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Achieving Emolliency and Sensory Effects By Sophisticated Cascading of Volatile Silicone Oligomers

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Introduction

The use of volatile ingredients, particularly in skin care products can provide significant benefit to consumers of these products. In this article we touch on the regulatory and health information about volatile cosmetic components, compare volatile silicones to volatile organics and illustrate the use of volatile silicone materials in skin-care with a few example formulations.

A Complicated Choice

The use and application of volatile silicones have long been a mainstay of numerous cosmetic and personal care products. In particular, their use in fragrances, antiperspirants and sunscreens, as well as in many other categories has made them a critical component for which there have not been other suitable substitutes.

In recent times, however, the low molecular weight-, cyclic silicone, known as D4, has come under scrutiny and questioned as to its safety. This question has led the industry to investigate and develop suitable alternatives which provide the unusual combination of physical and chemical properties of this material. The purpose of this paper is to offer alternatives to formulators for the responsible, foreseeable use of needed, alternative, volatile ingredients that provide essential properties in their products. We believe the "final" health issue assessment of the low molecular weight silicones is not yet agreed upon, in spite of the many different studies, regulations and directives that been published. To this point, this article will not be discussing these studies, or drawing conclusions about them. Rather, our purpose here is to simply address the emerging needs of the industry and propose alternatives if they become necessary.

Some Background on the Issues

In view of the very nature of their volatility, these types of volatile, cyclic, low molecular weight organosilicones have always endured significant scrutiny for their potential health and environmental effects.

In 2008 Health Canada expressed concern over studies showing possible negative health consequences of D4 and its potential for accumulation in the environment [1] Subsequent intensive scientific efforts have helped reduce these concerns. As a result the cosmetic review boards of both the North America and European Union have come to a common conclusion:

- The CIR (U.S. Cosmetics Ingredients Review) board stated that all of the cyclosiloxanes as currently used are acceptable in cosmetic formulations [2].
- The European Union Directorate General for Health and Consumer Scientific Committee on Consumer Safety (SCCS) came to essentially the same conclusion and "The SCCS is of the opinion that cyclomethicone (D4, D5) does not pose a risk for human health when used in cosmetic products" [3].

Due to the nature of the use and application of products in the cosmetic industry, formulators responsibly err on the side of caution when choosing ingredients for their products. For example, this has led to a trend away from the use of cyclotetrasiloxane D4, with cyclopentasiloxane D5, being used in its place based on the premise that the higher molecular weight silicone cyclic would be more acceptable. As can be seen in Chart 1, however, the evaporation rates of D5 are considerably lower. This poses a problem when a faster drying sunscreen is needed for instance. Formulators are now turning to the use of low molecular weight siloxanes alone or in combinations with cyclosiloxanes to enhance and augment the performance characteristics of their products.

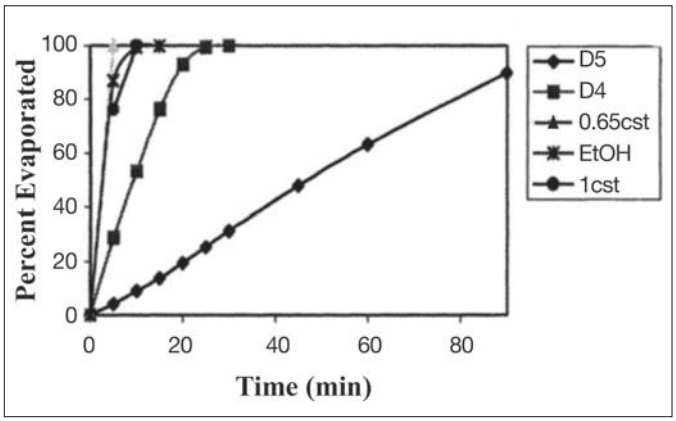

Chart 1 [4]

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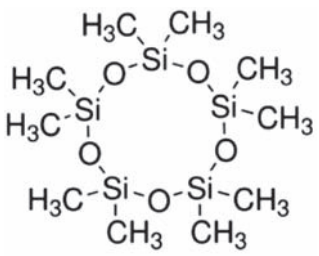
Through the use of this range of product volatilities, performance relative to increasing volatility can be enhanced. By means of the use of two or more volatile materials with different evaporation rates one can create a continuously changing viscosity profile of the product during its application. This is especially important for skin care products such as sunscreens and moisturizers. These products can be applied to the skin with low viscosity and low friction thereby providing a thin, uniform protective layer to the skin. As the volatile material evaporates the other properties of the formulation take-over to provide the intended benefits.

