Low outgassing materials for electro-optic and electronic systems

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This paper explores the need for low outgassing, thermally stable, high performance materials for electro-optic and electronic systems, citing various applications of low outgassing materials in electro-optic and electronic systems. This paper also describes the chemistry of silicone polymerization, identifying the source of outgassing components in silicones as well as the procedures for eliminating these volatile materials—solvent washing or wipe film evaporating.

WHITE PAPER

INTRODUCTION

In closed electronic and opto-electronic systems, volatile components can contaminate sensitive components. Smaller electronic packages with higher voltage requirements can produce excessive heat, and any components containing volatile chemical species can outgas under these conditions. Electronic systems can contain a variety of components at various operating temperatures. Cooler components behave like a cold soda can on a warm humid day, as they can become a conduit onto which these volatile components re-condense. Specific examples of military and comme rcial applications described below demonstrate the necessity for low outgassing materials that prevent contamination.

TECHNOLOGY AND TRENDS :

Traditionally, applications on satellites and the space shuttle employ low outgassing materials , as these applications encounter extraterrestrial environments that cause outgassing. These environments typically undergo extreme temperature cycling in a vacuum. However, use of low outgassing materials has recently branched out into electronic applications such as aircrafts, touch screens, and projectors. We investigate the market forces that are driving more terrestrial uses of low outgassing materials.

The military recognized certain components containing volatile materials can contaminate other traditional electronic packages, prompting them to write standard specifications for materials used to build electronic systems. The Department of Defense issued Mil-Std-883E test method standard for microcircuits, effective May 1, 1997. The purpose of this mil-spec is to standardize acceptance of materials used in microcircuit applications. In regards to outgassing of the cured material, the Department of Defense states materials must meet rigorous outgassing requirements.

The military continually relies on cutting edge technology, and expects to spend $12.7 billion on research and development of electro-optical systems through 2012. Electro-optical systems are now an integral component in the advancement of military technology. One such investment is the military's novel remote sensing technology, which combines wide field-of-view surveillance, near continuous sensing, and fast sampling with the added capability of spectral discrimination of events over the chosen electro-optical band. Currently, the directorate responsible for this systems is also working to miniaturize the sensor system using folded, high efficiency, reflective/refractive optical system concepts, increasing the field of regard with larger, fast framing focal planes. The risk of re -condensation of outgassed silicones or other materials in closed systems threatens the advancement of electro-optic systems such as the one described above, as outgassing can cause contamination or fogging of sensitive critical components.

Many non-military challenges exist when packaging sensitive electronic systems. For example, contamination cannot occur in microelectricalmechanical systems (MEMS) in the assembly, joining, and aging processes.

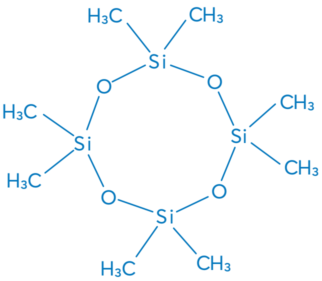
Low outgassing materials have become critical to the performance of commercial electro-optical system applications. Most notably, the fabrication of hard disk drive assemblies uses Pressure Sensitive Adhesives
(PSA's) because they offer an easy-to-use method for bonding components. New high-capacity drives use low outgas versions of PSA's, eliminating head corrosion and media fogging that causes hard drive failures. Other common uses of low outgassing pressure sensitive adhesives include bonding microfilters, flexible circuits, seals and labels.

SILICONE CHEMISTRY

Commercial production of silicone polymers often begins with polysiloxane cyclic and short chained siloxane oligmers, typically derived from the hydrolysis of chlorosilane monomers. While creating many specialized functional polymers and silicone resins begins with chlorosilane chemistry, this paper will focus on building polymers from the cyclic stage.

Polysiloxane cyclics can convert to high molecular weight polymers at temperatures of 250 to 300°C in closed systems. Thermal degradation of organic constituents on the silicon atom can create undesirable crosslinking, essentially forming non-linear structures. To achieve any appreciable amount of high molecular weight species, applying pressures of 1000 to 7000 kg/cm2 is required. Fortunately, more commercially viable options, such as the use of catalysts , can polymerize polysiloxane cyclics into linear, high molecular weight silicones at considerably lower temperatures and pressures.

