



Special Supplement to Silicone Spectator December 17, 2008

Cyclomethicone Free Silicone Fluids?

Editor's Note:

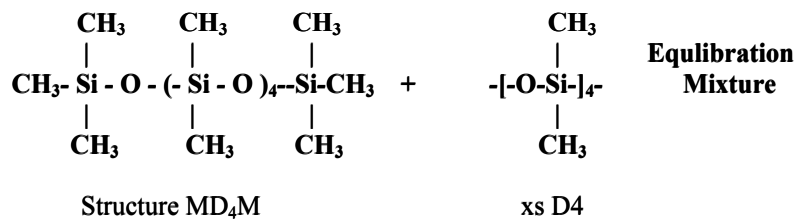
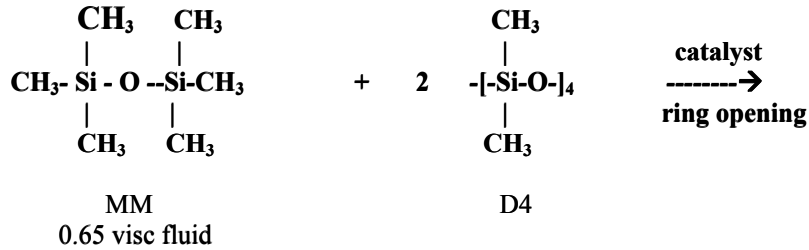
There has been considerable interest in making products that are free of cyclomethicone. Originally this was limited to D4, now D5 is coming under scrutiny. The molecular design will become more and more critical in choosing a compound that is not only free of cyclomethicone as prepared, but also will remain cyclomethicone free in formulation. This is due in part to the fact that silicone polymers are decidedly different from organic compounds. This difference is due to the fact that silicone fluids are produced by a process called equilibration. In practical terms one needs to engineer molecules that cannot re-equilibrate under formulation conditions to make cyclomethicone.

An article published in *Cosmetics and Toiletries* in 2003 (Vol 119 No. 5 p. 89-98) addressed the problem posed by equilibration. The article states: "It is also quite interesting to note that a "finished silicone fluid" may be placed in contact with D4 and catalyst and re-equilibrated to make a higher viscosity fluid. Conversely, a "finished silicone fluid" may be re-equilibrated with MM and catalyst to make a lower viscosity fluid. **Finally, silicone rubber may be decomposed into MM, and D4 via stripping of the product in the presence of catalyst. This property of silicone polymers makes them decidedly different from organic compounds.**"

The key thing to consider is that the result of equilibration always has cyclomethicone as a product.

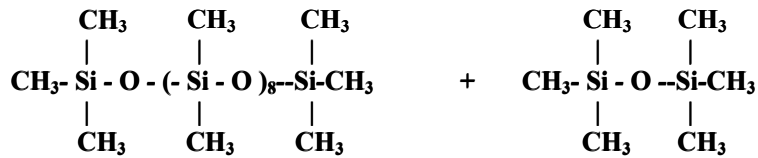
FIGURE 5: EQUILIBRATION REACTION SCHEME

Build up Process



^
| Catalyst
|

Breakdown Process



The original article is presented below.

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Editor

Published in Cosmetics and Toiletries 2003 Vol 119 No. 5 p. 89-98

Equilibration Reaction of Silicone Fluids

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Silicone fluids are used in many cosmetics and personal care products. This article looks at the synthesis of silicone fluids and evaluates whether that process can be viewed as an equilibrium reaction.

Silicone Fluids

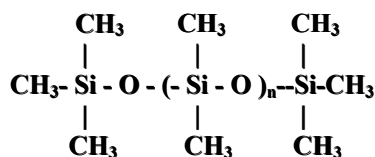
Silicone fluids are a class of compounds that have become known by a variety of names including silicone oils, dimethyl fluids, dimethyl polysiloxane, and polydimethyl siloxane. Silicone fluids have become an important class of materials over the years. These materials are unique in terms of chemistry when compared to hydrocarbon-based materials. While much has been learned about these compounds since they were developed in the 1940s, the available published data remains somewhat limited related to certain aspects of the chemistry.