The Critical Function: Uniform Film Formation with Good Sensory Properties

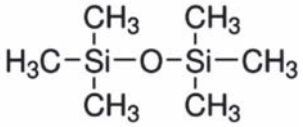
The volatile ingredients form an essential component of many products, especially in skincare and sun protection lotions. They lower surface tension, increase spreading tendency and act as a carrier for other ingredients which would otherwise be too viscous, tacky or insoluble in the formulation. Volatile siloxanes can impart the smooth spreading and ease of application in lotions and creams and can provide a smooth transition in spreadability without leaving an undesirable greasy or fatty feel. A combination of volatile siloxanes can provide a sequential evaporation effect. As each oligomer leaves, the sensation on the skin changes which can provide a luxurious feel. The use of three or more emollients with different spreading coefficients has been described as "cascading emolliency" [5]. A similar concept can be applied by utilizing the wide range of evaporation rates available in the volatile siloxanes family. By carefully selecting the concentration and ratio between the volatile ingredients the formulator can adjust the sensory profile over time to enhance the application and ultimate performance of the product. Rather than viewing the elimination of D4 as a problem it can be considered an opportunity to explore new ways to enhance the consumer experience. The clever formulator will be able to create unique and differentiated products which will provide real value to the customer.

The high spreading coefficient and resulting uniform film application can help enhance efficacy and the pleasant application process encourages usage by the consumer.

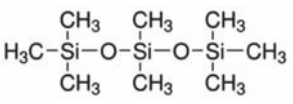
The formulators tools



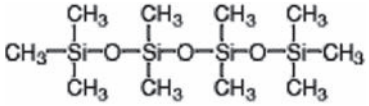
Cyclopentasiloxane



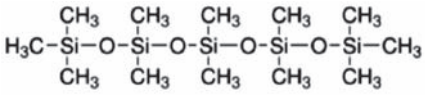
Hexamethyldisiloxane



Octamethyltrisiloxane



Decamethyltetrasiloxane



Dodecamethylpentasiloxane

Compound	MW (g/mole)	Vapor pressure (mmHg, 25°C)	Solubility (mg/L, 25°C)	Density (g/cm³, 20°C)	Viscosity (cst., 20°C)	Bp (°K)
D3	222	8.6	1.56	0.856	0.5	408.2
D4	297	0.99	0.56	0.953	2.4	448.7
D5	371	0.174	0.017	0.995	4.2	484.2
D6	445	0.03	0.005	0.966	7.7	518.1
MM	162	42.2	0.93	0.765	0.65	373.6
MDM	236	3.88	0.034	0.820	0.9	425.7
MD2M	384	.06	7×10^{-5}	0.867	1.4	503.1
MD3M	310	.43	0.006	0.854	1.7	467.1

Table 1: Properties of volatile siloxanes

Other Considerations

Fluid	Hvap (kJ/kg)
Water	2257
Isopropyl	779
Ethanol	846
D4	175
D5	163
SF1	184
SF2	150
SF 0.65	192

Table 2: Heat of vaporization [6]

Volatile materials such as alcohols and hydrocarbons can provide a cooling effect which is beneficial in some applications. Volatile silicones can achieve rapid evaporation while avoiding this potentially undesirable, chilling or cooling effect. The heat of vaporization in Table 2 is directly related to the amount of energy which is extracted from the surface of the skin which is perceived as cooling as the substance is volatilized. As the volatile siloxanes evaporate they remove very little heat from the skin, this result, combined with the light friction of a manual application process can leave the skin feeling warm and soothed. Alternatively in a spray application, the low heat of vaporization makes the application process much less unpleasant especially when applied to sun warmed skin.

