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The quest for D_5 replacements

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There are a number of applications in which a dry skin feel is important. Cyclomethicone compounds are commonly used in cosmetic products to provide a solvent that feels dry on the skin. The INCI name Cyclomethicone refers to a family of cyclic dimethyl siloxanes that includes Cyclotetrasiloxane (D_4), Cyclopentasiloxane (D_5) , and Cyclohexasiloxane (D_6), a family that has come under increased environmental scrutiny in recent years. Key areas where this family of materials is used include antiperspirants, colour cosmetics and as a base solvent to blend with fragrance oils and perfume oils. Cyclomethicone is a clear, odourless silicone. It leaves a silky-smooth feel when applied to the skin. Cyclomethicone compounds possess a cyclic structure rather than the chain structures of linear dimethyl silicones (dimethicone). Low heat of vaporization and low vapour pressure has led their use as cosmetic vehicles. In other words the feel correctly or incorrectly has been associated with volatility. However, the physical chemistry that results in the dry feel of cyclomethicone is a complex one. Volatility is but one aspect of the complex phenomenon that contributes to a dry feel in a solvent used in cosmetics. Other considerations that impact upon selection of a D_5 replacement include viscosity, surface tension reduction (which affects spreadability), flammability of the solvent, effects of the solvent on skin and cost. Clearly, a D_5 replacement that is flammable, defatting and expensive is unacceptable. Table 1 outlines the assumptions we used in evaluating the suitability of materials as D_5 replacements.

1. **Cosmetic products are used at ambient temperatures, making volatility measurements at high temperature irrelevant.**
2. **Flammable materials are highly undesirable in cosmetic formulations.**
3. **Dry feel is a consumer perceptible rather than a laboratory metric.**

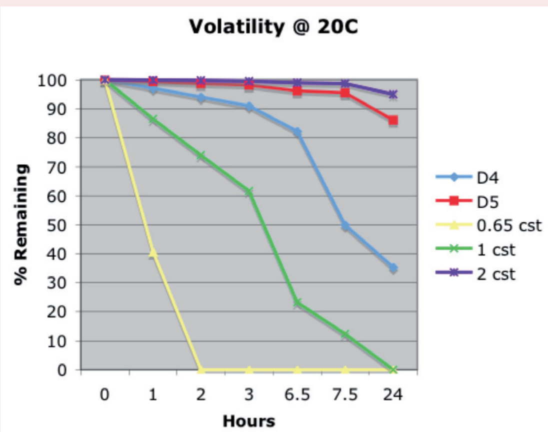
Table 1. Assumptions in evaluating D5 replacements.

VOLATILITY

Hours	D5 Cyclic	D4 Cyclic	0.65 cps	1cps	2cps
0.0	100.0%	100.0%	100.0%	100.0%	100.0%
1.0	99.4%	97.1%	40.6%	86.5%	99.9%
2.0	98.7%	94.0%	0.0%	74.0%	99.7%
3.0	98.1%	91.0%	0.0%	61.6%	99.5%
6.5	96.1%	82.2%	0.0%	23.3%	98.9%
7.5	95.5%	50.1%	0.0%	12.4%	98.7%
24	86.1%	35.3%	0.0%	0.0%	94.9%

Table 2. Percent remaining at 20°C.

Volatility is the ability of the compound being tested to evaporate under the temperatures at which the compound is used in formulation. For cosmetic products, this temperature is ambient (~25°C). It has generally been accepted that cyclomethicone compounds provided this feel because they evaporate quickly after helping to carry oils into the top layer of the epidermis. The ability to provide a product that (1) has the dry feel (2), is cyclomethicone free (3), is not capable of making cyclomethicone when exposed to catalyst and (4) is not flammable is a long felt need, un-satisfied need in the cosmetic industry. Volatility a contributor to dry feel, but more importantly, spreadability and low surface tension are major contributors to a dry feel. The assumption that volatility is required for dry feel is due to the fact that historically D_4 has a dry feel and is volatile. D_5 has replaced D_4 in formulations and consequently has been found acceptable in many cosmetic formulations as a D_4 replacement, but is it volatility that is primarily responsible for the dry feel? Personal care products are unique in that they are not applied at elevated temperatures as are many industrial products. It is therefore unreasonable to talk about volatility of a cosmetic solvent at elevated temperatures. The temperature of application is more typically 20°C than 200°C, yet we measure volatility at elevated temperatures. If one looks at a temperature of 20° the volatility more closely resembles what might occur in topical cosmetic products. Table 2 shows the percentage of material remaining over a 24 hour period at 20°C for several silicone compounds commonly evaluated as replacements for D_5. 0.65 cst fluid (INCI: disiloxane) and 1 cst fluid (INCI: trisiloxane) are volatile if one looks for all of evaporation of all the material in 24 hours. D_4, D_5 and 2 cst fluids are not volatile. However, it is also clear that D_4 >>D_5 > 2 cst. The problem with 0.65 cst silicone fluid is flammability. The data is presented graphically in Graph 2.



