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Outgassing of Silicone Heater Compounds



SILICONE TECHNOLOGIES DIVISION

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What is Silicone Outgassing?

Sources of Volatile Species

Outgassing is the volatilization of gaseous species from a material. It can be a significant problem in applications that are sensitive to contamination such as are common in the semiconductor, biomedical, and aerospace industries. In order to understand the outgassing associated with silicone, it is necessary to first examine the chemical origins of these volatile species.

Low Molecular Weight Siloxanes (LMWS)

In silicone, the bulk of outgassed species are LMWS. Low molecular weight siloxanes come from four primary sources:

The first source of LMWS is an intermediate in the polymerization reaction that leads to high polymer. Dimethyldichlorosilane is reacted to form dimethyltetramer or D4. The cyclic siloxane responsible for the majority of silicone outgassing. The dimethyltetramer ring is then opened and polymerized to high polymer. Generally high polymer is composed of linear siloxanes with molecular weight in the 300,000 to 800,000 g/mol range. To contrast, these linear chains have between 4,000 and 11,000 monomers each. The final polymerization reaction to high polymer is approximately ~85% efficient. Proprietary reaction mechanisms and post polymerization processes are used to clean the compound. Commercial grade silicone elastomers have as much as 5% residual low molecular weight siloxanes.

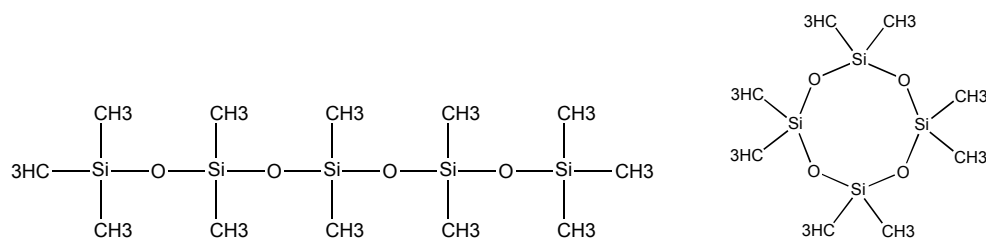


Figure 1. Examples of Linear and Cyclic Low Molecular Weight Siloxanes

The second source of low molecular weight siloxanes are the carrier for initiators, pigments and additives. Low molecular weight dimethyl silicone fluids are used almost exclusively as the carrier medium for masterbatches. Masterbatches are the preferred method for compounding because they increase the safety of working with an otherwise

hazardous substance. Masterbatches also increase the rate at which full dispersion occurs making compound easier and more efficient.

The third source of low molecular weight siloxanes arise from reinforcing and extending fillers used to increase the strength and modify certain physical properties of the final compound. The fillers are surface treated with silane and silanol molecules to make them compatible with the high polymer.

The fourth and final source of low molecular weight siloxanes arise from the high polymer. Thermal degradation leads to depolymerization of the high polymer which occurs by three mechanisms:

1. The first mechanism of depolymerization is termed "reversion". Reversion occurs when organic acids from the cure reaction coupled with high temperature attack the cured high polymer.

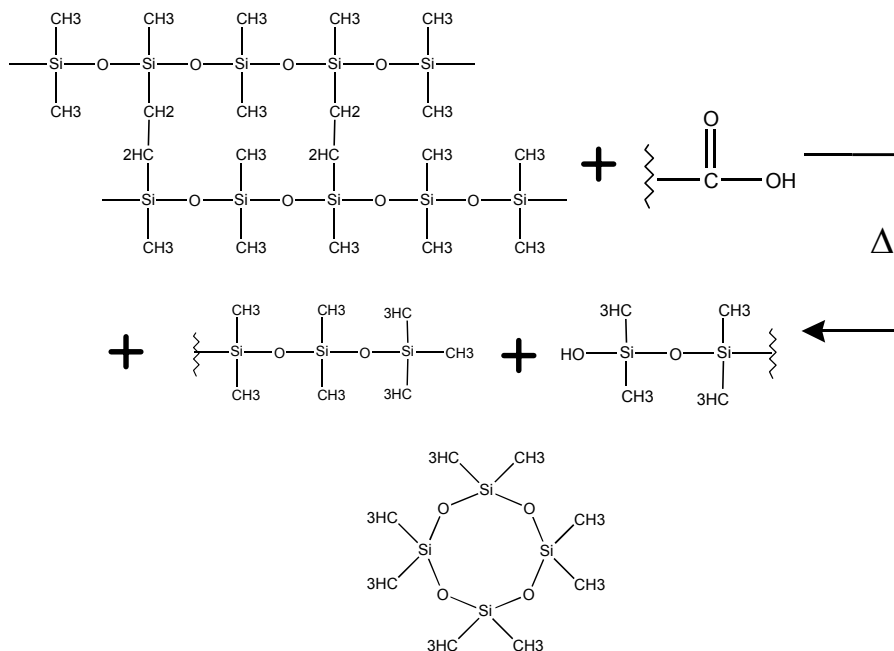
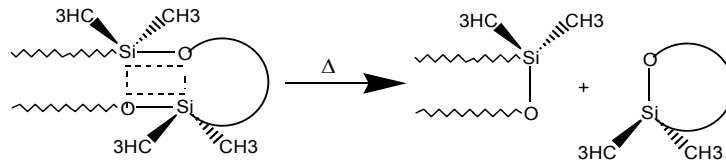


