Reducing or eliminating cyclomethicones from dimethicones

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Introduction

Silicones are often utilized in personal care products due to the performance benefits that they provide, including conditioning, slip, extended wear, shine and lubricity characteristics. More personal care product launches include the INCI name dimethicone than any other silicone offering. Dimethicones are silicone polymers that typically contain trace amounts of cyclomethicones, the starting molecules for silicone production. Historically cyclomethicones have also been used as stand-alone carriers or diluents in personal care products due to their inherent volatility, which is ideal not only for AP/Deo, but numerous other applications.

Cyclomethicones are a group of thermodynamically stable cyclic silicone molecules which are used in the manufacturing of the higher order polymers. The structures are small, volatile, cyclic versions of dimethicones with formulas: $[\sim Si(Me)_2O\sim]_n$. Although a range of structures from n=3 to n=6 is formed, the equilibrium ratio is about 85%/15% n=4/n=5. The structures where n=3 and n=6 represent less than 1.0% of the mixture. The majority components are colloquially termed D_4 (n=4) and D_5 (n=5).

In recent years cyclomethicones, namely octamethylcyclotetrasiloxane (D4), have been assessed by the Regulation on Registration, Evaluation and Authorisation of Chemicals (REACH). The Member States Committee of the European Chemicals Agency (ECHA) concluded that D4 is considered a Bioaccumulative substance. Further assessments are ongoing across multiple governments worldwide.

Current EU standards limit D4 and D5 to less than 0.1% for wash-off cosmetic products. The Global Silicones Council (GSC) explains that "It is noteworthy that outside of the EU no regulatory authority has imposed any restriction on the use of these substances in commerce, nor have they considered adopting such restrictive measures as requiring permission from the government to use these substances. D4, D5 and D6 are widely considered safe for human health and the environment when used as intended."[i]

According to the Silicones Environmental, Health and Safety Center (SEHSC), a sector group of the American Chemistry Council (ACC), "More than 99% of D4 is used as an intermediate to

[i] Global Silicones Council (GSC) News Release, "GSC Opposes EU Authorization Recommendation for D4, D5, D6; Potential ban on silicone substances in EU 'inconsistent with sound science'," https://globalsilicones.org, April 3, 2020.

make products that provide societal benefits from a variety of industries, including: transportation, building and construction, health care and electronics."[ii]

The benefits of cyclomethicones in personal care applications are numerous, including as diluents for wash-off conditioners and hair styling products, as carriers in AP/Deo products and as diluents for skin care products. When regulatory concerns regarding D4 arose many years ago, the industry first transitioned from using D4 to utilizing D5, but regulatory scrutiny has continued beyond D5 onto D6. The silicones industry challenges the validity of many of the concerns[iii] but the EU has taken action limiting the use of cyclomethicones and the personal care industry has reacted by formulating away from these products in some applications. Formulators seeking the desirable benefits of dimethicones have been faced with the challenge of achieving those benefits by other means, which in most cases is simply not possible.

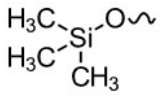
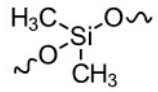
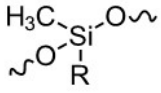
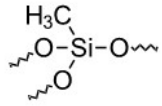
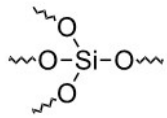
In the text that follows we demonstrate means for removing D4, D5 and D6 from standard silicone product offerings and outline the practical limitations to the final levels that can be reached. We also highlight innovative new families of non-dimethicone silicon-based products that are made without cyclomethicones.

Silicone Chemistry Basics

Silicones are manufactured from naturally occurring materials with quartz (silicone dioxide) as the typical starting silicon providing raw material. Silicon dioxide is reacted with carbon-based materials under high heat to form silicon metal. Silicon metal is then reacted with methylene chloride in the presence of a catalyst to produce chlorosilanes. The chlorosilanes are hydrolyzed with water to produce alkoxy silanes and subsequently polydimethylsiloxane (PDMS). The available basic constituents for silicone polymers directly impact the possible application range of the finished polymers.

[ii] "Final Results of D4 Environmental Monitoring Program Submitted to EPA," September 18, 2017, www.americanchemistry.com (accessed June 30, 2020).

