GE Silicones
Waterford, NY 12188

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Regarding the Evolution of Formaldehyde from Polydimethylsiloxanes.

Background

Formaldehyde is an oxidative decomposition product characteristically found during the thermal breakdown of most organic materials including polydimethylsiloxanes ("PDMS"). The formation of this material is indicative of polymer degradation.

Regulatory Perspective

Formaldehyde is subject to a variety of federal and state environmental, health, and safety requirements. The federal Occupational Health and Safety Administration ("OSHA") has promulgated regulations applicable to occupational exposure to formaldehyde. These regulations state that OSHA's hazard communication requirements apply to formaldehyde gas, all mixtures and solutions composed of greater than 0.1 percent formaldehyde, **and materials capable of releasing formaldehyde into the air, under reasonably foreseeable conditions of use, at concentrations reaching or exceeding 0.1 ppm.** 29 C.F.R. §1910.1048(m)(1)(i). GE Silicones has elected to include formaldehyde warning statements in the MSDSs and labels of many of its products because these products could possibly be subjected to conditions under which formaldehyde might be generated. Further, in small, unventilated areas, concentrations exceeding 0.1 ppm formaldehyde could possibly be achieved.

Quantitative Studies

Two recent studies[1,2] offer more quantitative data concerning the evolution of formaldehyde from Methyl Siloxanes.

Carnihan of GE CRD measured the amount of formaldehyde evolved from 350 cstk. PDMS fluid at various temperature and plotted formaldehyde yield vs. the inverse of temperature in an Arrhenius type plot. Filsinger[2] of Dow Corning did similar experiments using a more sensitive method so was able to measure formaldehyde at lower temperatures. He measured the formaldehyde levels in various polymethylsiloxane containing materials both at room temperature and at elevated temperatures. He also measured the amount of formaldehyde evolved during heating of various non-silicon organic polymers such as polystyrene, polyethylene, polypropylene and mineral oil.

The Data

The attached chart plots both GE data and DC data for polydimethylsiloxane, in an Arrenius type plot. The data (attached) were revised to the same units (% theoretical formaldehyde yield). We did not correct for the different heating times used for sampling and therefore assume that most of the formaldehyde is released within 15 minutes. We then used linear regression to obtain a relationship between the inverse temperature and log % formaldehyde yield. The correlation is reasonable (R2 = 0.9736) considering that different viscosity's and methods were used by DC and GE.

Here are estimated formaldehyde levels vs. temperature using the linear regression equation.

Temp. (deg. C)	*Temp. (deg. F)*	*% theoretical formaldehyde evolved*
150	302	0.000002
200	392	0.001
250	482	0.26
265	509	1.01
300	572	19
320	608	87

Conclusions

One can conclude that there is very little formaldehyde evolved until about 200°C (392°F).
One can also see from the DC data that PDMS evolves less formaldehyde than other thermally decomposing organic polymers such as polystyrene, polyethylene, polypropylene and mineral oil. The data for these polymers are on the attached chart.

Use Considerations

Though some manufacturers of cured silicone rubber products may allow a small amount of decomposition to occur (and therefore a small amount of formaldehyde to be formed) to enhance cure speed, such decomposition will eventually result in significant property degradation. For this reason, most will avoid conditions under which a significant amount of formaldehyde is formed.

Besides the temperature factor discussed above, the other significant factor influencing the rate of decomposition is the interaction of oxygen with the polymer. For formaldehyde to be formed, oxygen must be present and in contact with the polymer. Silicones can be heated to very high temperatures in an anaerobic environment without decomposition taking place. In an aerobic environment, the surface area of the polymer exposed to the air and the rate at which oxygen is dispersed through the polymer will have an impact on the rate of formaldehyde evolution. In the case of a silicone rubber, oxygen will only slowly diffuse into the polymer matrix. In the Dow Corning study, an agitated silicone fluid generated formaldehyde faster than a silicone rubber at the same temperature.

From a health and safety perspective, the level of exposure is of greater practical concern than the rates of evolution. The exposure will depend on the amount of formaldehyde formed and the characteristics of the room in which the activities are taking place. Amounts formed will depend on time as well as the rate of evolution. Exposing a silicone rubber to high temperature for an extended time will result in a higher amount of formaldehyde production than a brief exposure. The volume of the production area and the rate of air turnover are two of the most important room characteristics. A large room with good ventilation is much less likely to build up a high formaldehyde concentration than a poorly ventilated space.

Though calculating the levels of formaldehyde exposure is possible if one knows all the variable involved, GE Silicones recommends monitoring to determine if an operation meets applicable requirements, including OSHA requirements. Understanding the variables upon which the formaldehyde concentration depends, however, is important in the event that the recommended upper limit of formaldehyde exposure is detected. One can then decide which of the variables (*e.g.*, cure temperature, cure time, air turnover rate, number of pieces being cured at one time, oven ventilation efficiency) might be changed to reduce the formaldehyde concentration.

