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Low Outgas Silicone Pressure Sensitive Adhesive for Aerospace Applications.

By Bill Riegler, Product Director-Engineering Materials, Joan Meyer, Senior Chemist,
NuSil Technology -Carpinteria, CA.

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ABSTRACT

The need for a low outgas, thermally stable, high performance adhesive has initiated the development of a new experimental silicone Pressure Sensitive Adhesive (PSA) able to pass ASTM E-595, low outgassing requirements of 1% or less Total Mass Loss (TML) and 0.1% or less Collectable Volatile Condensable Materials (CVCM). The performance goals were to maintain performance under load at temperatures above 175°C and have similar properties to other low outgassed silicone PSA's as tested by peel, loop tack, shear, release force and Blunt probe tack.

KEY WORDS: Silicone, PSA, ASTM E-595, low outgas, Aerospace

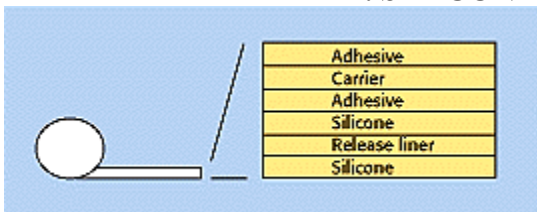
1. INTRODUCTION

The National Aeronautics & Space Administration (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 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.

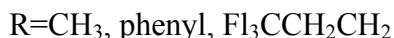
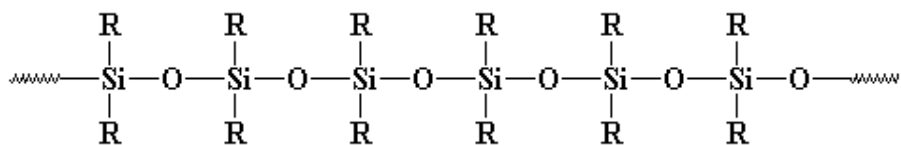
Pressure Sensitive Adhesives (PSA) are a whole category of adhesives defined as materials that adhere to a substrate temporarily when given some pressure and can be removed when needed without damaging the original substrate. They do not require activation by heat or water. A band-aid is a basic example of a pressure sensitive adhesive. All tapes are made from a PSA applied and cured on backing film. The chemistry used for the adhesive varies depending on the environment and application. Silicone PSA's incorporate a high molecular weight polydimethylsiloxane polymer and a tackifying silicone resin dispersed in a solvent system. As with any silicone adhesive, silicone PSA's are most appropriate when used in extreme temperatures ranging from -115 to 260°C.

A very unique and useful satellite repair product can be produced by combining the low outgas properties needed for a material used in space with the PSA technology incorporated into tapes. This paper details the development of an experimental low outgas silicone PSA and the various testing performed on the adhesive.

2. SILICONE PSA CHEMISTRY

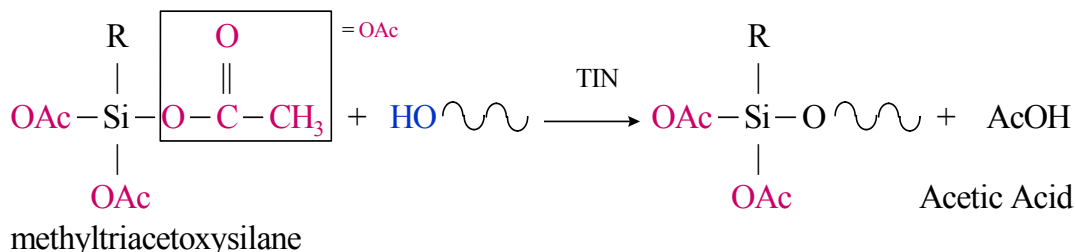


Silicone adhesives are over sixty years old (1), and oddly enough, ‘silicone’ is a misnomer. Normally the suffix ‘-one’ delineates a substance having a double bonded atom of oxygen in its backbone. Scientists initially believed that silicone materials contained double bonded oxygen, hence the use of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