Silicone fluids are sold by their viscosity. Commercial products range in viscosity from 0.65 centistokes to 1,000,000 centistokes. If the product is not made by blending two different viscosity fluids, the viscosity is related to molecular weight. Silicone fluids conform to the structure shown in Figure 1. The viscosity allows for an approximate calculation of the value of "n" as shown in Table 1.

Table 1. The "n" value for selected silicone fluids

Approximate Viscosity at 25°C (Centistokes)	Approximate molecular weight	"n" Value
5	800	9
50	3,780	53
100	6,000	85
200	9,430	127
350	13,650	182
500	17,350	230
1,000	28,000	376
10,000	67,700	910
60,000	116,500	1,570
100,000	139,050	1,875

FIGURE 1: GENERIC STRUCTURE OF SILICONE FLUIDS



These materials have found a home in many cosmetic products as outlined in Table 2.

Table 2. Cosmetic usage of silicone fluids¹

Product type	Desired effect	Use level
Skin Lotion	Desoaping	0.1%
	Rub-out	0.1 - 0.5%
	Protection	1 - 30%
	Feel	0.5 - 2%
Skin Cleaner	Lubricity	0.1 - 0.5%
	Wetting	0.1%
Antiperspirant	Anti-whitening	0.5 - 2%
	Detackification	0.5 - 2%
Preshave Lotion	Lubricity	0.5 - 2%
Aftershave Lotion	Feel	0.5 - 2%
Makeup	Water Resistance	1 - 5%
Shaving Cream	Reduce Razor Drag	0.5 - 2%

Synthesis

Silicone fluids are synthesized by the equilibration reaction of MM and cyclomethicone. Typical of the synthesis of fluids is the reaction in which one MM is reacted with one D4 compound to make MD₄M, a simple silicone fluid.

The reaction may be run with either an acid or base catalyst. In one method, the reaction is conducted at room temperature for 12 hours, with sulfuric acid as a catalyst resulting in a mixture of cyclic and linear fluid. If the catalyst is neutralized and the cyclic is stripped off, a stable fluid results. If the catalyst is not neutralized during stripping, the fluid will degrade.^{2,3}

The equilibration process is critical not only to the production of stable silicone fluids, but also as a means of introducing functional groups into the polymer. This is done using a process called hydrosilylation, a process used to make organofunctional silicone compounds.

It is also quite interesting to note that a “finished silicone fluid” may be placed in contact with D4 and catalyst and re-

equilibrated to make a higher viscosity fluid. Conversely, a "finished silicone fluid" may be re-equilibrated with MM and catalyst to make a lower viscosity fluid. Finally, silicone rubber may be decomposed into MM, and D4 via stripping of the product in the presence of catalyst. This property of silicone polymers makes them decidedly different from organic compounds.

Equilibration

It is thought that silicone polymers form in equilibrium with their reactants and could be pushed back towards the reactant side of the equation under the correct circumstances. The reactants are Si(CH₃)₃-O-Si(CH₃)₃ (MM) and -(Si(CH₃)₂-O)₄ or D4. Since D4 is a six-member ring, having alternate silicon and oxygen atoms, its reaction with MM gives linear polymers in the presence of MM and catalyst. To be a true equilibrium reaction when MM is added to an already existing linear polymer one might expect to get the equilibrium mixture of D4 and a smaller linear molecule. If an excess of MM is combined with a linear polymer chain one might expect to get a different polymer consuming the MM. Little is published on the nature of the reversibility of the reaction known as equilibration.

