



Bryant Rubber Corporation
1112 Lomita Boulevard
Harbor City, California 90710
Phone (310) 530-2530
FAX (310) 530-9143

Case Study: O₂ Sensor Failure

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How Low Volatile Silicone Technology improves performance in automotive electrical components

*By: Rick Ziebell – Materials Technologist
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Introduction:

Automotive O₂ sensors have been employed in the operation of engine systems for several decades. These systems control oxygen–fuel mixture ratios that are necessary to improve engine performance in both fuel economy and emissions control. The necessity for these sensor assemblies to be located so close to hot engine exhaust gasses created engineering design barriers. This became apparent when several major automotive companies recalled vehicles for replacement of these units. Failure Mode Effects Analysis's (FMEA) were performed and found that elastomeric sealing inadvertently caused circuit failures by deposition of conductive solids onto electrical circuitry. This was commonly labeled as an out-gassing phenomenon but analytical detection of these semi-volatile components has led to solutions in polymer chemistry optimization that profoundly impact today's electrical component designs.

Focus: Elastomers used in sealing automotive systems need both long-term chemical stability and high temperature resistance. In many cases, small amounts of impurities within these systems can have major effects on design quality. This paper demonstrates a technique for detecting volatile and semi-volatile compounds and then reviews aspects of silicone chemistry to arrive at a practical solution with regards to the performance of component circuitry.

FMEA - Materials Section:

Circuit boards taken from defective units were examined and found to have an unknown substance deposited on the metal contacts. Once the substance was removed and the circuit board assembly was put back together, the device was tested to be working within original diagnostic tolerances. This substance was analytically studied to determine its origin. Unfortunately, the substance contained many contaminants and it was debatable as to the source of all the chemical species found. The only applicable determination was that many species seem to be coming from inorganic and organic polymers. The sensor assembly is enclosed so in the contained unit, **Silicone Rubber** was the only suspect source. Simple extraction and weight loss analysis yielded little information. The fact that by-products of these substances were deposited on the surface of the assembly became a very difficult problem to reproduce.

Evaluation of new assemblies through heat cycling showed at least that the problem was related to temperature cycling. Indeed, precipitation of semi-volatile elements generated by the elastomer out-gassing was to blame. To satisfy the evaluation requirements of new materials for the O₂ sensor program, a new analytical method was developed.

Analytical Method: Direct Thermal Extraction (DTE) is performed using a Short Path Thermal Desorption System. Additional information on this method can be found in the reference section of this paper. Figure 1 shows a typical SPTDS graph. The spikes indicate unique volatile components.

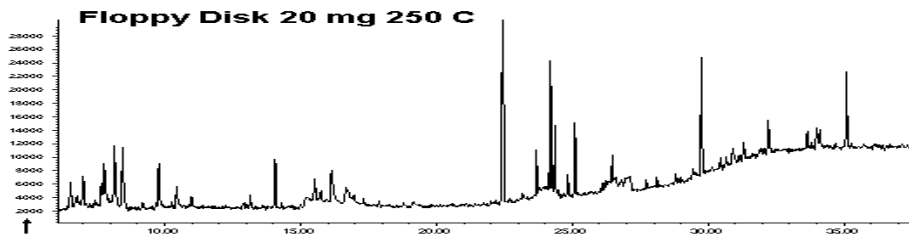


Figure 1. - Analysis of PBA Resin Via Direct Thermal Extraction

By running successive graphs at increasing temperatures observations can be made as to the quantitative and depositional aspects of these components. The Y-axis parts per million (ppm) and the X-axis show absorption wave length (nm). The area under the spikes can be used to provide relative quantitative estimates of the components. Using the temperature profiling technique, observation as to the deposition temperature and rates of deposition can be compared.

Case Study:

Analysis: Samples of the two suspect materials were pulled from assemblies and tested per DTE at temperature ranges that were normal with respect to the hot and cold conditions the O₂ Sensor commonly sees in operation.

