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Formaldehyde Generation from Silicone Rubber

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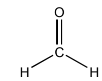
Figure 1 – Formaldehyde



The Occupational Safety and Health Administration (OSHA) defines formaldehyde as a hazardous chemical. It is characterized as a flammable, colorless gas with a pungent odor. Formaldehyde is considered and irritant, a sensitizer, and a potential carcinogen. Although silicone rubber generates formaldehyde through thermal oxidation, the rate at which it is produced is generally lower than that of many common materials. In aerobic atmospheres, silicone rubber begins generating formaldehyde at temperatures above 149^{o}C. Additionally, materials that are manufactured from formaldehyde; materials that contain formaldehyde in their composition; and/or materials that produce formaldehyde as a by-product of thermal oxidation also generate formaldehyde. During thermal oxidation of silicone rubber, the rate at which formaldehyde is generated is dependent on temperature and atmosphere. To establish the required engineering controls, it is possible to estimate the rate of formaldehyde generation for a particular process with knowledge of a few essential variables.

Silicone rubber is a polymer consisting of an inorganic siloxane (-Si-O-) backbone and two organic functional groups bonded to each silicon atom. The organic groups are most often methyl, but may include vinyl, phenyl, hydrogen, hydroxyl and/or trifluoropropyl. The type and quantity of organic functional group is varied to impart certain physical and/or chemical properties to the polymer. Most industrial grade silicones contain methyl groups with a few mole percent of vinyl groups. The methyl ($-CH_3$) groups are largely responsible for formaldehyde generation during thermal oxidation. Thermal oxidation of methyl groups begins at 149^{o}C with the formation of a peroxide on the methyl group followed by scission of the Si-C bond leaving a free radical on the silicon atom and a departing peroxide. The peroxide decomposes to a hydroxide ion and formaldehyde. A portion of the formaldehyde can decompose to carbon monoxide, hydrogen, carbon dioxide, and water. It is this portion of the mechanism that gives rise to the volatile organic products of the decomposition. The hydroxide ion and the free radical silicon atom can react with each other, or with other methyl groups, eventually leading to the decomposition of the methyl groups and the formation of non-volatile silicon dioxide. In addition to the volatile organic products listed, trace amounts of methanol and formic acid can also form during thermal oxidation[1]. Figure 2[2] illustrates said mechanism proposed by Andrinov.

Figure 2 – Andrinov Mechanism

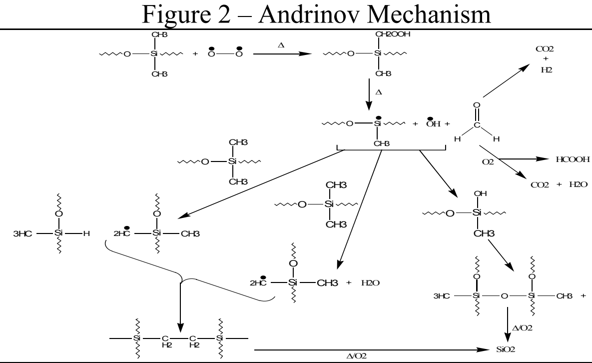


Table 1 contains the quantity of volatile organic compounds generated during thermal oxidation of a typical polydimethylsiloxane containing only methyl functional groups[3].

Table 1[3]	
Volatile Organic Compound	Quantity, %wt
Carbon monoxide	25
Water	17
Formaldehyde	4
Carbon dioxide	2
Methanol	trace
Formic acid	trace

Silicone rubber is not the only material that generates formaldehyde during thermal oxidation. Many common materials, such as polystyrene, polyethylene, polypropylene and mineral oil are capable of generating formaldehyde through thermal oxidation. Typically, these materials generate formaldehyde at rates greater than that of silicone rubber for a given temperature. Dow Corning has measured the formaldehyde generation rates of these materials at 200°C – 204°C using TGA-Hydrazine Polarography, a method which gives good sensitivity to formaldehyde in the presence of other aldehydes and carbonyl groups[4,5]. The Dow Corning results are summarized in Table 2 below.

Table 2[6]

Material	Temperature, °C	Formaldehyde Generation, µg CH_2O/g-hr
Polystyrene	204	50
Polyethylene	200	81
Polypropylene	200	435
Mineral oil	200	463

In addition to thermal oxidation, products that use formaldehyde as a building block or component in manufacturing processes are also sources of formaldehyde generation. For example, certain plastics, foams, coatings, insulations and building materials are fabricated from formaldehyde. Furthermore, cleaning agents, antiseptics, cosmetics, paints and pharmaceuticals contain it because of its preservative, bio- and fungicidal properties[7]. Formaldehyde is widely used in many materials making it difficult to avoid. Nearly 3% of all products in the Danish Product Registry Database directly use formaldehyde in their production[8].