Conclusions and Recommendations

The generation of formaldehyde is a complicated subject due to the number of variable involved. Because of this, GE Silicones can not give assurances that levels of formaldehyde above the OSHA limits are not being generated. It is our policy to advise customers of the potential for formaldehyde generation and recommend monitoring by a trained Environmental Health and Safety specialist if there is a concern.

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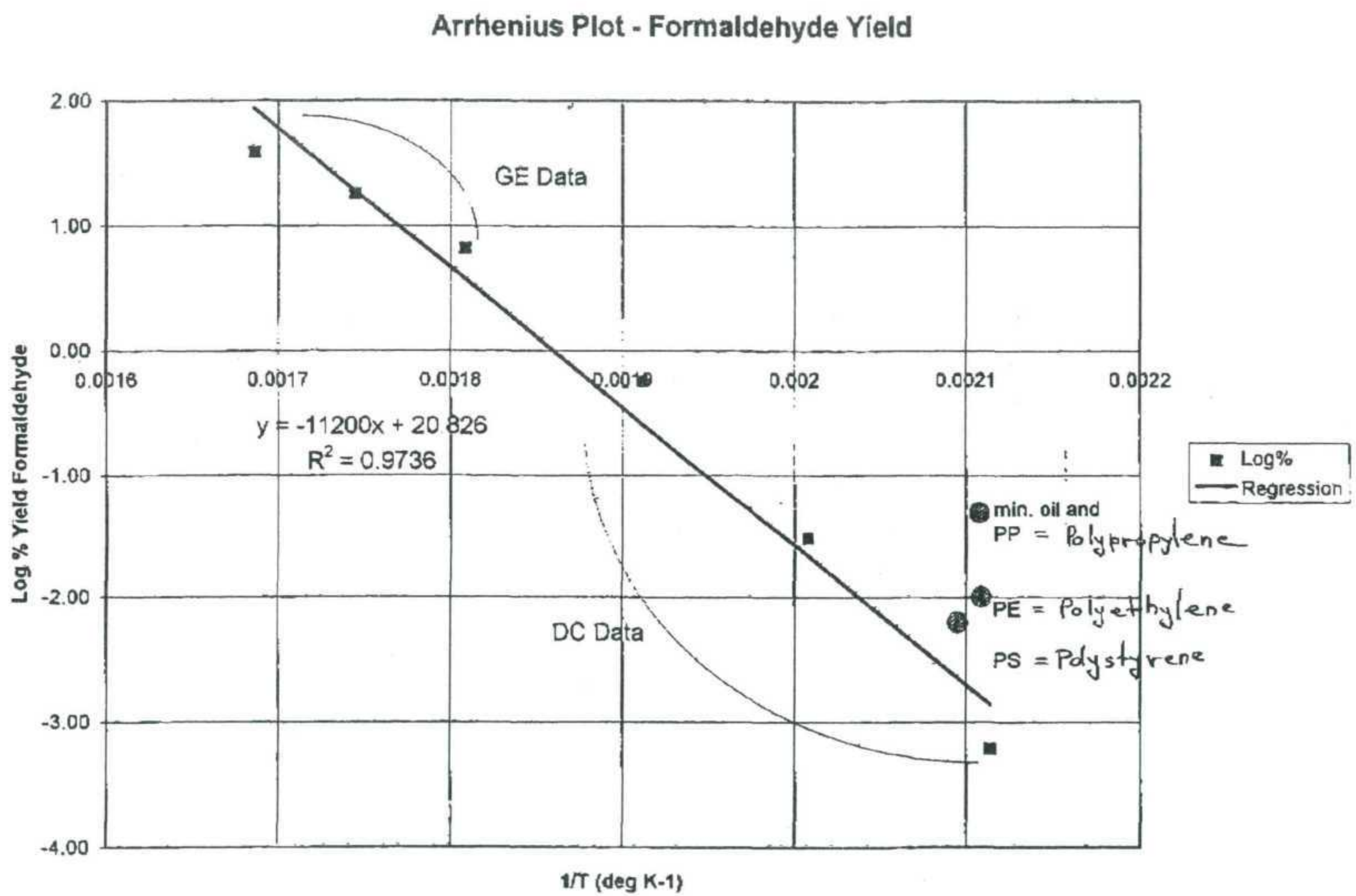
[1] Carnahan, J. "Oxidation of Dimethyl Fluids". GECRD private communication September 9.1994

[2] Filsinger, D.H., "Formaldehyde Levels Based on Bulk and Elevated Temperature Evolution Rate Measurements of Silicone Materials", American Industrial Hygiene Association Journal 56,, 1201 (1995)


Arrhenius Plot - Formaldehyde Yield
2.00
1.00
0.00
-1.00
-2.00
-3.00
-4.00
0.0016
0.0017
0.0018
0.0019
0.002
0.0021
0.0022
GE Data
DC Data
y = -11200x + 20.826
R2 = 0.9736
Log % Yield Formaldehyde
1/T (deg K-1)
Log%
Regression
min. oil and
PP = Polypropylene
PE = Polyethylene
PS = Polystyrene