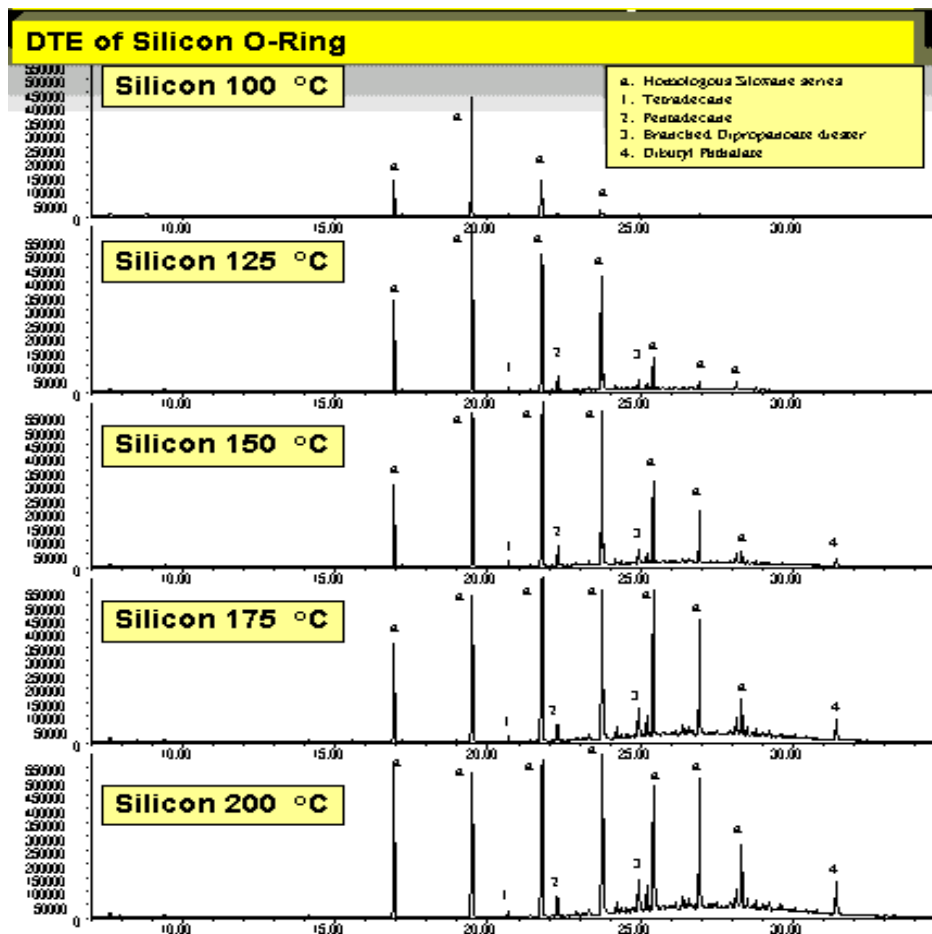


Figure 2. - Direct Thermal Extraction of Silicone Elastomer

This series of DTE graphs depict the increase in the amount of volatiles that are out-gassing from the elastomer. It is important to note that the semi-volatile components are the ones that do not show up on the cooler graphs but then become apparent in the warmer graphs. This means simply that when temperatures peaks above the liberation temperature, that component will out-gas and as the temperature decreases the precipitation will cause deposition on exposed surfaces. By definition we call this a semi-volatile component.

In an enclosed system these components can build up as the assembly is thermally cycled. As the thermal cycling reaches maximum temperature the liberation rate of the semi-volatile components is highest. In addition, when the minimum thermal cycling range falls below the gas phase precipitation temperature deposition will occur.

In the case of the O₂ sensor failures, dibutyl phthalate (item 4) in figure 2 shows peaks in temperatures above 125°C. This semi-volatile component is in the Handbook of Chemistry and Physics Reference and shows the boiling point to be exact at 340°C. The important note is that unexpectedly, the volatility of this component is much higher than the physical boiling point would suggest. Apparently, a eutectic condition exists that lowers the volatility temperature for this component that further increases the rate of evolution. The DTE graph accurately identifies the component and gives direct proof of its existence below the expected thermal conditions one might assume.

With this indication, a root cause is proven. Resolution to the problem was found to be more of a difficulty but was eventually achieved. The next sections of this report discuss in detail the chemistry of Silicone Rubber and will make direct recommendations to solve out-gassing problems.

Silicone Chemistry:

Silicone elastomers have wide application where high temperature and chemical resistance are needed. They have found use in a variety of performance-critical applications. O₂ sensor assemblies are just one such application. Heat cured silicones are commercially available in two types: millable high consistency silicone rubber and pumpable liquid silicone rubber. Optimization of silicone materials for these applications have led to the development of non-volatile silicones that greatly improves compatibility in systems that are poisoned by polysiloxane oil residues.

SILICONE ELASTOMER CHEMISTRY AND PROPERTIES

Silicone elastomers are proprietary compositions that contain silicone polymers, reinforcing and extending fillers, and cure ingredients.