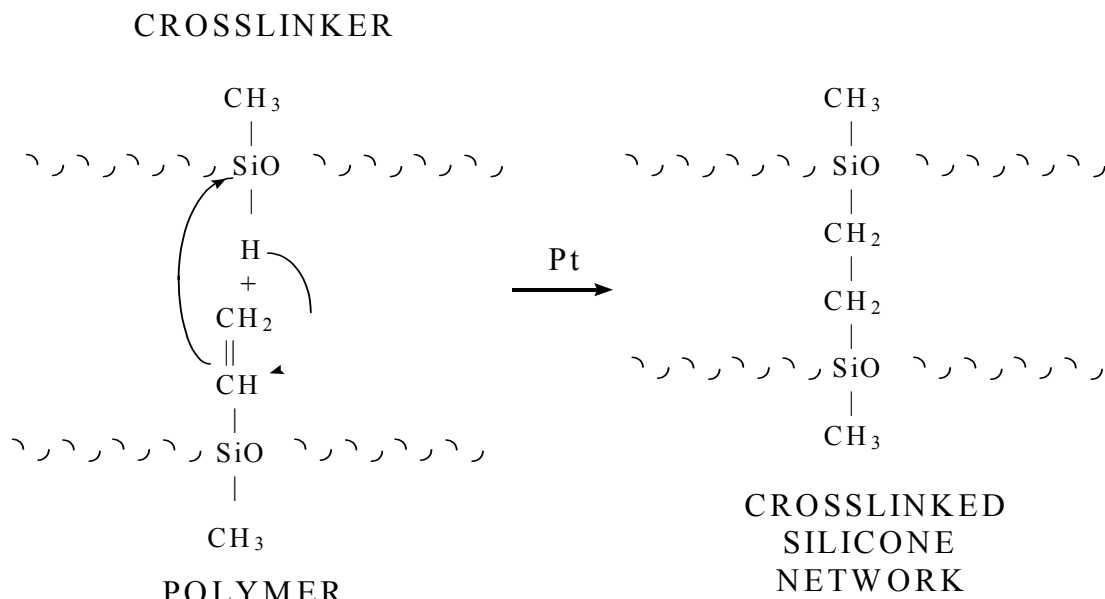
Polysiloxanes offer excellent elastomeric properties, a wide range of temperature stability (-115 to 260°C when phenyl substituted), fuel resistance (when Trifluoropropyl substituted), optical clarity (with refractive indexes as high as 1.60), low shrinkage (2-%), and low shear stress (2). Silicones are used in a wide array of applications due to these property advantages (1).

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 acetoxo (alkyltriacetoxysilane) or alcohol (alkoxy) crosslinked cure systems. The following demonstrates the reaction, which requires water to cure:



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.

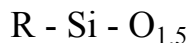


<Figure 1>

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.