[iii] Global Silicones Council (GSC) News Release, "GSC Opposes EU Authorization Recommendation for D4, D5, D6; Potential ban on silicone substances in EU 'inconsistent with sound science'," https://globalsilicones.org, April 3, 2020.

 = M group	Monofunctional groups typically act as chain terminators and provide the basis for hexamethyldisiloxane “MM” units.
 = D group	Di-functional groups typically act as chain extenders and make up the cyclomethicones (D4).
 = D* group R=alkyl	Reactive SiH groups provide reactive sites for the creation of multi-functional polymers.
 = T group	T-groups typically provide spacing units in the three-dimensional network.
 = Q group	Q groups provide additional spacing units and lend rigidity to the polymer network and potential film formation which is desirable in some applications.

Manufacturing Silicones, Using D4 as a Raw Material

Typical silicone product manufacturing for personal care applications involves the building of polymers from D4 as the starting point. Normally three monomers are used to make a silicone pre-polymer:

1. Hexamethyldisiloxane (or “MM”) which acts as an end group and determines the molecular weight and length of the polymer. The higher the charge of MM, the smaller the length of the silicone backbone will be.
2. D4, which provides the non-reactive dimethylsiloxane group (D group) which provides the hydrophobicity to the silicone backbone.
3. Methyl silicone hydride (D*) which will then have functional groups grafted on.

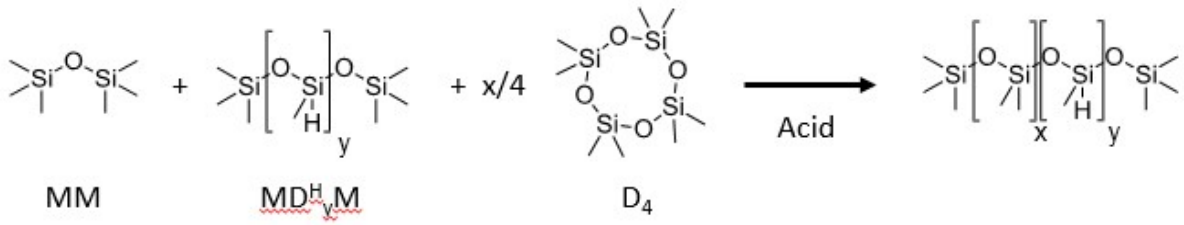


Figure 2. Re-distribution

The process to make the silicone pre-polymer is called a re-distribution process which results in the MM, D4 and D* reacting together to make a linear silicone polymer. This can also be referred to as a MDxD*yM polymer where x and y signify the number of D groups and D* groups. During this re-distribution process, although most of the D4 is consumed, some of the

thermodynamically stable D4 is re-formed along with D5 and D6. When the reaction has completed, residual levels of cyclomethicones (D4, D5 and D6) exist.

The silicone pre-polymer is then hydrosilated with a vinyl functional species to make a silicone copolymer.

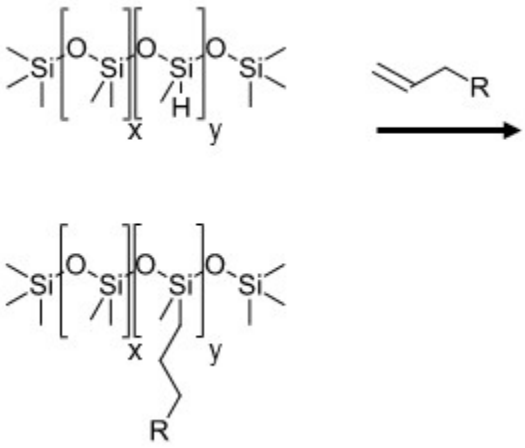


Figure 3. Hydrosilation

Where R is the functional group or polyether. Traditionally, the most common functional groups used in personal care are polyethers and these copolyols have the INCI name PEG/PPG Dimethicone. There can also be alkyl, quats, amines and other specialty functionalities on the silicone backbone.