This paper will use octamethyltetracyclosiloxane as the cyclic for the discussion. This molecule (Picture 1) is very reactive when compared to other organosiloxane compounds such as diphenylsiloxane cyclics, because of the relatively uninhibited access of a catalyst to the siloxane oxygen.



Picture 1:

Polymerizations can be catalyzed with either Brönsted or Lewis acids. The acid proton attacks the lone pairs of the siloxane oxygen, creating a scission (acidolysis) at the oxygen and silicon bond

$$HA \;+\; (R_2SiO)n \longrightarrow HOSiR_2(OSiR_2)_{n-1}\;A$$

This new ionic species may react with other similar species forming a siloxane bond. Other scenarios include the condensation of the two hydroxy functional siloxane units and the hydrolysis of the cation end of the polymer (all three scenarios are depicted below):

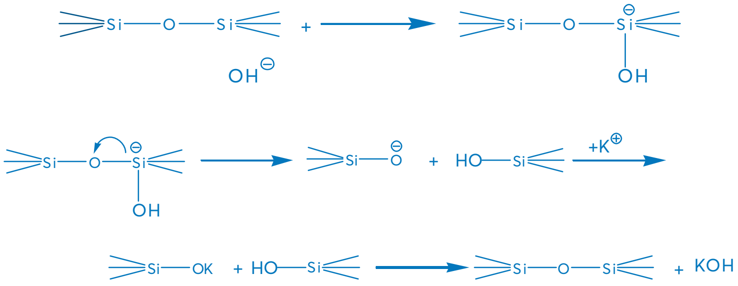
$$\sim SiOH + HA\ ?\quad \sim SiA\ + H_2O$$

$$\sim SiA + HOSi\sim ?\quad \sim SiOSi\sim + HA$$

$$\sim SiOH + HOSi\sim ?\quad \sim SiOSi\sim + H_2O$$

According to Noll (4), there is an energy gradient that favors macromolecules in these situations.

Using alkaline catalysts is another method of catalyzing a siloxane polymerization. The reaction proceeds differently than the Lewis acid catalysis. The base attaches itself to the silicon atom in the polysiloxane, cleaving the bond as shown below in Picture 2:

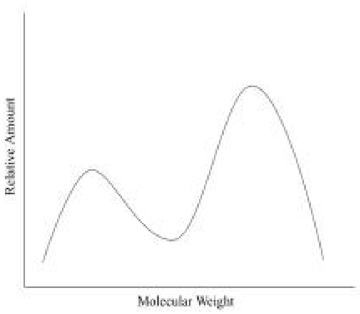


Picture 2:

Both reactions are equilibrium reactions, and in the presence of an end blocking or chain terminating species such as hexamethyldisiloxane, the reaction begins with an increase in viscosity.

This increase in viscosity occurs primarily because the rate of cyclic opening and polymerizations is greater than that of the end blocking molecule scission. The polymer chain forms and breaks through the course of the reaction. Typical reactions take several hours to reach equilibrium. In the case of polymerizations involving octomethyltetracyclosiloxane and hexamethyldisiloxane, an equilibrium mixture of roughly 85% linear polymers and 15% cyclics is present. The stoiciometric amounts of cyclics and chain terminating species in the reaction determines the molecular weight of the polymer . Small amounts of endblocking species create larger linear polymers, and conversely, large amounts of those species result in shorter, lower molecular weight polymers. After equilibrium, purging acid catalysts from the system stops the reaction, and elevated temperatures or carbon dioxide can deactivate alkaline catalysts.

As stated above, the product of the polymerization reaction is a mixture of cyclics, short chained linear molecules and higher molecular weight polymers. The length of the polymers, or molecular weight, is normally distributed, and gel permeation chromatography will show a bimodal distribution with a smaller, low molecular weight peak (representing cyclics and very short chained linears) and a larger peak representing the larger molecular weight polymers.



The species represented in the smaller peak and the lower molecular weight portion of the larger peak can outgas in extreme operating environments. The two processing techniques described below achieve removal of these species.