Potential concerns

Flash point	Degrees Celsius
Acetone	-20
Ethanol	13
IPA	12
SF 0.65	-1
SF 1	30
SF 1.5	57
SF 2	87

Table 3: Selected flashpoints

The flash point of volatile silicones is considerably higher than organics with a similar evaporation rate. This makes them inherently safer, especially when used in high concentrations in a formulation. For example, ethanol has an evaporation rate approximately the same as Andisil SF 1 but ethanol has a flashpoint of 13°C versus the siloxane flash point of 30°C. Table 3 compares the flashpoints of selected organic and silicone-based volatile ingredients.

Other volatile materials are offered to the industry and welcomed by the formulator as a way to increase the number of tools available for formulation [7]. The versatility of the family of silicone coupled with their unique combination of sensory properties continues to make them valuable components of skincare formulations [8].

Conclusions

As raw material suppliers take up the challenge of meeting the expectations of today's formulators new materials and concepts are constantly under evaluation. Responsible suppliers strive to provide alternatives suitable for the most conscientious formulator. Formulators work to meet their responsibility to differentiate their products and satisfy their customers.

Cross Reference to the different nomenclatures for siloxanes

INCI	IUPAC	Trade	Short
Cyclotetrasiloxane	Octamethylcyclotetrasiloxane	CM 40, D4	D4
Cyclopentasiloxane	Decamethylcyclopentasiloxane	CM 50, D5	D5
Disiloxane	Hexamethyldisiloxane	DM 0.65; SF 0.65	MM
Trisiloxane	Octamethyltrisiloxane	DM 1; SF 1	MDM
Dimethicone	Decamethyltetrasiloxane	DM 1.5; SF 1.5	MD2M
Dimethicone	Dodecamethylpentasiloxane	DM 2; SF 2	MD3M

Cross-reference table between BRB and ABSS product numbers used in example formulations.

BRB	ABSS	INCI
BRB DM 0.65	Andisil SF0.65	Disiloxane
BRB DM 5	Andisil SF 5	Dimethicone
BRB DM 10	Andisil SF 10	Dimethicone
BRB CM 50	Andisil D5	Cyclopentasiloxane
BRB CM56-S	Andisil D56	Cyclopentasiloxane (and) Cyclohexasiloxane
BRB 6373	Contact	Cyclopentasiloxane (and) PEG/ PPG-18/ 18 Dimethicone
BRB SG 506	Contact	Dimethicone (and) Dimethicone/Vinyl Dimethicone Crosspolymer
BRB TMS-30D	Contact	Dimethicone (and) Trimethylsiloxysilicate
BRB TMS-50C	Contact	Cyclopentasiloxane (and) Trimethylsiloxysilicate

Suggested formulations

Clear Sun Mist

Formulation S140721-13

Skin Care Issue date: August 6th, 2014

Description

Clear Sun Mist is an anhydrous and alcohol free spray on sunscreen which provides broad spectrum protection against UV ray.

Benefits

Clear Sun Mist delivers long-lasting broad spectrum UV protection with a unique, luxurious crystal clear mist. It also infused with vitamin E that enhances the benefits of sunscreen to help keep skin healthy and youthful-looking. The continuous spray mist instantly disappears into skin, leaving skin feeling fresh with no greasy residue.

Featuring

BRB CM 50: Provide light and dry skin feel.
BRB TMS-50C: Act as film former. Give wash off resistance effect.
BRB 0.65: Act as high volatile carrier and aid in spreadability.

Formulation

No	Ingredients	INCI	Suppliers	Dosage (%)
A1	Parsol MCX	Ethylhexyl Methoxycinnamate	DSM	10.00
A2	Parsol 1789	Butyl Methoxydibenzoylmethane	DSM	4.00
A3	Parsol 340	Octocrylene	DSM	6.50
A4	Crodamol GTCC	Caprylic/Capric Triglyceride	Croda	10.00
A5	Fancol IH-CG	Isohexadecane	Elementis	30.00
A6	Vitamin E Acetate	Tocopheryl Acetate	DSM	0.50
A7	BRB CM 50	Cyclopentasiloxane	BRB	8.00
A8	BRB TMS-50C	Cyclopentasiloxane (and) Trimethylsiloxysilicate	BRB	2.00
A9	BRB DM 0.65	Disiloxane	BRB	29.00

* Estimated SPF 25 (calculated by sunscreen simulator)

Procedure

1) Add phase A one by one into bulk. Mix well after each addition.