Removing Cyclomethicones From Silicone Products

Cyclomethicones provide positive performance benefits in some applications, but are less desirable due to existing or pending regulations in other applications. Processes exist allowing manufacturers to reduce levels of cyclomethicones that are naturally occurring from the reaction processes. Since cyclomethicones are volatile in nature, the standard processes involve heating the finished silicone polymers and vacuuming off the cyclic species. Two standard methods exist:

1: Bulk Stripping: Silicone polymers are heated in bulk vessels with agitation and under vacuum, removing the volatile silicones. Stripping at temperature and under vacuum typically results in residual cyclomethicone levels below 0.1%.

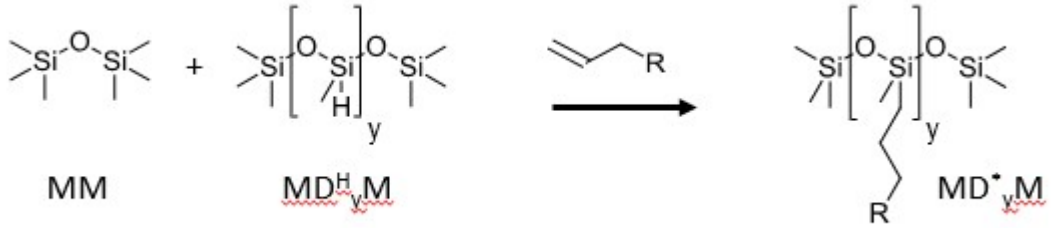
2: Wiped Film Evaporator Stripping: An available advanced processing method entails forcing silicone polymers through equipment creating a thin-film while heating and under vacuum. The high surface area of this so called thin-film stripping can yield cyclomethicone levels below 0.01%, which is well below current regulations.

Manufacturing Cyclomethicone-Free Silicones

As detailed many silicone polymers can contain cyclomethicones as part of standard reaction processes. Manufacturers have a way to greatly reduce the level of cyclomethicones via stripping, but it is typically not possible to remove cyclic species entirely.

Cyclomethicone-free silicone products offer an alternative to silicones manufactured with cyclics as a starting raw material and assure formulators and consumers alike that zero cyclomethicones are present in finished products. These "cyclic-free" products offer a solution for regulations already in place, and those regulations that may be pending, regarding the inclusion of cyclics or cyclics as bi-products in cosmetic applications.

In this process silicones are made using only MM and D^{H*}, but no D4 cyclics.



As can be seen in the Methicone structure, since no D4 is used there are no dimethylsiloxane groups (or D groups) and therefore are no residual cyclics in the final product.

Methicones offer an ideal solution for formulators seeking the benefits provided by silicones as they eliminate the concerns regarding existing and potential regulations. Formulators need not worry that cyclics are present as the starting raw materials for manufacturing methicones ensures that no volatile silicones are present in the finished products.

Siltech offers commercial methicones and is expanding this product line even further to meet the growing needs of formulators.

Siltech has also recently begun exploration with the use of T and Q groups referenced earlier in this document. These so called MTQ silicon resins, with branched silicone groups, provide a range of performance attributes that differ from the already outlined methicone products.

Silsurf Q25315-O is the newest methicone product launched by Siltech. This MQ silicon resin-based product behaves in many ways like traditional dimethicone copolyols, but with zero cyclomethicones. The product is an excellent Oil-in-Water (O/W) emulsifier and pigment dispersant. The unique properties allow for cold processing and resultant formulations exhibit a light, powdery skin feel. This exciting new material carries the INCI name PEG/PPG- 12/12 Dimethylsiloxysilicate.

The addition of T groups to the range of starting materials is Siltech's latest area of research and provides additional tools to the silicon chemists to innovate exciting products for the personal care industry, absent of any regulatory concerns.

Conclusions

Current and potential pending regulatory pressures on cyclomethicones have resulted in concerns for formulators and a reduction in usage. Processes exist for reducing cyclomethicone values well below the requisite limits with traditional sparging and state of the art wipe film evaporators. Siltech alternatively offers new structures that are absent cyclomethicone, yet offer traditional and even improved benefits of silicones for personal care.

About Siltech

Siltech specializes in the development, manufacturing and marketing of a full line of organo-functional silicone compounds and related products for a wide range of personal care applications. Siltech offers solutions for improving functional attributes such as wetting, conditioning, emulsification, film formation and more in cosmetic formulations and specializes in customization to meet customer needs. With more than 30 years of experience and two manufacturing facilities, Siltech remains committed to supporting the growing personal care industry.