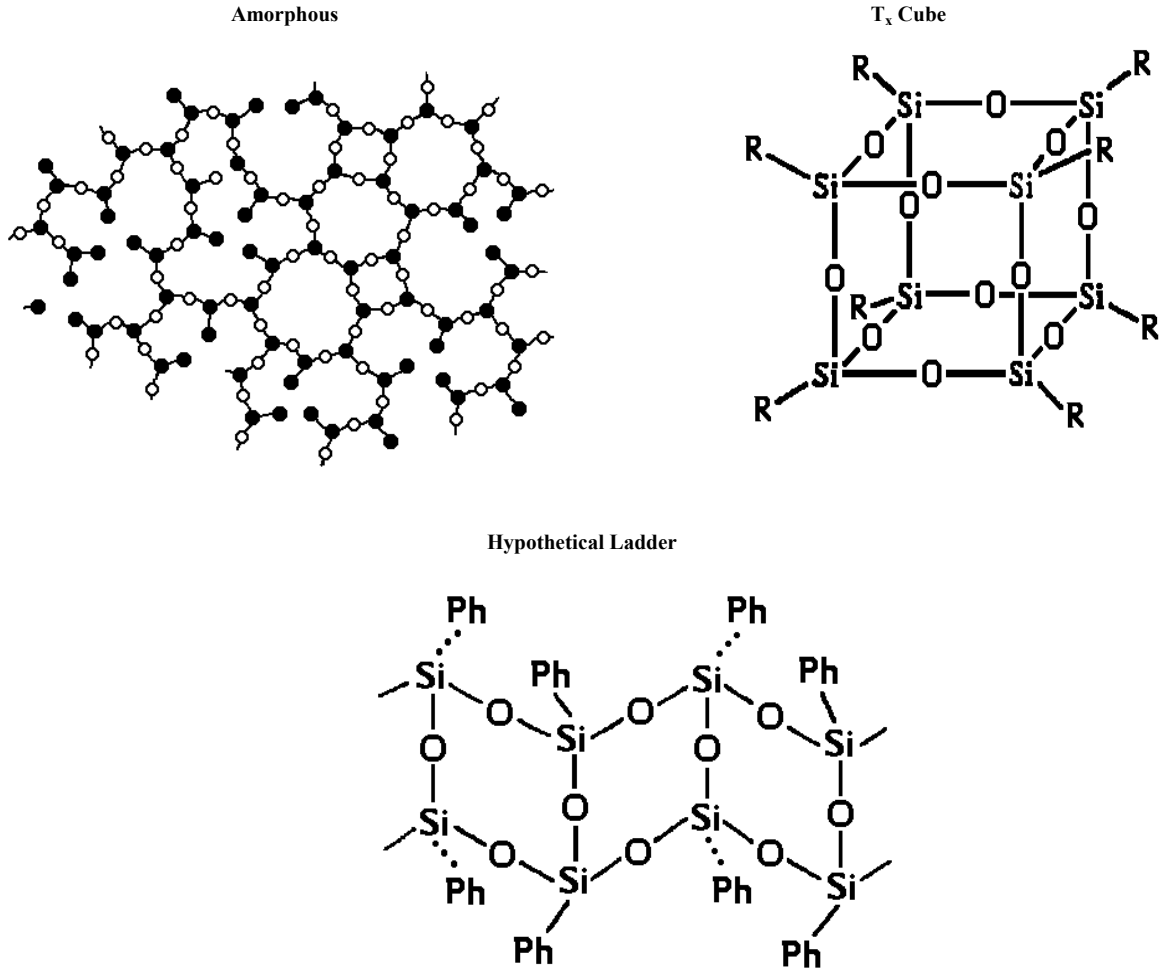
As mentioned above, silicone PSA's incorporate a polydimethylsiloxane polymer with a high molecular weight and a tackifying silicone resin dispersed in a solvent system. The main goals for resin manufacture are finding the ideal molecular weight and resin functionality. Resins with high molecular weights and increased functionality give a PSA very good cohesive properties, but may compromise the adhesive properties. On the other hand, resins with low molecular weight and decreased functionality give better adhesive properties but compromise cohesive properties. These properties can be altered by adjusting the amounts and types of starting materials for the resin.

Silicone resins, also called Polysilsesquioxanes, are highly crosslinked siloxane systems with the empirical formula:



Both the Polysilsesquioxane and T-resin names can be derived from the empirical formula. The root "sesqui" indicates the one and a half stoichiometry of the oxygen bond to silicon. T-resin indicates the trisubstitution of silicon by oxygen. Silicone resins are also named by the organic, or "R," group.

Sample Resin Structures (2):



Adding resin provides several benefits to a silicone polymer. It can strengthen the physical properties of the final adhesive produced because it increases crosslink density and reinforces the polymer. A resin can reinforce silicone polymers in three ways:

- (1.) Covalent bonding through the hydrosilation, condensation or peroxidic crosslinking of functional groups on the resin with functional groups on the polymer.
- (2.) Hydrogen bonding of the silicone polymer with silanol groups on the surface of the resin.
- (3.) Chain entanglement of the resin and the polymer.

The low intrinsic viscosity of the resin can also provide viscosity control by decreasing the polymer's viscosity. Finally, the resin provides optical clarity. Polymer and resin refractive indexes can be matched to result in an optically clear material.

The following are some standard applications where resin addition is used:

- ❖ Intra Ocular Lenses (IOL): Resin reinforced optically clear materials with a range of refractive indexes and viscosities.
- ❖ Pressure Sensitive Adhesives (PSA): Silanol (OH) functional resins provide the bulk of the cohesive strength in PSAs.
- ❖ Protective Coatings / Encapsulants / Electrical Insulators: Due to surface toughness, resins are widely used as protective coatings and encapsulants. When used in conjunction with specific fillers, they can be used where a non-conducting or dielectric material is required.
- ❖ Adhesives: Alkylamine resins can increase adhesive properties to various substrates. Resins also add structure and strength to CV grade adhesives.