Processing

Wiped film evaporation can process silicone materials utilizing polymers with viscosities under 500,000 cps. Most formulations of liquid silicone elastomer systems contain polymers of this size. Polymers or materials with viscosities higher than this amount typically require a process called solvent extraction. These materials are typically high consistency rubbers or PSA's.

A distillation process known as wiped film evaporation can remove low molecular weight fractions of polymerizations. The wiped film apparatus is typically an evacuated chamber with heated walls and a central cooling finger designed for condensing low molecular weight molecules. After the polymerization reaction is complete, the material is driven into the heated chamber and wiped onto the heated chamber walls. This exposes a thin film of the polymerization to heat under vacuum conditions. Higher molecular weight silicones continue to migrate down (or wipe down) the chamber wall, while the low molecular silicones condense on the cold finger and are routed to a collection vessel.

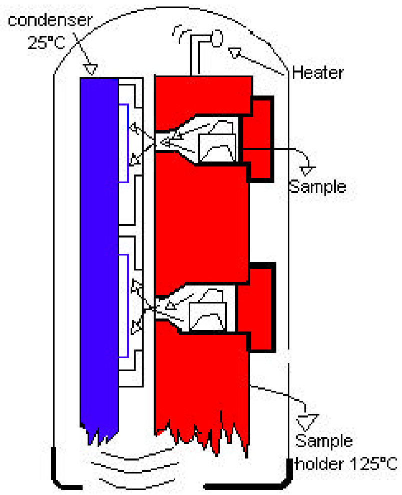
Depending on the type of equipment, several attempts may be required to remove a sufficient amount of low molecular weight silicone species to pass Total Mass Loss (TML) and Collected Volatile Condensable Material (CVCM) requirements—standard criteria for low outgas materials limit materials' TML to 1.0% and CVCM to 0.10%. While low TML's can be achieved with a minimal amount of processing, CVCM's may require extensive processing to meet required specifications.

As stated above, making a silicone polymer via an equilibrium method, a portion of monomer remains and a population of short-chained oligomers forms in addition to the main product. This portion varies depending on the type of siloxane polymer and constitutes the volatile condensable material. These volatile condensable materials are the specific moieties that need to be removed to produce a low outgassing material. If not removed, they will separate from the main polymer and contaminate the surrounding environment, leaving a silicone residue.

When the polymer in question is of larger molecular weight, such as those in a PSA, it can be difficult to remove the volatile condensable materials by the conventional stripping methods. A solvent washing technique is used instead. Essentially, solvent washing is a form of extraction involving multiple solvents with varying solvating abilities. Due to the nature of the polymer prior to extraction, a second solvent immiscible with a bulk polymer but miscible with the first solvent is used to remove low molecular weight volatile condensable material. In addition, it is difficult to perform a simple single solvent exaction due to the high molecular weight of the polymer. The multiple solvent method allows the extractant to reach and solvate this lower molecular weight fraction and remove it from the bulk. The washing process may need to be repeated several times, dependent again on the type of siloxane polymer involved. This process is shown in Appendix A.

Testing

The American Society for Testing and Materials' (ASTM) test method E595 provides a standard for testing 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 within a test stand (see Picture 3). 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-hour 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' TML to 1.0% and CVCM to 0.10% . To adhere to these requirements, NuSil Technology performs this as a standard, lot-to-lot test for low outgassing materials.



Picture 3. Diagram of ASTM E595 Test Stand

Materials

Even after additional processing, low outgassing materials perform to the same level, or exceed, non-outgassing materials. Several tests were performed on materials to demonstrate the similarities of low outgassing and non-outgassing materials. The results of these tests show the excellent physical properties of low outgassing materials.

