finger designed for condensing low molecular weight molecules. Polymer is driven into the heated chamber and wiped onto the chamber walls. This exposes a thin film of the polymer to heat under vacuum conditions. The low molecular weight materials condense on the cold finger and are separated to a collection vessel. Depending on the size of equipment and the ultimate use of the polymer, one to multiple passes through the distillation process can be performed to remove a sufficient amount of low molecular weight species based on the ultimate requirement of polymer. To produce the *ultra low outgassing*™ materials, more low molecular weight linears need to be removed via distillation (Figure 5). This adds more processing time to achieve these lower levels.

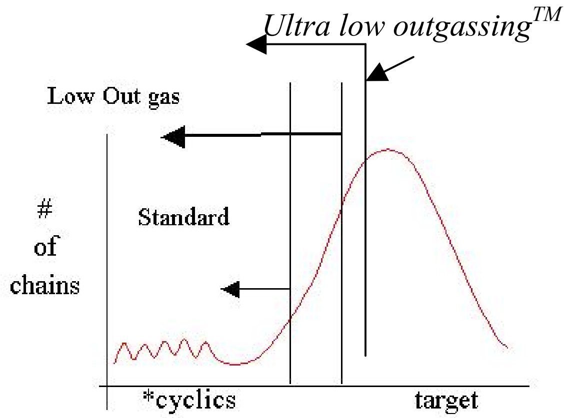


Figure 5: Schematic showing removal of volatile species of a standard silicone versus a low and ultra low outgassinging silicone.

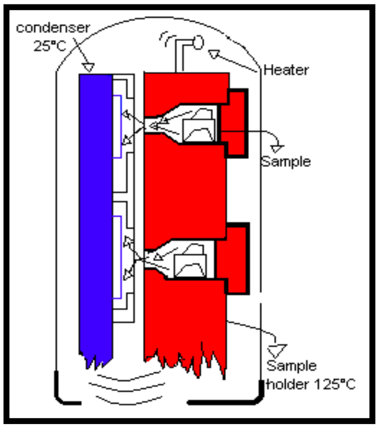
Once the low or ultra low outgassed polymer is produced, silica is added as a reinforcing filler to improve the physical properties of the adhesive. This form is called the base. In a one-part system, catalyst and crosslinker are added to the base. For a 2-part, crosslinker and inhibitor are added to half of the base to create Part B. Catalyst is added to the remaining half of the base creating Part A.

4. LOW OUTGAS TESTING

As mentioned in the Abstract, ASTM E-595 is used to verify all silicone adhesives for extraterrestrial use. The test involves each material sample undergoing preconditioning, conducted at 50% relative humidity and ambient atmosphere for twenty-four hours. The sample is weighed and loaded into a compartment (see *Figure 6*) within a test stand (*Figure 7*). The sample is then heated to 125°C at less than 5 x 10^{-5} torr for 24 hours. Any volatile components of the sample outgas in these conditions. The volatiles escape through an exit port, and if condensable at 25°C, condense on a collector plate maintained at that temperature. The samples are post-conditioned in 50% relative humidity and ambient atmosphere for a twenty-four hour minimum. The collector plate and samples are then weighed again to determine the percentage of weight change, determining TML% and CVCM%. Standard criteria for low outgas materials limit materials' Total Mass Loss (TML) to 1.0% and Collected Volatile Condensable Material (CVCM) to 0.10%. For the *ultra low outgassed*™ materials, the specification will be

< 0.1% TML and <0.01% CVCM. To adhere to these requirements, NuSil Technology will perform this as a standard, lot-to-lot test.