Three factors affect the silicone resin properties:

(1.) Choice of Chlorosilanes,

- Choosing alkyl groups. Methyl / Vinyl / Phenyl.
- Cross linking level. Hardness / Elasticity. (3)
- Larger alkyl substituents cause a slower cure rate and a softer resin.
- Resins with higher phenyl content display heat stability, oxidation resistance, toughness of the finished film and retention of flexibility upon heat aging (4).
- Resins with higher methyl content impart flexibility, water repellence, faster cure rates, chemical resistance, and gloss retention.

<Figure 2> The Effect of Silanes on the Properties of Silicone Resin Films (5)

Property	MeSiCl ₃	PhSiCl ₃	Me ₂ SiCl ₂	Ph ₂ SiCl ₂	MePhSiCl ₂
Hardness	increase	increase	decrease	decrease	decrease
Brittleness	increase	great increase	decrease	decrease	decrease
Stiffness	increase	increase	decrease	decrease	decrease
Toughness	increase	increase	decrease	decrease	decrease
Cure Speed	much faster	some increase	slower	much slower	slower
Tack	decrease	some decrease	increase	increase	increase

(2.) Degree of Cure, and

(3.) Manufacturing Process Conditions.

Cure and processing conditions frequently make predicting specific resin properties very difficult.

Silicone PSA's will typically crosslink further by curing after removing the solvent. Two systems are currently available: platinum catalyzed and peroxide catalyzed. The

platinum catalyzed system follows the same reaction as shown in *Figure 1* and the curing is typically done in a single oven at 100 to 150°C.

The peroxide cure system is more common and employs benzoyl peroxide, or 2,4-dichlorobenzoyl peroxide, as a catalyst to drive a free-radical reaction and achieve cure. The curing is normally done in a multi-zoned oven. Solvent removal is achieved through a gradual increase in temperature, starting at 60 to 90°C to ensure that the peroxide catalyst does not cure solvent into the PSA. The temperature is then increased to 130 to 200°C, eliminating the peroxide through decomposition. A high crosslink density PSA can be better achieved through peroxide curing due to the ability to increase peroxide levels up to 4%. However, as discussed in the introduction, an increase in cohesive strength will lower tack performance. These trade-offs are adjusted based on the application.

Fabricators of tapes and adhesive backed components, take the liquid PSA and either wet coat in sheet form, for small applications or in roll form (pilot coaters and full width production coaters) when large quantities are required. The PSA adhesive may be applied on one or both sides of a substrate such as Kapton®, Mylar®, Nomex®, foils, foams, and rubbers or it can be coated directly onto a release film. Coat weights on supported film range from 0.0003” to over 0.010” thick. When the adhesive is coated directly onto a release film, this is called an unsupported PSA transfer film. Common post production processes include: die cutting, laser cutting, component assembly and automated pick and place solutions for difficult to apply parts and materials.

3. PSA APPLICATIONS

There are many benefits to using a PSA instead of liquid adhesives. Possibly the most important being the cleanliness of using PSA's. Liquid adhesives are messy and difficult to apply exactly where needed. Therefore they usually require cleanup afterwards. Also, using a PSA tape requires no cure time and can be die cut to match any unique configuration. Another big benefit is the consistent bond line offered by the PSA. Obtaining a consistent bond line with a liquid adhesive can pose a challenge, especially when adhering a large surface area. The great benefits of using a PSA can be seen when looking at the many PSA applications.

In 1968 a researcher by the name of Dr. Spence Silver working for the 3M company invented a pressure sensitive adhesive, which was later applied to one of the most famous uses of PSA's, the Post-it® Note.



The U.S. Postal Service created one of the largest usages of this technology (estimated at 14% of total US consumption) when it switched from moisture activated adhesive stamps to PSA stamps (*Reference 6*).

The medical industry is a prominent and long-time user of PSA's. An early use was hospital tape, a natural rubber filled with tackified zinc oxide. Other current uses include electrocardiogram patches, transdermal drug delivery patches, ostomy mounts, burn dressings, and protective pads.