Typical properties / Additional information

Parameter	Unit	Value
Appearance		Clear light yellow liquid
Viscosity at 25°C	cPs	N/A
pH		N/A
Sensory attributes		Light and dry

Please note that this formulation has passed 2 months stability at 45°C.

Magic Water Bead Cream

Skin Care Issue date: Nov 6th, 2013

Description

Magic Water Bead Cream is a water-in-silicone emulsion which provides hydrating to your skin.

Benefits

By rubbing Magic Water Bead Cream onto your skin, it forms water drop on your skin.

Featuring

BRB 6373: Act as water-in-silicone emulsifier.
BRB CM 56-S: Provide light and dry skin feel.
BRB SG 506: Provide excellent powdery and smooth skin feel. Also help to build up viscosity.
BRB DM 10: Aid in spreadability. Provide emolliency to skin.

Formulation

No	Ingredients	INCI	Suppliers	Dosage (%)
A1	DI water	Aqua		78.40
A2	Sodium Chloride	Sodium Chloride	Merck	1.00
A3	Glycerin	Glycerin	Local supplier	5.00
B1	BRB 6373	Cyclopentasiloxane (and) PEG/ PPG-18/ 18 Dimethicone	BRB	5.50
B2	BRB CM56-S	Cyclopentasiloxane (and) Cyclohexasiloxane	BRB	5.00
B3	BRB SG 506	Dimethicone (and) Dimethicone/ Vinyl Dimethicone Crosspolymer	BRB	1.50
B4	BRB DM 10	Dimethicone	BRB	3.00
C1	Phenochem	Methylparaben (and) Ethylparaben (and) Propylparaben (and) Butylparaben (and) Phenoxyethanol	Sharon Laboratories	0.50

Procedure

1) Mix A1-A3 well.
2) Mix B1-B4 separately.
3) Add phase A slowly into phase B while stirring
4) Add C1 into bulk and mix well

Typical properties / Additional information

Parameter	Unit	Value
Appearance		White cream
Viscosity at 25°C (spindle 5, speed 10)	cPs	32,000
pH		N/A
Sensory attributes		Light, soft and hydrate

Please note that this formulation has passed 3 months stability at 45°C.

Radiant CC Cream

Formulation C130923-04

Color Cosmetics

Issue date: July 6th, 2014

Description

Radiant CC Cream is light a water-in-silicone emulsion which provides colour correcting properties onto your skin.

Benefits

Radiant CC Cream provides skin a glowing, healthier look and even skin tone. Suitable for all day long wear as it contains BRB TMS-30D which form a film onto skin upon drying. This film helps to reduce water loss.

Featuring

BRB CM 50: Impart soft and dry skin feel.
BRB DM 5: Aid in spreadability. Provide emolliency to skin.
BRB 6373: Act as water-in-silicone emulsifier.
BRB TMS-30D: Act as film former. Give long lasting effect.
BRB SG 506: Provide excellent powdery and smooth skin feel. Also help to build up viscosity.