Silicone Polymers. The polymers used in silicone elastomers are of the general structure depicted in Figure 3, where R represents –OH, –CH₃, or an aryl group. The degree of polymerization (DP) is the sum of subscripts x and y. In high consistency silicone rubber elastomers, the DP is typically in the range of 5000 to 10,000. Thus, the molecular weight of the polymers—generally called gums—used in the manufacture of high consistency silicone rubber elastomers ranges from 350,000 to 750,000 or greater. In liquid silicone rubber elastomers, the DP of the polymers used typically ranges from 10 to 1000, resulting in molecular weights ranging from 750 to 75,000. R' represents the pendant functionality of the polymer where cross-linking takes place, which is usually a, –CH=CH₂ alkenyl group. The ratio of y/x gives the relative reactivity index of the polymer expressed in mole percent. For liquid polymers this is generally a blend of high (20-mole %) and low (0.2-mole %) polymers to achieve an optimum resinous matrix. Typically, the low functionality polymer is used to the greatest degree. For high consistency rubber polymers, the functional index is lower (less than 0.2-mole %). The blend of multiple functionality polymers is minimized in high consistency rubber as compared to liquid silicone rubbers. The relatively low reactivity index in liquid silicone rubber can produce a fair degree of volatility due to the non-reactivity of lower DP oligomers occurring in the polymer. By comparison, the relatively higher DP of high consistency rubbers provides ample reactivity to tie in the chains during the cross-linking process. This produces lower volatility in high consistency rubber materials.

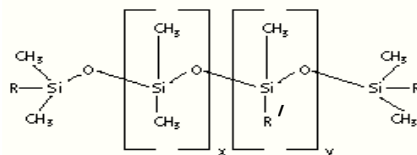


Figure 3. Chemical structure of typical silicone elastomers

Reinforcing Fillers. Many manufacturers use reinforcing fillers to add strength to the finished elastomer product. Typically, these fillers are amorphous fumed silicas, although the use of precipitated silicas has increased in recent years. Particle sizes of standard reinforcing fillers normally fall within the range of 5 to 20 nm in diameter. The reinforcement that occurs is the result of interaction between the polymer and the filler, whose surface typically has silanol functionality. Because of the hydrogen bonding initiated by this silanol functionality, the interaction between polymer and filler can actually become so significant that it results in elastomers that are extremely stiff, giving the appearance of a cross-linked system. This phenomenon—commonly referred to in the industry as crepe--

can be reversed, because it is possible to break down the hydrogen bonding through the addition of shear energy in the form of mixing or milling.

To achieve a level of polymer and filler interaction that provides a stable product, while maintaining the reinforcing nature of the filler in the elastomer, a treatment or pacification of the silanol species on the reinforcing filler is necessary. This is typically carried out either through the addition of silanol-endsblocked polydimethylsiloxane oligomers or via a capping reaction using reactive silanes or silazanes.

Extending Fillers. In order to impart particular performance attributes to silicone elastomers, extending fillers are sometimes employed. These fillers add to the desired performance of the elastomer while reducing the overall cost. Since extending fillers are more readily added to high consistency silicone rubber the resultant cost is considerably lower than compared to liquid silicone formulations.



Low viscosity liquid silicone rubbers.



High consistency rubbers and polymer additives: Photos: Dow Corning Corp.

CURE MECHANISMS

Two major cure mechanisms are used in the manufacture of silicone rubber elastomer products: free radical cure and addition cure.

Free Radical Cure Free radical cure systems employ peroxide catalysts that are either vinyl specific or nonspecific in nature. Adding heat causes the peroxide to decompose into two free radical-containing components, which then react with either an alkyl or a vinyl species along the polymer backbone, transferring the free radical to the silicone polymer. The cross-linking mechanism is terminated by the reaction of the free radical on the polymer chain with an alkyl species on another polymer chain.

Nonspecific peroxides-such as bis(2,4-dichlorobenzoyl) peroxide or benzoyl peroxide-do not require the presence of vinyl or other unsaturated alkyl species in the polymers making up the elastomer formulations. Vinyl specific peroxide catalysts-for example, dicumyl peroxide or 2,5-bis(tert-butyl peroxy)-2,5-dimethyl hexane-require the presence of vinyl or other alkenyl species in the polymers contained in the elastomers.

A serious drawback to the use of peroxide cure in silicone materials is that it leaves residues in the cured elastomer, including acid by-products (a reactive species such as **dibutyl phthalate** known as a phthalic acid group) and polychlorinated biphenyls (PCBs). The acid residue cannot be completely removed causing a potential

decomposition of the silicone backbone (chain scission) that creates additional volatility. Excessive volatility adversely affects other elements of the device the part is used in.

There are not any commercially available liquid silicone rubber elastomers that use the free radical peroxide cure mechanism. Table I lists typical properties obtained in high consistency silicone rubber elastomers cured via peroxide.