In order to evaluate the nature of the equilibrium, a study was undertaken which included:
 Reacting MM and D4 and building it up to a viscosity of 350 centistokes, and also to 1,000 centistokes;
 Adding MM to break down the 1,000 centistoke fluid made in step 1 and also to break down a commercially obtained 1,000 centistoke fluid;
 Neutralization of the catalyst, followed by;
 Analysis via Gel Permeation Chromatography of the products to determine the linear polymer concentration and the concentration of D4 found in each.
 One objective is to determine if the composition of product made by build up is the same as the composition made by the break down process. Specifically, the concentration of D4 will be of major interest. One possibility is that there will be a comparable amount of D4 present regardless if the process is build up or break down. Another possibility is that since commercial 1,000 centistoke product is stripped of D4 after processing, the break down product may be very low in D4.

The build up reaction is shown in Figure 2. The break down reaction is shown in Figure 3.

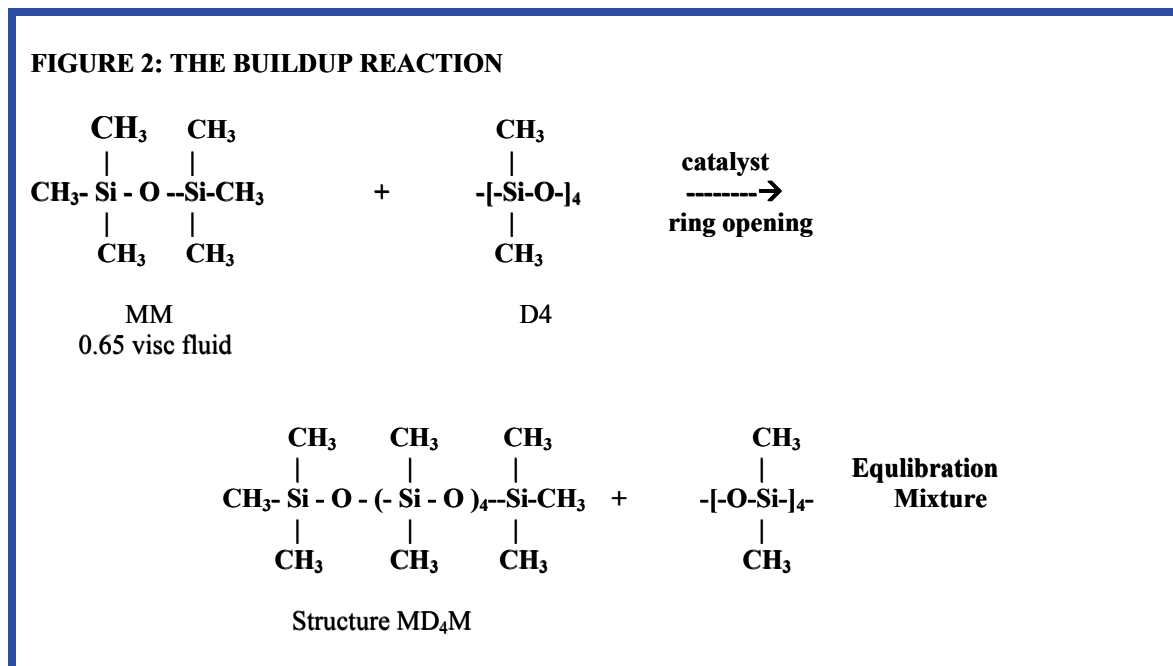
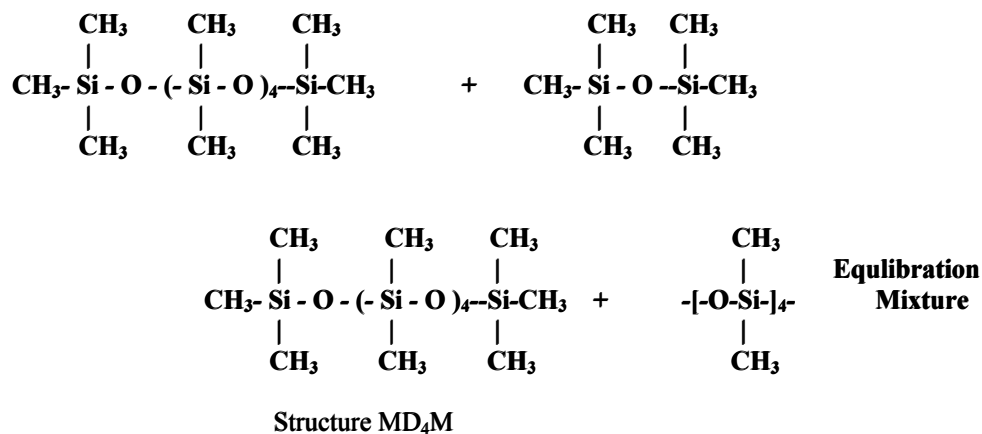