Graph 2.

Since the cosmetic industry has accepted D_5 as a replacement for D_4 and it is clearly is much less volatile at temperatures that the consumer is likely to encounter, the dry feel must be caused by other factors.

STRUCTURES AND PROPERTIES

Silicone nomenclature. Linear compounds

For compounds that have only methyl groups, terminal groups are referred to as M units, internal groups are D units. The structure is given in Figure 1.

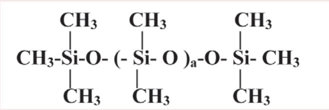


Figure 1. Linear silicone.

Cyclic siloxanes	Linear siloxanes
D3: hexamethylcyclotrisiloxane	MM: hexamethyldisiloxane
D4: octamethylcyclotetrasiloxane	MDM: octamethyltrisiloxane
D5: decamethylcyclopentasiloxane	MD2M: decamethyltetrasiloxane

Table 3. Description of silicones.

MM: hexamethyldisiloxane - The average value of a is 0.
MDM: octamethyltrisiloxane - The average value of a is 1
MD2M: decamethyltetrasiloxane - The average value of a is 2

Cyclic silicone compounds

Cyclic compounds are named by the number of Si atoms in the ring. The structure of D_5 is shown in Figure 2.

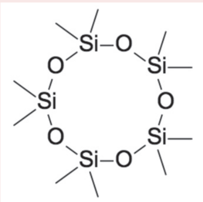
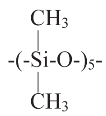


Figure 2. Structure of D5.

Material	Bp(°C)	MP(°C)	CAS	EINECS	Hazard
D4	175	17.5	556-67-2	209-136-7	Combustible
D5	210	-38	69430-24-6	209-136-7	Combustible
MM	153	12	107-46-0	203-492-7	Flammable
MDM	194	-80	107-51-7	203-497-4	Combustible
MD2M	112	-70	141-63-9	205-492-	Combustible

Table 4. Properties of silicones.

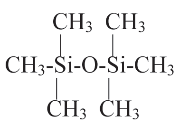
Name: Decamethylcyclopentasiloxane (INCI: Cyclopentasiloxane)



CAS 69430-24-6
Flash Point: 164°F
Flammability: Combustible

Table 7. D5.

Name: Hexamethyl disiloxane (INCI: Disiloxane)

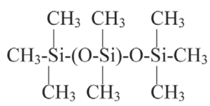


CAS#: 107-46-0

Flammability of the Product: Flammable.
Flash Point: 30.2°F
Flammable Limits: LOWER: 8% UPPER: 10.3%

Table 5. 0.65 cst Silicone Fluid (MM).

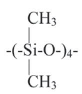
Name: Octamethyltrisiloxane (INCI: Trisiloxane)



CAS 107-51-7
Flash Point: 86 °F
Flammable Liquid

Table 8. 1 cst Silicone Fluid.

Name: Octamethylcyclotetrasiloxane (INCI: Cyclotetrasiloxane)

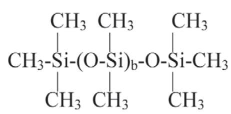


CAS: 556-67-2

CAUTION! Adverse liver and reproductive effects reported in animals.
Combustible liquid and vapor.
FLASH POINT: 138 °F
FLAMMABLE LIMITS IN AIR - LOWER (%): 0.4 %(V).
FLAMMABLE LIMITS IN AIR - UPPER (%): 11.7 %(V).

Table 6. D4.

Name: Decamethyltetrasiloxane



CAS 141-63-9
Flash Point: 188.6 °F
Combustible Liquid

Table 9. 2 cst Silicone Fluid.

SURFACE TENSION

One of the key properties that make silicone interesting in personal care products is its ability to lower surface tension. Fatty compounds have a surface tension of about 30 dynes/cm^2. Silicone compounds have a surface tension of about 20 dynes/cm^2. This is because the fatty compounds have primarily methylene groups(-CH_2-) at the interface, while silicones have methyl groups (-CH_3). Figure 2 shows the many methyl groups present on a silicone polymer. In fact, the compounds shown above all have surface tension values between 22 and 25 dynes/cm^2.