Clear Encapsulants:	**CV-2500**	**R-2615**
Durometer, Type A	45	
Tensile Strength	900psi	1100psi
Volume Resistivity	1x1015	1x1015
Collected Volatile Condensable Material	0.01%	0.25%
Total Mass Loss	0.05%	0.80%

Thermally Conductive Elastomers:	**CV-2960**	**R-2930**
Durometer, Type A	60	80
Tensile Strength	200psi	260psi
Volume Resistivity	125%	20%
Collected Volatile Condensable Material	0.01%	0.08%
Total Mass Loss	0.04%	0.46%

High Temperature Clear Encapsulants:	**CV16-2500**	**R-2655**
Durometer, Type A	40	40
Tensile Strength	500psi	800psi
Volume Resistivity	100%	125%
Collected Volatile Condensable Material	0.01%	0.87%
Total Mass Loss	0.05%	2.03%

Pressure Sensitive Adhesives:	**CV-1161**	**Med-1356**
Collected Volatile Condensable Material	0.07%	2.11%
Total Mass Loss	0.30%	5.09%

CONCLUSION

Many of the rapidly growing industries mentioned above demonstrate the need for low outgassing materials. Low outgassing silicones provide these industries with beneficial physical properties including flexibility/stress relief, thermal stability, moisture resistance, low ionic impurity levels, and high permeability to gases and high overall purity. These properties help ensure protection of other sensitive components in electronic packages.

This paper was able to confirm the need of low outgassing materials in the market by citing various applications for low outgassing materials. An explanation of the chemistry, procedures, testing and comparisons proves the performance quality of low outgassing materials, even after additional processing.

Author Biographies:

Bill Riegler is the Product Director-Engineering Materials for NuSil Technology, the 45 largest privately owned silicone manufacturer in the World. Bill has been in the silicone industry for almost twenty years with various positions at NuSil and the silicone division of Union Carbide, which has become the OSi Specialties Group of GE Silicones. Bill has a B.S. in Chemistry from the University of California at Santa Barbara and a Masters in Business from Pepperdine University.

Steve Bruner is the Marketing Director at NuSil Technology. He has a BA in Chemistry from The University of Colorado and a Masters in Business from Pepperdine University. Steve has been with NuSil almost ten years.

Rob Thoma ier is the Research Director at NuSil Technology. Rob has close to fifteen years in silicone R&D experience. He has a B.S. in Chemistry from UCLA.

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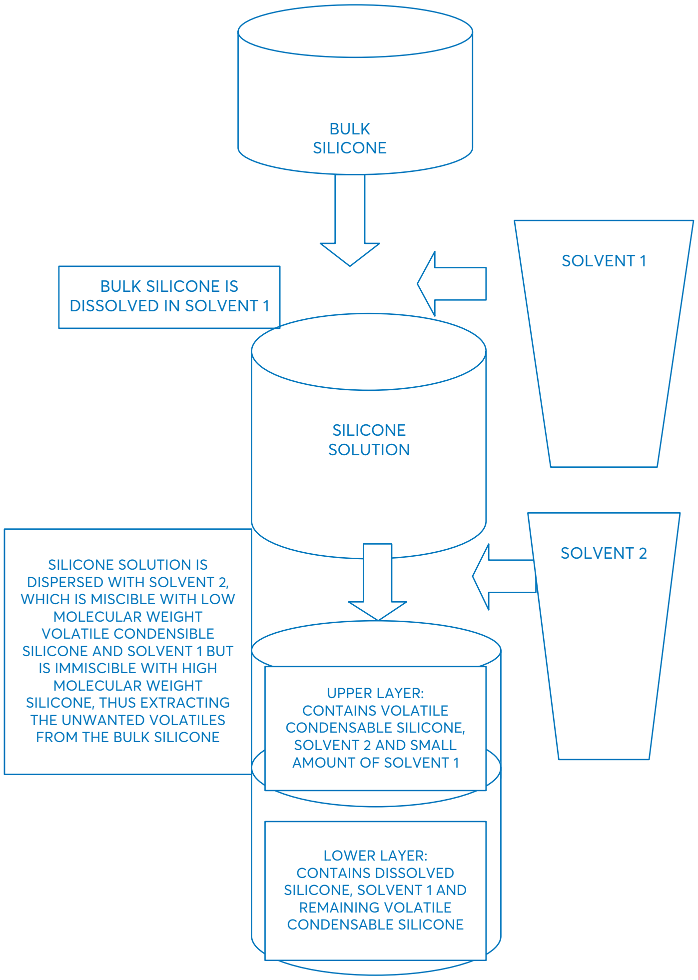

Appendix A : Solvent Wash Process Diagram