Consumer Solutions

The Beauty of Silicone in Skin Care Applications

Isabelle Van Reeth

Pharmacist (Free University or Brussels) and Skin Care Global Technology leader

Introduction

Silicones are a very broad chemical family and not just a single material. Silicone is a generic term for Si-based materials. The most well-known structure is a polymer that contains silicon and oxygen atoms. The main chain is Si-O with attached methyl groups. The structure is shown in Figure 1.

The variations on the structure to the right are almost endless, making silicone chemistry almost as broad as carbon chemistry.

The following modifications can be made: variation of molecular weight and addition of organic functionalities (polyether, alkyl, amino, etc.), resulting in a range of materials, from volatile fluids to gums, waxes and elastomers. The INCI dictionary documents more than 500 silicone materials derivatives, illustrating the diversity of this chemical family. Table 1 gives an overview of the most common INCI names for different silicones materials. These polymers can be oil- or water-soluble.

Figure 1: Polydimethysiloxane (Dimethicone) structure

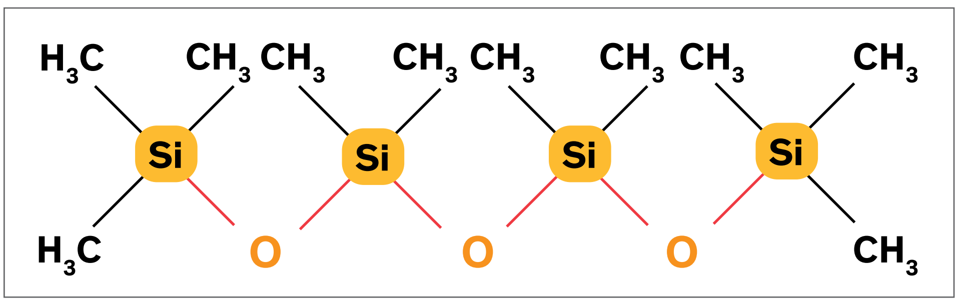


Table 1: Most common INCI names for silicone materials

Types of Silicones	Description	INCI Names
Volatile Silicones	Low molecular weight cyclic and linear siloxanes	Cyclomethicone, Cyclopentasiloxane, Cyclohexasiloxane, Trisiloxane, Dimethicone
Silicone Fluids	Linear siloxanes with or without functionalities	Dimethicone, Dimethicone copolyol, Aminodimethicone
Silicone Gums	High molecular weight fluids siloxanes	Dimethicone, Dimethiconol
Silicone Gels	Slightly X-linked siloxane network	Dimethicone crosspolymer, Vinyl dimethicone crosspolymer
Silicone Resins	Three dimensional siloxane network	Trimethysiloxysilicate, Polymethylsilsesquioxane, Polypropylsilsesquioxane

The Si-O bond is very stable, not easily oxidized and therefore inert, an advantage when in contact with biological tissues. The bond length of Si-O is 0.163 nm and the angle is 130°, larger than the bond length of C-C (0.154 nm) and angle (112°), allowing oxygen and water vapor to permeate and therefore not interact with the skin function regulating water vapor and O_2 exchange.[1] The permeability of silicone polymers has been well documented in-vitro and in-vivo.[2] To decrease the permeability of silicones, the addition of organic functionalities such as alkyls groups is required. By varying the type and the amount of alkyls groups on the Si-O backbone, semi-permeable to occlusive materials can be obtained.[3] Indirectly related to permeability, several silicones including dimethicone, stearoxy simethicone, simethicone copolyols and cyclomethicone have been demonstrated to be noncomedogenic.[4,5] Their low surface tension allows silicones to spread very well while conferring hydrophobicity. As a consequence of these physical and chemical properties, polydimethylsiloxanes (dimethicone) from 350 – 12,500 cSt viscosity are listed in the FDA Monograph: "Skin Protectant Drug Products for Over-the Counter Human use; Diaper Rash Products," issued in 1990. The level needed for a protection claim is as low as 1%. As an example for barrier function, Dimethicone is used in foams formulated for the relief of irritation from dermatoses such as atopic and allergic contact and barrier creams designed to prevent skin sensitization to allergens.[6]