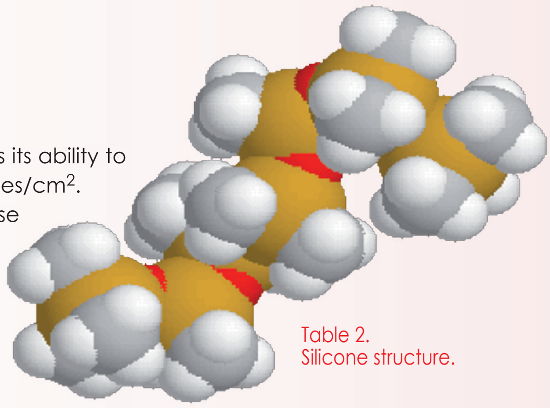
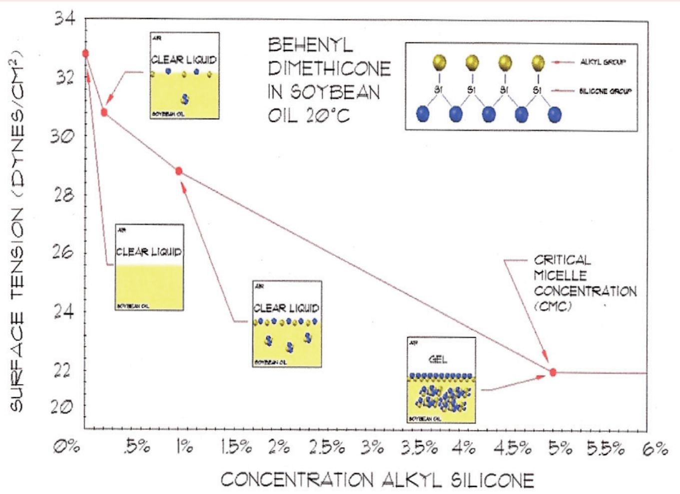


Table 2.
Silicone structure.

AMPHIPHILIC COMPOUNDS

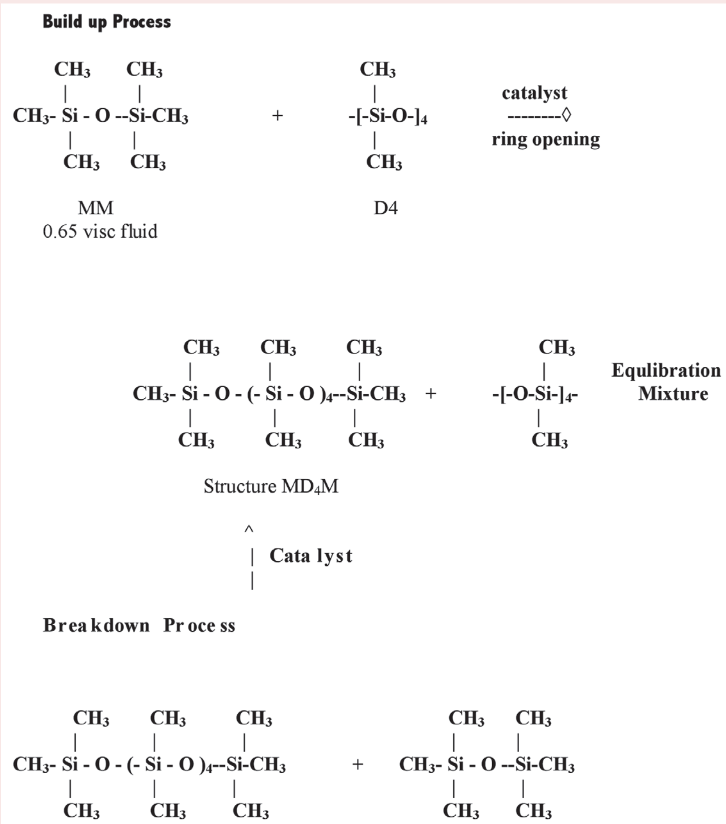


Graph 1. Behenyl dimethicone in soybean oil.

Silicone compounds that contain alkyl groups are amphiphilic, that is, they possess groups on the same molecule that would be insoluble in each other if mixed in pure form. Despite the fact that alkyl silicones are soluble (clear) in oils, they are surface active. Alkyl silicones when added to oils including triglycerides even at low concentrations, lower surface tension. This lower surface tension together with low viscosity, results in a dry skin feel because of efficient spreading. Graph 1 shows the effect of adding a C_{22} alkyl silicone to soybean oil. As the concentration of alkyl silicone is increased, the oil forms a gel.

The dry effect achieved on the skin by the efficient reduction of surface tension of a natural oil using low concentrations of alkyl silicone is a patent pending, valuable formulation tool for the formulator. Not only has the approach of replacing D5 with combination of natural oils and a small amount of alkyl silicone been used to replace D_5, the replacement is more green than D_5, (due to the fact that natural oils are present) , not flammable, effective in many formulations, and is cost effective because the majority of the material used is a relatively inexpensive natural oil.

Silicone equilibration



Scheme 1. Equilibration reaction scheme.