Due to advances in PSA Technology, the automotive market has introduced PSA's in a number of areas, replacing mechanical bonding. A few examples are side mirror adhesion, air bag inflators where a silicone PSA is used to hermetically seal the propellant, flexible circuit adhesion, and harmonic tire labels. Automotive wire harness systems, which consist of approximately 3500 linear feet of wire per car (1), are an important application requiring PSA's. Silicone PSAs are also used in engine compartments because of their high temperature resistance.

Flat panel displays (FPD) have benefited greatly from PSA technology, specifically by utilizing optically clear silicone adhesives. Uses include bonding different flexible components in the display (including reflective and anti-reflective films, filters, transfectors and diffusers) and laminating surface treatment films to the outer surface of touch screens for enhanced durability.



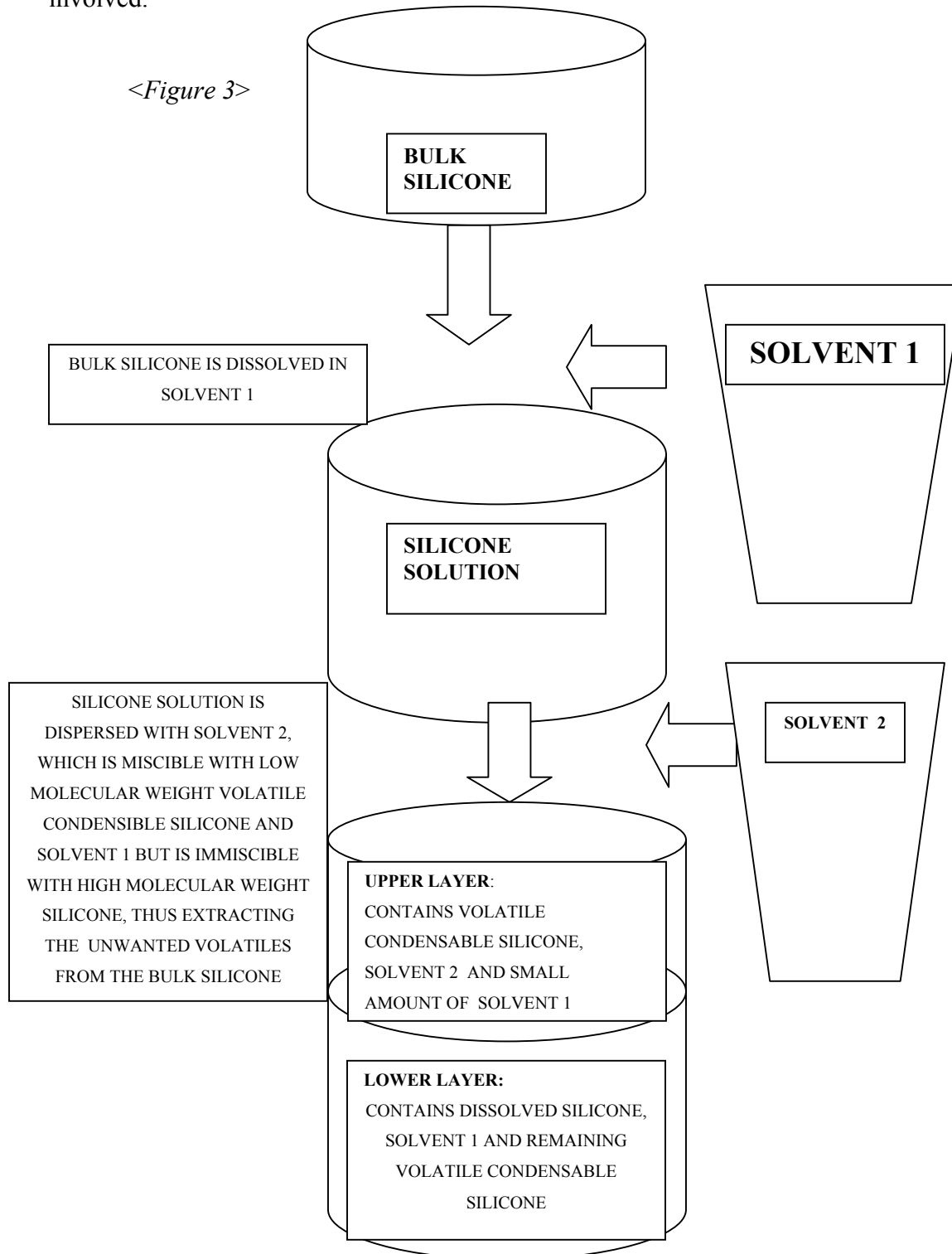
PSA's are widely used in the fabrication of hard disk drive assemblies because they offer an easy to use method for bonding components. Low outgas versions are used in new high-capacity drives to eliminate head corrosion and media fogging, which cause hard drive failures. Another common use is bonding microfilters, flexible circuits, seals and labels.