Addition Cure. Both high consistency silicone rubber and liquid silicone rubber can be addition cured. The addition cure mechanism-known as hydrosilylation-involves the addition of a silicon hydride (*SiH) to an unsaturated carbon-carbon bond in the presence of a noble metal catalyst. The most commonly used of these hydrosilylation catalysts are based on platinum, although palladium and rhodium catalysts are also available. In order for the cure to occur, the silicone polymers contained in the elastomers must include a vinyl or other alkenyl functionality. Elastomers featuring the addition cure system are supplied as two-part or one-part systems. The chemical species for curing are of the general description: a noble metal catalyst, a silicon hydride-functional cross-linker and an inhibitor to provide working time for shelf life and pot-life considerations.

The major advantage of addition cure for elastomers is that the cure reaction produces no by-products. Therefore, volatility in the elastomer is minimized. A postcure cycle is sometimes performed to stabilize the hydrosilylation chemistry and enhance the properties of the finished product. The postcure operation oxidizes away the noble metal catalyst and removes virtually all the low DP fraction of polymers. This imparts to addition cured high consistency rubber the optimum, by far, in low volatility performance.

ASTM Reference	Test	High Consistency Silicone Rubber Grades ^a		
		A	B	C
D 792	Specific gravity	1.12	1.15	1.20
D 2240	Durometer hardness, Shore A (points)	36	49	66
D 412	Tensile strength (psi)	1280	1445	1150
D 412	Elongation (%)	800	655	600
D 624	Tear strength, die B (ppi)	110	175	210

^a Silastic Medical Grade ETR Elastomers (Dow Corning Corp.); A = Q7-4535, B = Q7-4550, C = Q7-4565.

Table I. Typical properties obtained in high consistency silicone rubber elastomers cured via peroxide

ASTM Reference	Test	High Consistency Silicone Rubber Grades ^a				
		D	E	F	G	H
D 792	Specific gravity	1.11	1.12	1.15	1.20	1.20
D 2240	Durometer hardness, Shore A (points)	24	35	49	64	76
D 412	Tensile strength (psi)	1255	1395	1550	1155	1170
D 412	Elongation (%)	1255	1170	900	895	670
D 624	Tear strength, die B (ppi)	185	210	260	255	250

^a Silastic BioMedical Grade ETR Elastomers (Dow Corning Corp.); D = Q7-4720, E = Q7-4735, F = Q7-4750, G = Q7-4765, H = Q7-4780.

Table II. Typical properties obtained in high consistency silicone rubber elastomers with addition cure.

ASTM Reference	Test	Liquid Silicone Rubber Grades ^a				
		I	J	K	L	M
D 792	Specific gravity	1.12	1.12	1.12	1.14	1.16
D 2240	Durometer hardness, Shore A (points)	27	39	43	49	59
D 412	Tensile strength (psi)	1205	1300	1230	1375	1375
D 412	Elongation (%)	830	705	515	690	515
D 624	Tear strength, die B (ppi)	125	210	205	250	265

^a Silastic Liquid Silicone Rubbers (Dow Corning Corp.); I = 7-6830, J = 7-6840, K = Q7-4840, L = Q7-4850, M = 7-6860.

Table III. Typical properties obtained in liquid silicone rubber elastomers with addition cure.

Tables: Dow Corning Corp

Case Study Conclusion:

The semi-volatile component, dibutyl phthalate, was determined to be a by-product contaminate from silicone rubber. Additional research found that the material was a HCR peroxide cured silicone rubber. Additionally, the silicone was originally post cured at 200°C for 4 hours prior to assembly into the O₂ sensor unit. While some of the dibutyl phthalate was evolved in the post cure process, it was not completely reduced.

Evaluation of silicone chemistries lead to the discovery of **low volatile platinum cured silicone rubber**. This class of silicone rubber contains none of the acid by-product, dibutyl phthalate. Platinum cure is a much cleaner curative and produces no semi-volatile components in temperature ranges between 0 and 200°C.

The manufacturer was able to simply change the material used in the O₂ sensor gasket to this low volatile material and continue supplying the part. In the design review, it was determined that additional systems would be evaluated to determine if silicone was the best material of choice. Silicone rubber, with its high degree of temperature resistance, was determined to be the best material after low volatility was addressed.

Summary:

Today, the necessity of performance demands that great care be taken to minimize the effect of systemic component contamination. All too often, the diagnosis of system failure has caused much waste in terms of engineering design. We have in this case, examined the effects of silicone chemistry as a potential contamination source. Through optimization of chemistry, a three-decade magnitude reduction in volatility makes for ease in design level engineering.