Figure 6 . Low outgas test chamber



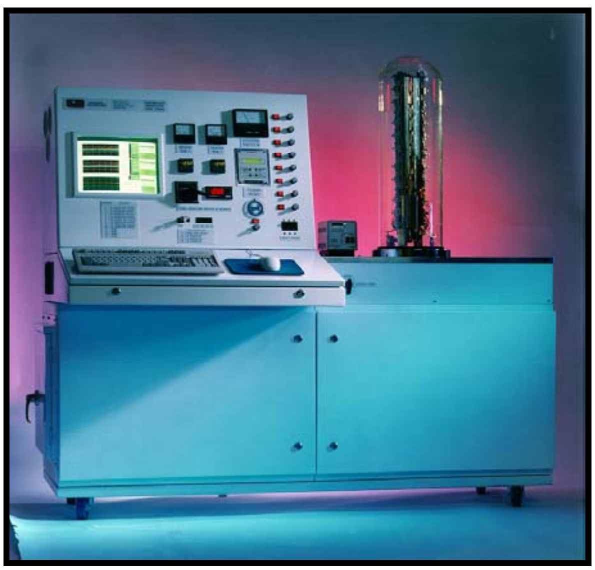


Figure 7. Low outgassed test stand

5. STANDARD PROPERTIES

Seven materials are being initially produced to the *ultra low outgassing*™ specification. These materials were chosen because: they had previously been produced to these low outgas levels, these tighter specifications can be consistently achieved with these materials, and many Material Space Engineers would be interested in these materials.

Tabel 1, *Ultra low outgassing*^{TM} Standard Properties

	SCV1-2599	SCV-2590	SCV-2590-2	SCV1-2590	SCV2-2590	SCV-2596	SCV1-2596
Thermal Conductivity, W/mK	1.25	NA	NA	NA	NA	NA	NA
Electrical Conductivity, ohm-cm	NA	NA	NA	NA	NA	5	0.004
Durometer, Type A	70	45	50	50	40	75	75
Tensile, MPa	1.3	6.2	6.2	5.5	3.5	2.4	2.5
Elongation, %	35	150	150	80	100	75	50
Viscosity, cP	paste	8000	8000	3000	4000	95000	paste
CTE, ppm/C	225		370	400	490	580	215
TML	< 0.1%	<0.1%	<0.1%	< 0.1%	<0.1%	<0.1%	< 0.1%
CVCM	<0.01%	< 0.01%	< 0.01%	<0.01%	<0.01%	<0.01%	<0.01%
Color	White	Clear	Black	Clear	Clear	Black	Tan
Cure system	Platinum	Platinum	Platinum	Platinum	Platinum	Platinum	Platinum

6. COMPARATIVE ANALYSIS

The Table below compares physical properties of an ultra low outgassed material to its similar low outgassed version. This analysis demonstrates that removal of more low molecular weight linears to achieve the ultra low outgas specification for TML and CVCM, does not alter the properties of the finished adhesive and sealant.

Table 2, Comparison of low outgassing to *ultra low outgassing*^{TM} materials

	CV15-2500	SCV1-2590
Durometer, Type A	50	50
Tensile, MPa	5.5	5.5
Elongation, %	90	90
Viscosity, cP	3000	3000
CTE, ppm/C	400	400
TML	< 1%	<0.1%
CVCM	<0. 1%	< 0.01%
Color	Clear	Clear
Cure system	Platinum	Platinum
TGA Takeoff	353°C	353°C
%Transmission, 400nm	>90%	>90%

7. CONCLUSION

The Aerospace community sees a need for *ultra low outgassing*^{TM} silicone adhesives and sealants for use in space applications. These new specification requirements of 0.1% TML and 0.01% CVCM will allow more materials to be used on a spacecraft when necessary, longer life of the solar cells due to lower contamination, and lower risk for optical applications. Based on property data and comparison study, these *ultra low outgassing*^{TM} materials have no negative effects from the removal of more low molecular weight linears. Further studies will be performed on these new materials at higher temperatures and longer exposure.

8. REFERENCES

(1) Aerospace Bibliography, NuSil Technology Document
(2) ASTM E-595
(3) NASA SP-R-0022A
(4) ESA PSS-014-702
(5) Space News, January 21, 2002
(6) Space News, March 10, 2003
(7) M.Bodeau, "Root-Cause of the 702 Concentrator Array Anomaly," Presentation at 2003 Space Power Workshop, Redondo Beach, CA April 2003
(8) M. Eskenazi, A. Jones & R.Jain, "Cellsaver Qualification Testing and Contamination Analysis", 1st International Energy Conversion Engineering Conference, Portsmouth, VA, August 2003

(9) B.Riegler, J.Meyer, "Low Outgas Silicone Pressure Sensitive Adhesives for Aerospace Applications", 36th International SAMPE Technical Conference, May 2004.
(10) B. Riegler, et al, "Accelerating Cure of Silicone Adhesives", 34th International SAMPE Technical Conference, November 2002.
(11) Siloxane Polymers Stephen Clarson & J. Anthony Semlyen (PTR Prentice Hall. Copyright 1993)