4. SOLVENT WASHING TECHNIQUE

When a silicone polymer is made via an equilibrium method, there is a portion of monomer that remains and a population of short-chained oligomers formed in addition to the main product. This portion can vary 10-20% 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 they are not removed they will separate out 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 that used in a PSA, it can be difficult to remove these 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 required for the PSA, a solvent is used to disperse the polymer prior to extraction. A second solvent, which is immiscible with the bulk polymer but miscible with the first solvent, is used to remove low molecular weight volatile condensable material. In addition, it is also difficult to perform a simple single solvent extraction 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.



5. 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 3*) within a test stand (*Figure 4*). The sample is then heated to 125°C at less than 5×10^{-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

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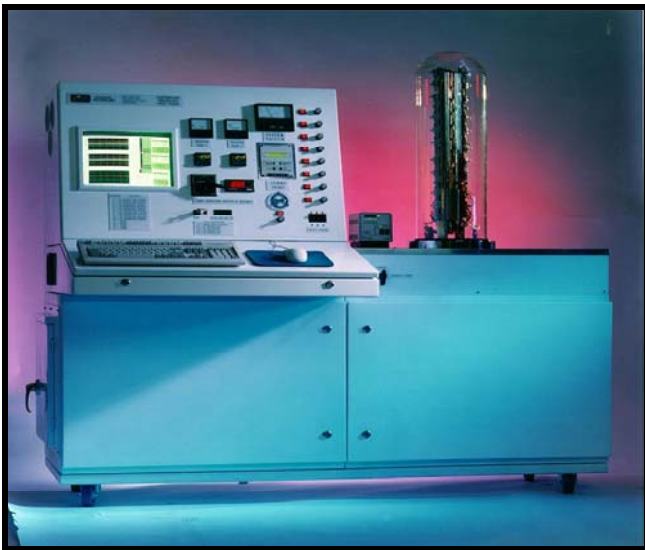


Figure 4

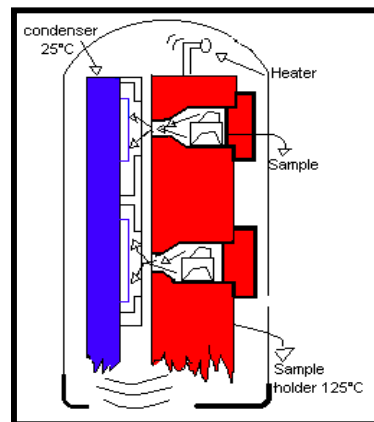


Figure 3

6. LOW OUTGAS SILICONE APPLICATIONS

The following is a short list of ASTM E-595 compliant silicones used in Aerospace applications:

Benjamin Rodini, Jr, Swales Aerospace, “**Development of a Lead-Coded Composite Mask for Gamma-Ray Detection**,” 34th International SAMPE Technical Conference, November 4-7, 2002. CV10-2568 adhesive used to bond lead tiles to composite face sheets on the Burst Alert Telescope sent on NASA’s SWIFT satellite in 2003.

Paul Wienhold and David Persons, John Hopkins Applied Physics Lab, “**The Development of High Temperature Composite Solar Array Substrate Panels for the Messenger Spacecraft**,” 34th International SAMPE Technical Conference, November 4-7, 2002. CV-2568, CV3-2289, CV5-2568 for cell and Optical Solar Reflectors (OSR) bonding on solar array.

Campbell, William A. Jr., and John J. Scialdone, “**Outgassing Data for Selecting Spacecraft Materials**,” NASA Reference Publication 1124, Revision 3, September 1993. CV-2946, CV-1142, CV-1142-1, CV-1142-2, CV-1500, CV-2187, CV-2500, CV-2500-2, CV-2510, CV-2520, CV-2566, CV-2567, CV-2568, CV-2644, CV-2646, CV-2942, CV-2948, CV-8151, CV1-2960, CV4-2500.