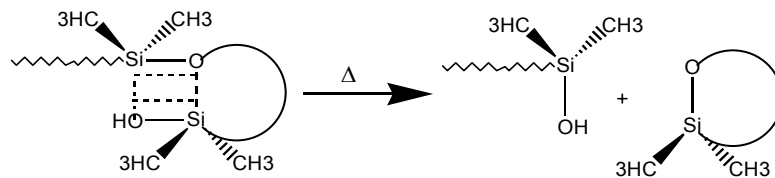
Figure 2 shows is a simplification of the mechanism of reversion. Organic acids attack the crosslinks between silicone chains allowing the chains to break in to smaller linear chains and cyclics. If the molecular weight of the fragments is low enough, typically 12 monomers or less, the molecule will volatilize.

2. The second mechanism of depolymerization is chain scission. This process can occur in several ways:

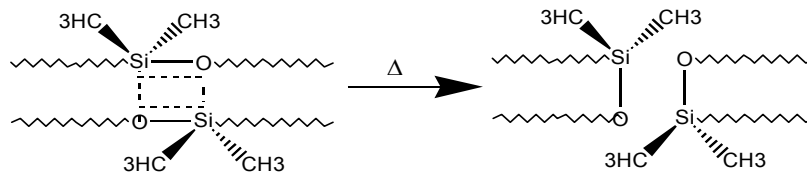
a. Random Cyclic Formation



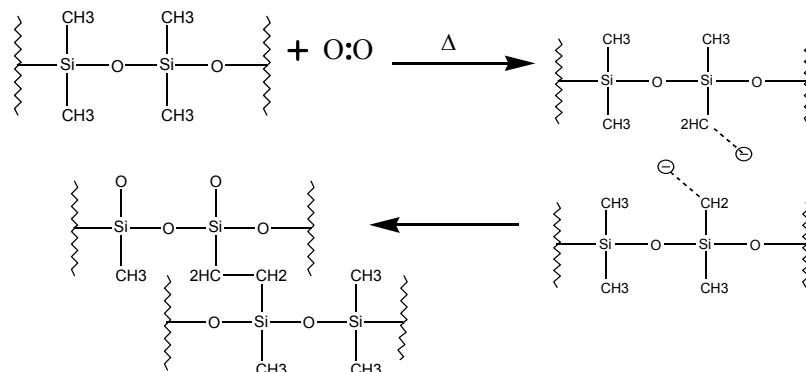
b. End Initiated Cyclic Formation



c. Intermolecular Chain Scission



3. The third mechanism for depolymerization is oxidation and excessive crosslinking as shown in the reactions below. In this mechanism, free radical oxygen is responsible for oxidizing silicon atoms which lead to the breakup of monomer units and eventually results in surface oxidation.



Organic Acids (Initiator By-Products)

The remainder of silicone outgassing arises from the decomposition product of the organic peroxide used to cure the elastomer. The peroxide by-products of the cure reaction are organic acids. The organic acids readily volatilize from the cured product during post cure and are not seen as outgassing except in non-post cure products. Removal of organic acids is critical to stabilize the cured product. If not removed, the organic acids will attack the polymer causing reversion during service. Some of the typical initiators used are:

- 2,4-dichlorobenzoic acid is the by-product of di(2,4-dichlorobenzoyl) peroxide. Bis(2,4-dichlorobenzoyl) peroxide is commonly used as a catalyst because of its low activation temperature and high activity. It is also an efficient crosslinker in open air situations.

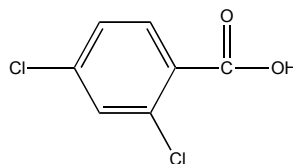


Figure 4. 2,4-dichlorobenzoic acid.

- Benzoic acid is the by-product of benzoyl peroxide. If benzoic acid is not removed through post cure it will migrate to the surface of the polymer where it crystallizes. These crystals are commonly referred to as “bloom”.

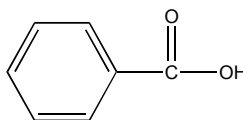


Figure 3. Benzoic acid.

- 4-methylbenzoic acid is the by-product of di(4-methylbenzoyl) peroxide. Di(4-methylbenzoyl) peroxide is similar to di(2,4-dichlorobenzoyl) peroxide except for the chlorine side groups of the benzene ring. This peroxide addresses the ever growing concern surrounding the use of halogenated chemicals.