FIGURE 3: THE BREAKDOWN REACTION

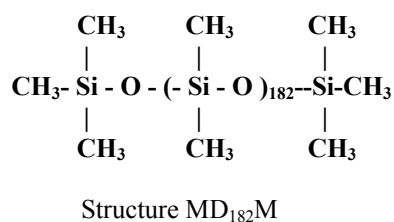


What is not clear from the literature is if the equilibrium mixture made by the build up process is the same as that of the break down product. If the reaction is a true equilibrium, it should not matter which path the reaction takes, but should be only determined by the ratio of reactants introduced. On the other hand it is possible when one breaks down a pre-existing silicone polymer, the silicone polymer might be the same but no D4 would form. This would mean the reaction is not a true equilibrium.

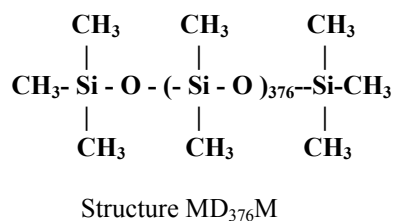
The average structures of the two silicone fluids used in this study are shown in Figure 4.

**FIGURE 4:
AVERAGE STRUCTIONS OF SILICON FLUIDES USED IN THIS STUDY**

(a) Average structure of 350 viscosity polydimethyl siloxane



(b) Average structure of 1000 viscosity polydimethyl siloxane



If the silicone polymer made by the break down process results in no D4, a cyclic free product might be possible by breaking down higher molecular weight polymers with MM. This is very important to the cosmetic industry because cyclic silicones are not desirable in cosmetic products. Many companies go through different synthesis to minimize the concentration of cyclic in their final product.

Methods and Materials

In our study we used the five samples described in Table 3.

Table 3. Materials used in the study

Sample	Description	Material (in parts)				
		D4		MM	H ₂ SO ₄	NaHCO ₃
A	1000 Viscosity Build Up Product	99.4	6.6	5.0	15.0	
B	350 Viscosity Break Down Product from commercial 1000 viscosity fluid		0.6	5.0	15.0	99.4
C	1000 Viscosity Build Up Product broken down to 350 Viscosity	99.4	0.6	5.0	15.0	
D	350 Viscosity Build Up Product	98.8	1.2	5.0	15.0	
E	Commercial 350 Viscosity control					

* = Fluid-1000, a commercial 1000 centistoke silicone fluid

** = A commercial 350 centistoke silicone fluid

Procedures for samples A, B, C, D:

1. Combine the amounts of MM and D4 in a 400 mL flask.
2. Stir well.
3. Add sulfuric acid.
4. Mix for 24 hours (under good agitation for sample A).
5. Slowly add sodium bicarbonate. Foam will be encountered requiring venting of carbon dioxide.
6. Filter.

The equipment used for gel permeation chromatography analysis included an HPLC pump^a, a differential refractometer detector^b and a column heater module^c. The columns were Styagel HR 3, 1 and 0.5 in series with a flow rate of 1.0 mL/min, a mobile phase THF, a column temperature of 55°C and a detector temperature of 45°C. Waters HPLC Pump Model 515. Waters Differential Refractometer Detector Model 410. Waters Column Heater Module,

Results

The results of the gel permeation chromatography analysis are presented in Table 4.