P. Tegehall, B. Dunn, “**Influence of Flux Residues and Conformal Coatings on the Surface Resistance Properties of Spacecraft Circuit Boards**”, July 1992. ESTEC study as part of the International Conformal Coating Programme at the Swedish Institute of Production Engineering Research, showing the benefits of CV-1144-0 as a conformal coating for circuit boards.

M. Eesbeek, ATOX tests on McGhan coating for STSA cushion, December 1989. Effectiveness of CV-1144-0 as an Atomic Oxygen protective coating.

J. Scialdone, C. Clatterbuck, M. Ayres-Treusdell, G. Park, D. Kolos, “**Atomic Oxygen and Space Environment Effects on Aerospace Materials Flown with EOIM-III Experiment**”, NASA Technical Memorandum 104636, 1996. CV-1144-0 and CV-2500 on Delrin, CV-1144-0 and CV-2500 on Silver coated Teflon, CV-1142, CV-1500 and CV-2566 on AL, CV-1144-0 and CV-2500 on Kapton H film, and CV-1144-0 on Beta cloth.

B. Banks, S. Rutledge, K. Groh, M. Mirtich, L. Gebauer, R. Olle, C. Hill, “**The Implications of the LDEF Results on Space Station Freedom Power System Materials**”, 5th International Symposium on Materials in a Space Environment, September 1991. CV-1147 as an Atomic Oxygen protective coating.

J.Kleiman, Z.Iskanderova, “**Technological Aspects of Protection of Polymers and Carbon-based Materials in Space**”, 8th International Symposium on Materials in a Space Environment, June 2000. CV-1144 as an Atomic Oxygen protective coating in LEO.

S.Rutledge, P.Paulsen, J.Brady, “**Evaluation of Atomic Oxygen Resistant Protective Coatings for Fiberglass-Epoxy Composites in LEO**”, 34th SAMPE Technical Conference, May 1989. CV-1144 outperforms other coatings as AO protective coating for Space Station Freedom solar array mast.

J.Denman, L.Maloon, “**Protective Coating for the Ku-Band Reflector**”, 31st International SAMPE Symposium, April 1986. CV-1144 chosen superior over others as AO protective coating for reflector on Space Shuttle.

H.Burns, A.Whitaker, R.Linton, “**Atomic Oxygen Resistant Protective Coatings for the Hubble Space Telescope Solar Array in Low Earth Orbit**”, Surface and Coatings Technology, 1989, pgs 627-636. CV-1144-0 as AO protective coating for Hubble Telescope solar array.

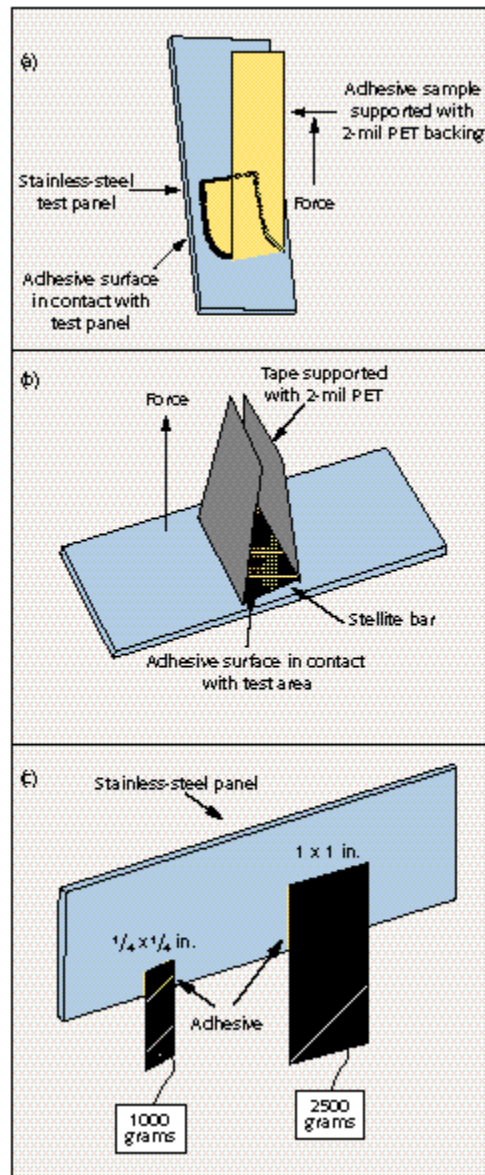
F.Gargano, “**Electrical and Geometrical Test on Wafers and Ladders of the GLAST Tracking System**”, 4th International Conference on Radiation Effects on Semiconductor Materials, Detectors and Devices, July 2002. CV-1142 and CV-2500 used to dam & fill encapsulate wafer assembly for the GLAST LAT gamma ray telescope