The selection of the right type of silicone elastomer for a specific use is of great concern. There is little observable difference between peroxide cured high consistency silicone rubbers, addition cured high consistency silicone rubbers, and liquid silicone rubbers, in terms of typical physical properties. However, the materials differ significantly in terms of compatibility with electronic devices.

Liquid silicone rubber is by design, a low molecular weight polymer that contains a significant fraction of volatile oligomers of non-reactive chains that impart volatility 1000 times that of high consistency silicone rubber. Free radical cure systems using organic peroxides produce acid by-products of the reaction that make the elastomer unsuitable by volatilizing acidic residuals in very high levels. **Addition cured high consistency elastomers yield the best performance providing low volatility as compared to any other silicone type (see next page for BRC formulation test data).**

References:

Direct Thermal Extraction (DTE) is performed using a Short Path Thermal Desorption System. The short path system is unique in that the sample is trapped or placed in a glass lined tube that becomes part of the injection syringe. This results in a very short transfer line (the needle) between the heated sample and the GC injector. The technique of Direct Thermal Extraction permits the analysis of solid samples without any prior solvent extraction or other sample preparation. The solid sample to be analyzed is inserted directly into the Glass Lined Stainless Steel (GLT) Thermal Desorption Tube between two quartz wool plugs. The Desorption Tube with the sample enclosed is purged with carrier gas to remove all traces of oxygen, after which the sample is heated to a predetermined set temperature and sparged into the GC injection port. The sample is then cryo-trapped at the front of the GC capillary column for a period of 5 to 10 minutes. When this is completed, the components are eluted from the GC capillary column via a temperature program cycle, and are detected via a GC detector or mass spectrometer. The Direct Thermal Extraction technique is useful for identifying trace residues of volatiles and semi-volatiles.

The relationship between vapor pressure and temperature allows the volatility of potential impurities to be approximated by heating the matrix from which they arise. While this estimate may not be strictly quantitative, it can give a good idea of the types of contaminants that are likely to arise in a given application, as well as provide a basis for comparison of the impurities generated by different materials. In processes where both high temperature and low pressure are present, the volatility of a given contaminant is expected to be further exaggerated.

In this work, several types of elastomers and plastics were evaluated using Direct Thermal Extraction. Qualitative and quantitative information about compounds which may evolve from samples can be obtained by heating them directly in the Short Path Thermal Desorption (SPDS) system followed by gas chromatography/ mass spectrometry (GC/MS) analysis.

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Photos and Tables from Dow Corning Corporation, Midland Michigan



High Consistency Addition Cured Silicone Rubber

Bryant Rubber Material:	5317-40	5317-60	5319-40	5319-60
Material Grade (Durometer)	40	60	40	60
Material Description	General Purpose	General Purpose	High Strength	High Strength
<u>Original Properties:</u>				
<i>Durometer (Shore A)</i>	41	62	38	61
<i>Tensile (psi)</i>	770	694	1300	1475
<i>Elongation (%)</i>	876	509	688	525
<i>Tear Die B (ppi)</i>	103	85	131	152
<i>Modulus @ 100% (psi)</i>	127	237	121	245
<i>Spec. Gravity</i>	1.28	1.40	1.08	1.21
<i>Resilience (Bayshore)</i>	59	52	67	62
<u>Heat Age Properties (70hrs @ 200°C):</u>				
<i>Durometer (Shore A)</i>	43	65	44	64
<i>Tensile (psi)</i>	520	485	1125	1210
<i>Elongation (%)</i>	325	215	598	442
<i>Tear Die B (ppi)</i>	43	53	140	161
<i>Modulus @ 100% (psi)</i>	158	243	153	285
<u>Compression Set In Air: (70hrs @ 150°C):</u>				
<i>Set (%)</i>	7	3	9	8
<u>Compression Set In Glycol Fluid: (5 days @ 60°C):</u>				
<i>Set (%)</i>	25	23	18	17
<u>Electrical Properties:</u>				
<i>Volume Resistivity (ohm-cm)</i>	1.4 E 13	2.9 E 15	1.9 E 12	1.1 E 12
<i>Dielectric Strength, (volts/mil)</i>	328	409	653	631
<i>Arc Resistance (seconds)</i>	215	185	428	485
<u>Volatility (TGA in Air):</u>				
<i>Weight Loss 2 hr. @ 150 °C (%)</i>	0.0	0.0	0.0	0.0
<i>Weight Loss 2 hr. @ 175 °C (%)</i>	0.23	0.20	0.32	0.29
<i>Weight Loss 2 hr. @ 200 °C (%)</i>	0.32	0.31	0.41	0.39
<i>Degradation Temperature (°C)</i>	350	380	335	341