Table 4. Results of the gel permeation chromatography analysis

Sample	Description	D4	Time	Polymer	Time	Sum
A	F1000 BU	3.05	23.97	96.95	15.29	100.00
B	F350 BD	5.29	23.38	94.71	15.57	100.00
C	BU 1000 BD 350	10.39	23.34	89.61	15.66	100.00
D	F350 BU	4.65	23.45	95.35	15.64	100.00
E	F350 Control	1.58	24.10	98.42	15.76	100.00

Discussion

Both the build up mechanism and the break down mechanism had a comparable quantity of cyclic products present. The break down from 1,000 to 350 had 5.29% cyclic silicones present before distillation, while the build up product had 4.65%. The commercial 350 viscosity product had less cyclic silicones present in it, at 1.58%. This is related to the degree of strip used after the catalyst is neutralized. It is surprising to see that a product that was built up, neutralized but not stripped, followed by a break down had twice as much cyclic silicone as the direct build up. The build up to 350 had 4.65% and the build up and break down had 10.39%. It appears that in the case of this sample there were in fact two different mechanisms occurring simultaneously, a build up and a break down, giving different equilibration concentrations of product. One of the other products had MM, D4, and linear silicone present at the same time, representing a different reaction sequence.

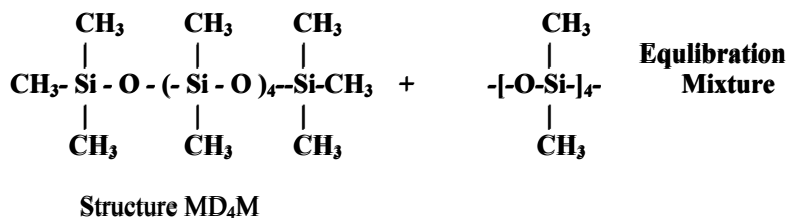
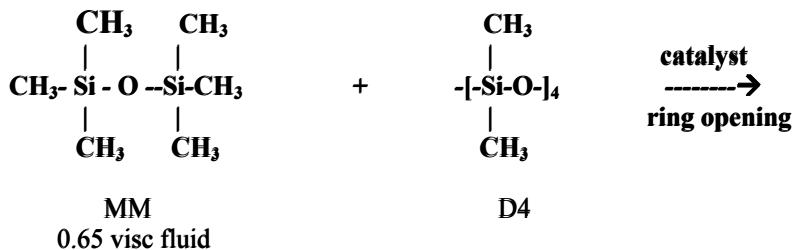
Conclusions

Reference to the results in Table 4 suggests several interesting conclusions.

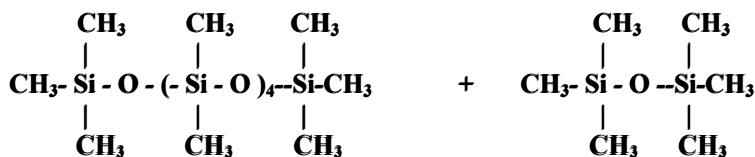
1. There are two different ways to make a 350 viscosity dimethyl polysiloxane – by build up (Sample D) or break down (Sample B). They result in the same mixture of D4 to polymer. Figure 5 shows the two reactions and the common product mixture

FIGURE 5: EQUILIBRATION REACTION SCHEME

Build up Process



Breakdown Process



2. Commercial 350 viscosity silicone is stripped to reduce the % D4 to under 2% (Sample E), from the original level of around 5% (Samples B and D).

3. The equilibrium mixture of dimethyl polysiloxane having a viscosity of 1,000 (Sample A) has a lower concentration of D4 in the equilibrium mixture than the 350 viscosity product (Sample D).

4. The surprising result is Sample C, the product in which a 350 viscosity dimethyl polysiloxane was built up to 1000 viscosity and then broken down to 350 viscosity. That sample had a very high level of D4 – twice the expected amount based on Samples B and D.

***Acknowledgments:** The authors would like to gratefully acknowledge Mr. Rick Vrckovnik of Siltech Corporation Canada for running the various chromatographic analyses.*

References

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Published in *Cosmetics and Toiletries* 2003 Vol 119 No. 5 p. 89-98



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