Formulation

No	Ingredients	INCI	Suppliers	Dosage (%)
A1	FAS50EYSI-E	Iron Oxides (C.I. 77492) (And) Cyclopentasiloxane (And) PEG/PPG-18/18 Dimethicone (And) Triethoxycaprylylsilane (And) Tocopheryl Acetate	Kobo	0.18
A2	FAS55ERSI-E	Iron Oxides (C.I. 77491) (And) Cyclopentasiloxane (And) PEG/PPG-18/18 Dimethicone (And) Triethoxycaprylylsilane (And) Tocopheryl Acetate	Kobo	0.23
A3	FAS60EBSI-E	Iron Oxides (C.I. 77499) (And) Cyclopentasiloxane (And) PEG/PPG-18/18 Dimethicone (And) Triethoxycaprylylsilane (And) Tocopheryl Acetate	Kobo	0.04
A4	BRB CM 50	Cyclopentasiloxane	BRB	4.00
A5	BRB DM 5	Dimethicone	BRB	8.00
A6	Parsol MCX	Ethylhexyl Methoxycinnamte	DSM	5.00
A7	TiO2 CR 50SC34	Titanium Dioxide	Yamaguchi	6.00
A8	Talc	Talc	Yamaguchi	2.00
A9	Mica (YSS-010PS31)	Mica	Yamaguchi	2.50
A10	BRB 6373	Cyclopentasiloxane (and) PEG/ PPG 18/18 Dimethicone	BRB	10.00
A11	BRB TMS-30D	Dimethicone (and) Trimethylsiloxysilicate	BRB	2.00
A12	Bentone Gel VS-5	Cyclopentasiloxane (and) Disteardimonium Hectorite (and) Propylene Carbonate	Elementis	3.00
A13	BRB SG 506	Dimethicone (and) Dimethicone/ Vinyl Dimethicone Crosspolymer	BRB	7.00
B1	DI Water	Aqua		46.25
B2	Glycerin	Glycerin	Local supplier	2.00
B3	Sodium Chloride	Sodium Chloride	Merck	1.00
C1	Phenochem	Methylparaben (and) Ethylparaben (and) Propylparaben (and) Butylparaben (and) Phenoxyethanol	Sharon Laboratories	0.80

Procedure

1) Add phase A1-A11 into bulk. Homogenize well. Make sure all powder material is well dispersed.
2) Then, add in A12 & A13. Homogenize well.
3) Prepare phase B in a separate beaker.
4) Slowly add step 3 into step 2. Viscosity will increase gradually.
5) Then, add in C1. Mix well

Typical properties / Additional information

Parameter	Unit	Value
Appearance		Beidge cream
Viscosity at 25°C (spindle 4, speed 10)	cPs	14,000
pH		N/A
Sensory attributes		Light, good spreadability

Please note that this formulation has passed 3 months stability at 45°C.

Perfectly Clear Gel Moisturizer

Skin Care Issue date: Nov 6th, 2013

Description

Perfectly Clear Gel Moisturizer is a clear water-in-silicone emulsion which provides hydrating to your skin.

Benefits

Perfectly Clear Gel Moisturizer makes skin soft and supple after application.

Featuring

BRB 6373:	Act as water-in-silicone emulsifier.
BRB CM 56-S:	Provide light and dry skin feel.
BRB SG 506:	Provide excellent powdery and smooth skin feel. Also help to build up viscosity.
BRB DM 10:	Aid in spreadability. Provide emolliency to skin.

Formulation

No	Ingredients	INCI	Suppliers	Dosage (%)
A1	BRB 6373	Cyclopentasiloxane (and) PEG/ PPG-18/ 18 Dimethicone	BRB	5.50
A2	BRB CM56-S	Cyclopentasiloxane (and) Cyclohexasiloxane	BRB	5.00
A3	BRB SG 506	Dimethicone (and) Dimethicone/ Vinyl Dimethicone Crosspolymer	BRB	1.50
A4	BRB DM 10	Dimethicone	BRB	3.00
B1	DI water	Aqua		35.22
B2	Sodium Chloride	Sodium Chloride	Merck	1.00
B3	Propylene Glycol	Propylene Glycol	Local supplier	48.63
C1	Neolone 950	Methylisothiazonlinone	Dow Chemical	0.10
C2	Protectol BN	Bronopol	BASF	0.05

Procedure

1) Mix well A1-A4.
2) Mix B1-B3 separately.
3) Add phase B slowly into phase A while stirring.
4) Add C1-C2 into bulk and mix well

Typical properties / Additional information

Parameter	Unit	Value
Appearance		Clear gel
Viscosity at 25°C (spindle LV4, speed 6)	cPs	80,000
pH		N/A
Sensory attributes		Light & non-tacky

Please note that this formulation has passed 3 months stability at 45°C.

The Product Safety Data Sheets for **BRB** products should be obtained from your **BRB** office prior to use. ATTENTION: Before handling, read product information, Product Safety Data Sheets and container labels for safe use, and any physical and/or health hazard information.

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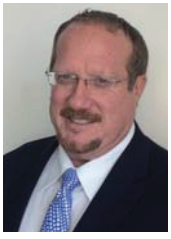

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