Silicone fluids are most often made by the equilibration of D_4 and MM. The equilibration refers to a catalytic polymerization process that works by a combination of ring-opening and condensation of siloxane bonds. The products of the reaction always include raw materials that are reacted. The excess raw materials can be stripped off in a subsequent step after catalyst is removed. The reaction is has been shown to be an equilibrium that can be established with acid, base or other catalyst (1). The reaction pathways are shown in Table 3. Silicone fluids are stripped of residual D_4 before sale, to low non-zero percent replacements for D_4 or D_5. concentrations. However, the fact that the reaction is reversible means that in formulation it does not matter how well the fluid is stripped, there is always a possibility for D_4 to be formed if acid, base or other catalysts are present. This observation should make the formulator cautious when using low molecular weight silicone polymers as Dimethicone compounds are often made using D_4 as a reactant. They have two methyl groups on each Si, as shown in Figure 4. Methicone compounds are not made using D_4 as a reactant. They are made by hydrosilylation an Methicone compounds conform to the structure in Figure 5 and have only one methyl group on each

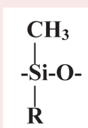


Figure 4. Dimethicone unit.

repeating siloxane unit. Our patent pending approach to replacing D_5 is achieved using a silicone that is a methicone not a dimethicone. The mechanism of action is similar to what was illustrated in Graph 1: the silicone lowers the surface tension of natural oils at low concentrations making the blend have similar properties to D_5. Ethyl methicone (Silwax D-02) conforms to the generic structure shown in Figure 6.

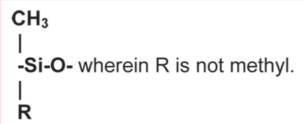


Figure 5. Dimethicone unit.

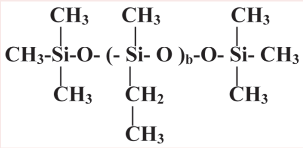


Figure 6. Ethyl methicone.

Since it is a methicone, not a dimethicone, it is not made using D_4. So it cannot re-equilibrate into D_4 regardless of the formulation. Additionally, ethyl methicone chosen for low viscosity, spreadability and low surface tension in the organic chosen, have the following properties making them of interest when used in combination with esters or triglycerides as D_5 replacements:

- Low surface Tension.
- Low concentration needed in oils to make silicone like (siliphilic).
- Does not gel oil.
- Not flammable.
- Can be used alone or in properly selected ester.
- Effective at less than 5 percent in many oils.
- Cost effective

Antiperspirant application

Both formulations were found to be similar to the control in terms of cosmetic aesthetics. D_5 has also been replaced in several other formulations shown on the right.

Antiperspirant w/D5 Replacement

Formulation FA800

Phase	Ingredient	INCI Name	A %w/w	B %w/w	C %w/w
Part A	Reach AZP-908 (Summit Research)	Aluminum/Zirconium Tetrachlorohydrex-GLY	24.00	24.00	24.00
	Silsurf DMC-AP (Siltech)	PEG/PPG 18/6 Dimethicone	2.50	2.50	2.50
Part B	DC-245 (Dow Corning)	Cyclopentasiloxane	30.00		
	Silwax D02 (Siltech)	Ethyl Methicone			30.00
	Silwax D02 (Siltech)	Ethyl Methicone			0.90
	Soybean Oil	Glycine Soja (Soybean) Oil			29.10
Part C	Fancol IH-CG (Fanning)	Isohexadecane	9.00	9.00	9.00
	Probutyl 14 (Croda)	PPG-14 Butyl Ether	9.00	9.00	9.00
	Castorwax NF (Vertellus)	Hydrogenated Castor Oil	2.50	2.50	2.50
	Protomate 400-DS (Protameen)	PEG-8 Distearate	1.00	1.00	1.00
	Crodacol S-95 NF (Croda)	Stearyl Alcohol	18.00	18.00	18.00
Part D	270764 Talc USP 300 BC 127 (Brenntag)	Talc	3.00	3.00	3.00
	Cab-O-Sil M-5 (Cabot)	Silica	0.50	0.50	0.50
Part E	Fragrance Blue Musk (Lebermuth)	Fragrance (Parfum)	0.50	0.50	0.50
			100.00	100.00	100.00

Procedure:

1. In a side vessel, combine Phase A ingredients. Impeller mix to uniformity.
2. In main vessel, heat Phase B ingredients to 70°C under agitation. Continue mixing and add Phase A. Bring to 75°C.
3. Combine Phase C in side vessel, heat to 85°C under impeller agitation and mix to uniformity.
4. Add Phase C to AB under homogenization. Maintain batch at 80°C.
5. Pre-combine Phase D. Add to batch under homogenization. Begin cooling.
6. Add Phase E at 70°C under homogenization. Continue cooling.
7. Pour batch into sticks at 65°C.
8. Heat-treat surfaces.

REFERENCES AND NOTES

1. A.J. O'Lenick et al, *Cosmetics and Toiletries*, **119(5)**, pp. 89-98 (2003).