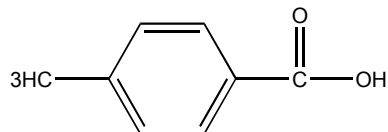
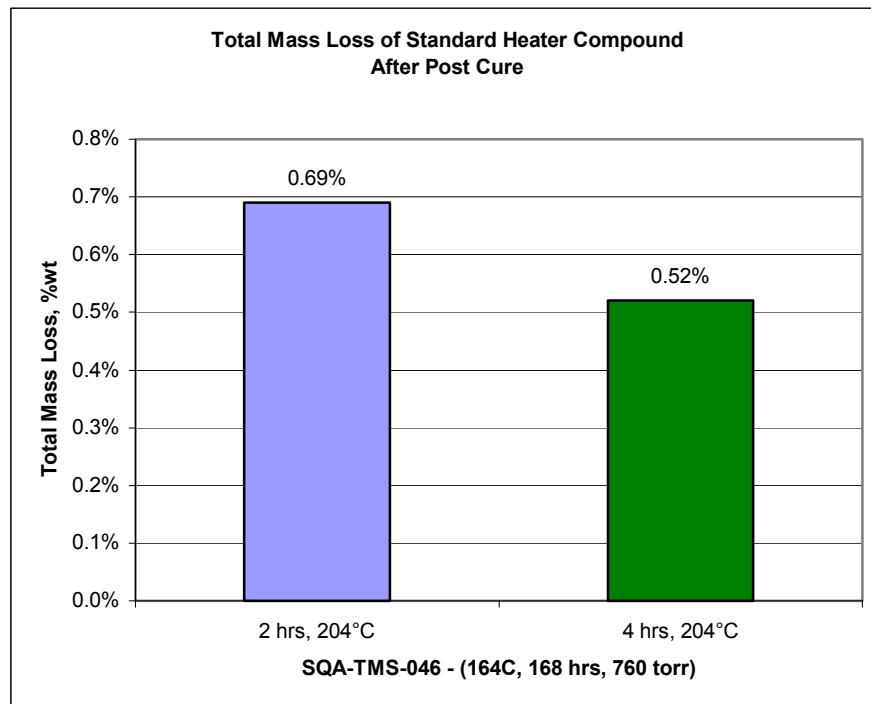


Figure 5. 4-methylbenzoic acid.

Quantity and Rate of Outgassing

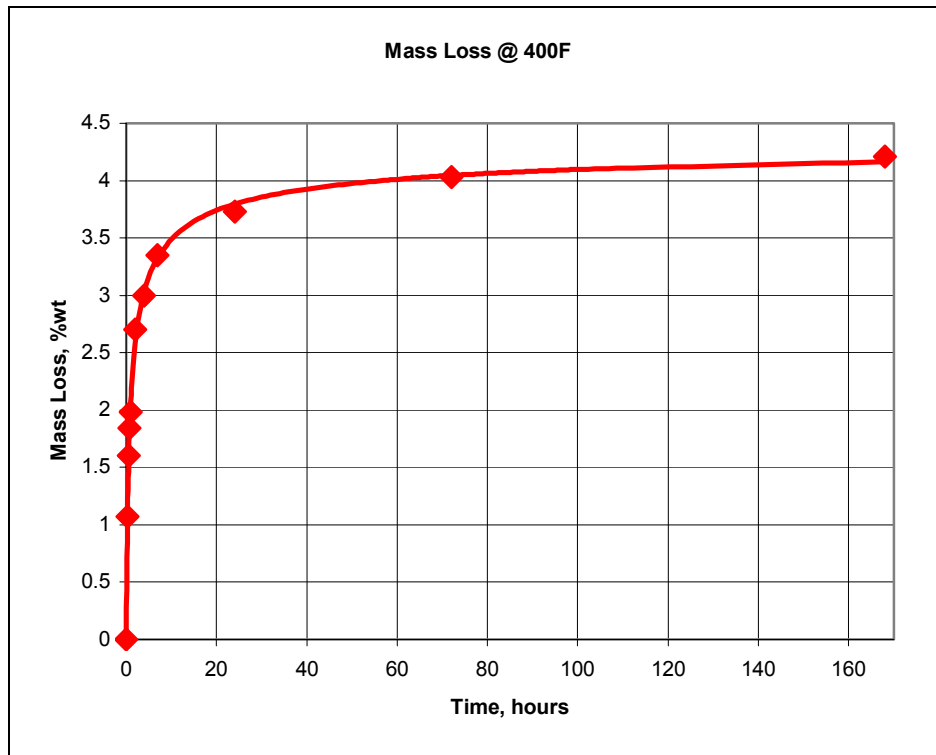
Total Mass Loss After Post-Curing

The following figure gives the total mass loss data for a typical heater compound material after typical post-cures. The total mass loss represents the amount of material lost after 168 hrs at 164°C and atmospheric pressure. Samples consisted of discs that were 1" in diameter and 0.076" thick. Only one surface of the disc was exposed during outgassing tests.



Rate of Outgassing Without Post-Curing

The chart below shows rate of mass loss of a standard heater compound without any post-curing. The data below shows that after approximately 160 hours of time the rate of outgassing decreases to about 19 ppm/hr.



Last Revised: February 10, 2004