The rate at which thermal oxidation of silicone rubber generates formaldehyde is dependent on atmosphere and temperature. Formaldehyde generation only occurs in aerobic atmospheres where oxygen is present. Higher temperatures equate to greater rates of formaldehyde generation during thermal oxidation. In addition to the organic materials listed in Table 2, Dow Corning also measured the formaldehyde generation rates from several silicone materials using the same TGA-Hydrazine Polarography method[9]. It was discovered that a dimethyl silicone fluid generated < 5 µg CH_2O/g-hr at ≤ 197°C. The rate increased to 245 µg CH_2O/g-hr at 225°C and to 1418 – 4627 µg CH_2O/g-hr near 250°C. Similarly, a high-consistency silicone rubber generated < 3 µg CH_2O/g-hr at 200°C, 14 µg CH_2O/g-hr at 204°C, and 1200 µg CH_2O/g-hr at 254°C. This demonstrated the relationship between temperature and formaldehyde generation of silicone materials -- including high-consistency silicone rubber. Furthermore, a dimethyl, phenylmethyl silicone fluid and a trifluoropropyl silicone fluid were analyzed between 200°C – 204°C. The two silicone fluids yielded < 5 µg CH_2O/g-hr and 48 µg CH_2O/g-hr, respectively. The established order of thermal stability for functional groups commonly used in silicones is phenyl > vinyl > methyl > trifluoropropyl[10]. This is in agreement with the results obtained by Dow Corning[11] and supports the thermal oxidation resistance of certain organic functional groups on the silicone backbone.

The concentration of formaldehyde for a particular manufacturing process can be estimated using the following equation provided factors such as workplace volume, air exchange in an 8-hour shift, and sources of formaldehyde are known[12]. This equation can help estimate the level of employee exposure to formaldehyde. The equation can also aid in determining if routine sampling or constant monitoring in the work place is warranted. Lastly, the equation can help determine if work place engineering controls and updated operating procedures are necessary.

Formaldehyde level, ppm $= x + y + z * \left(\frac{1}{V * A}\right) * \left(\frac{1}{1000}\right) * \left(\frac{1}{1.24}\right)$ ref: 13

Where:

x = formaldehyde released from products that contain formaldehyde in there composition, µg
y = formaldehyde released from products that release formaldehyde, µg
z = formaldehyde generated from products that generate formaldehyde thermally, µg
V = volume of workplace, m^3
A = air exchanges in an 8-hour shift

Formaldehyde is thermally generated from many materials -- including high consistency silicone rubber. However, the rate at which silicone rubber generates formaldehyde is substantially lower than many common materials. Silicone rubber begins to generate formaldehyde at temperatures as low as 149^{o}C, but does not appreciably generate formaldehyde until ~200^{o}C and above. At these temperatures, other materials have already achieved significantly greater formaldehyde generation rates. It is possible to estimate potential formaldehyde levels for a particular manufacturing process if the sources of formaldehyde are known. To minimize employee exposure, knowledge of potential formaldehyde generation levels can aid in the implementation of appropriate engineering controls and standard operating procedures.

Endnotes

1. Petar R. Dvornic, *High Temperature Stability of Polysiloxanes*, Silicon Compounds: Silanes and Silicones, Barry Arkles, Gerald Larson, Gelest Catalog 3000-A, Silanes & Silicones, 2004 pp 427.
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3. Dvornic, 427.
4. Daniel H. Flisinger (Dow Corning), Formaldehyde Levels Based on Bulk and Elevated Temperature Evolution Rate Measurements of Silicone Materials, American Industrial Hygiene Association Journal 56 (1995): pp 1201.
5. C. Stevens (Dow Corning), Generation of Formaldehyde – Where Does It Come From?, Dow Corning Report (01/1995) pp 2.
6. Flisinger 1207.
7. FormaCare Sector Group. FormaCare, about formaldehyde, common uses [Online]. Available: (http://www.formaldehyde-europe.org/pages/common_uses.uses.0.html) [2005, 12, 27]
8. Stevens 1.
9. Flisinger 1201 - 1207.
10. Dvornic 428.
11. Flisinger 1201 - 1207.
12. Stevens 3.
13. Stevens 3.