NEW LOW STRESS FILM ADHESIVE FOR AEROSPACE APPLICATIONS REQUIRING LOW OUTGASSING

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ABSTRACT

Low stress liquid adhesives based on silicone chemistry have been used for years in the aerospace industry requiring low outgas, ASTM E-595 requirements (1). The applications include coverglass adhesives, mirror bonding, potting of electronic parts and many more. Silicones are valued for their dependability during extreme temperature cycling and inherently low modulus characteristics. Aerospace Engineers working on applications that require precision bond lines for adhesion or sealing applications have struggled with liquid silicone systems. The lack of uniform bond thickness and mess/clean-up issues result in significant process inefficiencies.

Film adhesive technology solves many of these problems. Films can be produced to an exact thickness specified by the customer. If many of the same components are going to be adhered to, a die cut of the film could be obtained and reproduced to improve the efficiency of applying adhesive. Mess and clean-up are non-existent.

The problem until recently is that low stress, low outgassing silicone film adhesive versions were not available. This paper will characterize new film adhesives and compare with similar liquid materials; CTE, High/low temperature resistance, adhesion, etc. The possibility for future novel applications will also be discussed.

KEY WORDS: Silicone Polymers, Film Adhesives, Outgassing

1. INTRODUCTION

The National Aeronautics & Space Administration (NASA) recommends all adhesives used in extraterrestrial environments be tested by ASTM E-595 (2). 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 space applications. 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 Total Mass Loss (TML) of 1.00% and a maximum Collected Volatile Condensable Materials (CVCM) of 0.10% have been used as screening levels for rejection of materials.

Film adhesives are a whole category of adhesives defined as adhesives with a specified and consistent bond thickness that does not change (3). They often require heat or an activator to instigate the chemical reaction for cure.

2. SILICONE CHEMISTRY

Silicone adhesives are over sixty years old (1), and oddly enough, ‘silicone’ is a misnomer. Normally the suffix ‘-one’ delineates a substance having a double bonded atom of oxygen in its backbone. Scientists initially believed that silicone materials contained double bonded oxygen, hence the use of ‘silicone.’ However, scientists have found that silicones are really inorganic polymers, having no carbon atoms in the
backbone, and therefore should be named ‘Polyorganosiloxanes.’ The diagram below shows their typical structure (FIGURE 1):

![Chemical structure of polyorganosiloxanes](image)

**Figure 1 – Structure of polyorganosiloxane; R=CH₃, phenyl, F₃CCH₂CH₂**

Polysiloxanes offer excellent elastomeric properties, a wide range of temperature stability (-115 to 260°C when phenyl substituted), fuel resistance (when Trifluoropropyl substituted), optical clarity (with refractive indexes as high as 1.60), low shrinkage (<1%), and low shear stress. Silicones are used in a wide array of applications due to these property advantages (4).

One-part adhesives are the most common silicone adhesive and are used in diverse applications from bathtub caulking to adhering pace maker leads. These one-part adhesives are based on acetoxy (alkyltriacetoxyisilane) or alcohol (alkoxy) crosslinked cure systems. The following demonstrates the reaction, which requires water to cure:

![Chemical reaction diagram](image)

Addition cure adhesives, based on a two-part platinum catalyst system, do not require moisture or open air to cure. Both parts generally contain a vinyl functional silicone polymer with the platinum catalyst added to the material’s Part A and a hydride functional crosslinker and inhibitor added to Part B. Often both parts 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).
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. FILM ADHESIVE CHEMISTRY

A film adhesive is manufactured very similar to a low outgassed addition cure liquid adhesive. A polymer is made to meet the ASTM E-595 outgas limits, < 1.0% TML and <0.1% CVCM. These polymers used as the primary building block, are created with polyorganosiloxane cyclic and short-chained siloxane oligmers (see Figure 3). The use of catalysts can polymerize polysiloxane cyclics into linear, high molecular weight silicones at low temperatures and pressures.

This is an equilibrium reaction, and in the presence of an end blocking or chain terminating species such as hexamethyldisiloxane (Figure 4), 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. 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 linear, and a larger peak, representing the larger molecular weight polymers (See Figure 5). The species represented in the smaller peak and the lower molecular weight portion of the larger peak can outgas in extreme operating environments. Following E-595, CV- materials, these species are eliminated to prevent contamination.

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 the low outgassing requirement of E-595.

Once the low outgassed polymer is produced, silica is added as a reinforcing filler to improve the physical properties of the adhesive. Crosslinker and inhibitor are added to this silica filled base and calendared into a sheet. The catalyst, in the activator Part B, is applied to both the substrate and the film adhesive if possible. The film adhesive is then laid onto the substrate as smoothly as possible with a weight or roller added to apply some pressure. See Figure 6 for a diagram.
The activator with the catalyst diffuses throughout the silicone sheet and allows cure. Thin films can also be cured at room temperature.

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 7) within a test stand (Figure 8). 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%. To adhere to these requirements, NuSil Technology performs this as a standard, lot-to-lot test.
5. FILM ADHESIVE TESTING

Because these film adhesives are used as adhesives, testing related to the adhesive strength of these materials on substrates is primary. ASTM D-1002, Apparent Shear Strength of Single-Lap-Joint Adhesively Bonded Metal Specimens by Tension Loading, was used as our test method reference. This standard has been approved for use by the Department of Defense (5).

An aluminum panel is cut into a lap configuration, 1 inch wide by 4 inches long. Six strips of each substrate were prepared to make 3 test panels. Panels were cleaned with isopropanol to remove dirt, grease or particulates. The activator, Part B is added to one square inch area on one end of each lap panel as described above and let to sit for at least 30 minutes. The film adhesive was placed on the panels, covering the applicator. The two panels were pressed together forming a sandwich (See Figure 9). This sandwich then has a 1lb weight placed on it for 30minutes. The panels were then placed in an air-circulating oven set at 65°C for a four-hour cure. The equipment used to test for lap shear value was an ISTRON Model 1011 with MTS data acquisition and 1000-lb load cell installed (See Figure 10).

Figure 8. Low outgas test stand.

Figure 9 – Lap Panel configuration
6. COMPARISON WITH LIQUID ADHESIVES

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<th>Low outgas Film Adhesive (6)</th>
<th>Low outgas Liquid Adhesive (7)</th>
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<tr>
<td>CVCM</td>
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7. CONCLUSION

The development of a low outgas silicone film adhesive, combining the low outgas properties needed from a material used in space with the consistent bond thickness and no mess of a film adhesive, was concluded and characterized. The low outgassing requirements of 1% or less Total Mass Loss (TML) and 0.1% or less Collectable Volatile Condensable Materials (CVCM) were achieved. When compared to liquid adhesives most properties are very similar with the exception being tensile and tear which are greater. The use of a thicker base in the film adhesive allows for this increased strength. The thicker the bondline the greater the lap shear strength. The aerospace industry now has a thermally reliable, low outgassed film adhesive that can be used in a variety of applications common to satellite manufacturing. The material comes in a number of forms and thicknesses. Future work could be performed to incorporate electrically and/or thermally conductive fillers into the base to develop further unique films.
8. REFERENCES


(2) Something about NASA E-595

(3) Definition of film adhesive


(6) Product Profile for NuSil Technology LLC CV-2680-12

(7) Product Profile for NuSil Technology LLC CV2-2289-1

Bill Riegler is the Product Director-Engineering Materials for NuSil Technology LLC, the eighth largest silicone manufacturer in the world. Bill has been in the silicone industry for over twenty years with various positions at NuSil and the silicone division of Union Carbide, which has now become a part 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.

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