7. PSA PROPERTY TESTING

The Pressure Sensitive Tape Council (PSTC), made up of 29 North American PSA tape manufacturers, was organized to control and monitor the PSA market and its products. Three primary Test Methods were developed to compare PSA's on a performance basis. The first is adhesion, the measure of the bond strength of the PSA to a substrate. Some PSA applications require strong adhesion, for example when used in an ostomy bag. Others require being able to be easily removed, such as in band-aids. PSTC-101 is the test method for 180 or 90° peel adhesion (see Figure a).

The second is tack, described as the initial attraction of the PSA to a substrate without any pressure applied. Tack properties are measured using PSTC 16, the Loop Tack Test (see Figure b). Tack testing can also be measured via Blunt Probe Tack Test (ASTM D 2979, not pictured) where a probe is applied to the PSA and the force to withdraw that probe is measured.

The third test is Static Shear, PSTC 107A. Shear is defined as the strength of the PSA itself, or the material's strength. A stainless steel or aluminum panel is used to attach the PSA cut in 1/4" or 1" wide strips with a 1" overlap, and a weight is attached to the hanging end. Weights can weigh from 50 to 2500grams (See Figure 5c). Static Shear can also be done at elevated temperatures, for example 175°C for 24 hours, to estimate how the PSA strength holds up with temperature. Typically, as shear strength is increased, tack and adhesion properties decrease (8).



<Figure 5 (a) 180 or 90 peel, (b) loop tack test, and (c) shear>

6.MATERIAL PROPERTIES

Several tests were performed on materials to demonstrate the similarities of CV and non-CV PSA's with regard to bond strengths. Additional tests were performed to determine if the developed PSA met the goals of the research study.

Despite the processing steps required to produce a PSA that meets the 1 % or less Total Mass Loss (TML) and 0.1% Collectable Volatile Condensable Materials (CVCM) requirements, it was found the properties of the low outgas PSA were similar to a non-CV analogue. Below is listed a table of basic comparison (MED1-1356 is a NuSil Technology part number for a PSA used primarily in skin (topical) bonding applications and does not meet CV requirements)

	MED1-1356	CV-1161
T- Peel Test (ppi)	6	9.9
Shear Test (pass/fail) @ 175° C	Fail	Fail
Blunt Probe Tack Test (lbs)	1.2	Not Tested
TML %	Fail	0.12
CVCM %	Fail	0.027

The development of a PSA that passes the shear test described above was tested for the same properties. The results of this testing are below:

	PSA2-9911-20
T-Peel Test (ppi)	2.2
Shear Test (pass/fail) @ 175° C	Pass
Blunt Probe Tack Test (lbs)	0.7
TML %	0.10
CVCM %	0.017

8. CONCLUSION

The development of an experimental low outgas silicone PSA, combining the low outgas properties needed from a material used in space with the PSA technology incorporated into tapes, was initiated, and from preliminary testing looks very promising to achieve the proposed criteria to be used as a very unique satellite repair product.

The targets were for the silicone PSA to pass standard low outgassing requirements of 1% or less Total Mass Loss (TML) and 0.1% or less Collectable Volatile Condensable Materials (CVCM). The performance goals were to maintain performance under load at temperatures above 175°C, and have similar properties to other low outgassed silicone PSA's as tested by peel, loop tack, shear, release force and Blunt probe tack.

The next stage in this developmental cycle is making multiple lots to obtain an accurate view of the material's properties. A fabricator like Fralock will need to be involved in supplying commercial-like samples for application testing.

A special thanks to NuSil Technology Technical Writer, Alex Kurnellas and Scott Tucker, CEO at Fralock, San Carlos, CA., for their insights.

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