History of Silicones in Skin Care

The use of silicones in skin care started as early as 1953, when Revlon commercialized a hand cream called Silicare with the following positioning: "Silicare forms an invisible glove to protect your hands. Its amazing water-repellent power keeps detergent water away."[7]

In the 1960s, the use of volatile silicone dramatically improved the overall quality of antiperspirant products. Silicones eliminate transfer of antiperspirant salts, resulting in reduced staining of clothes, a nonstinging sensation (no alcohol) and good spreadability, allowing good distribution of the active salt and improved aesthetics.[34]

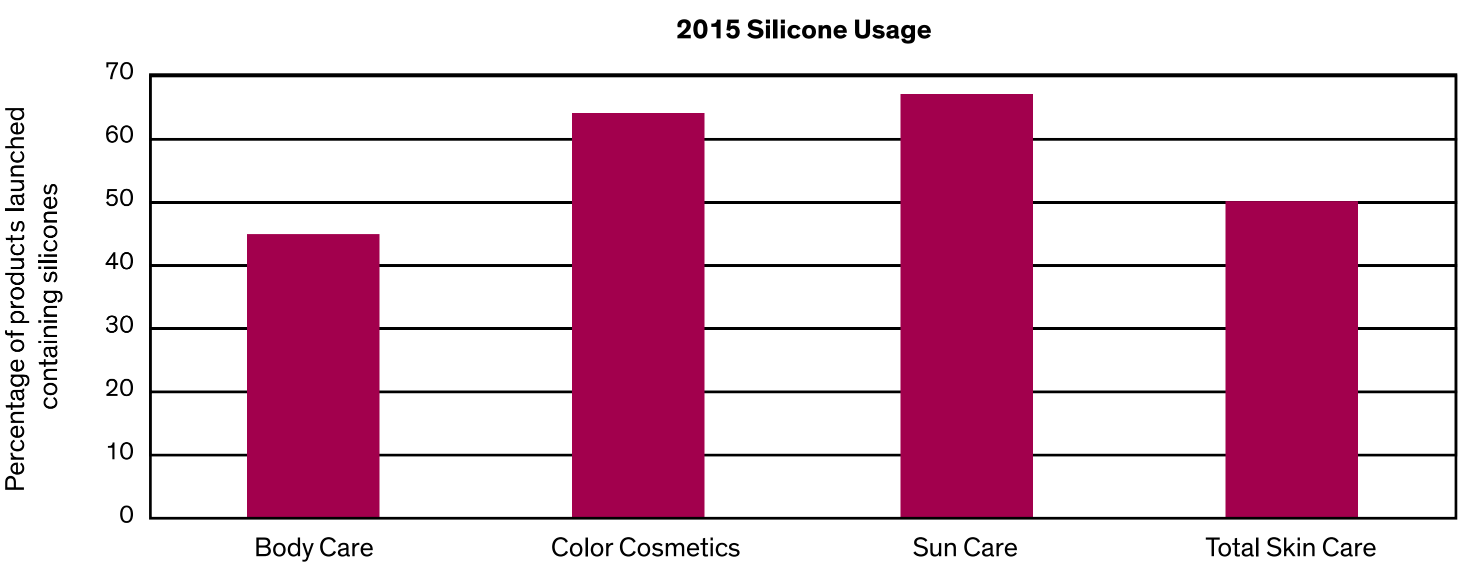
From the 1980s onward, the use of silicone materials expanded to all skin care segments and was recognized as a turning point, allowing an entirely different feel and solubility characteristics, offering new possibilities versus conventional organic materials.[8]

In the mid 1990s, silicone resins combined with volatile silicones were introduced in makeup formulations claiming to last all day. Volatile silicones evaporate, leaving the pure pigments held in place by a film of silicone resin, resulting in color adhesion to lips for 8 to 10 hours. Revlon demonstrated the transfer resistance of its Ultima II formulation using a "Kiss Test." Panelists were instructed to apply the lipstick, wait 5 minutes and then kiss the back of their hand, with the result that most of them reported hardly a trace of color.[9]

At the turn of the 21st century, the introduction of silicone elastomers offered unique replacements and modification of properties for traditional high oil and fatty alcohols systems, which had dominated formulations up until that time. This allowed formulations to deliver exceptional aesthetics while providing additional benefits such as soft focus and line-filling without the oiliness attributed to traditional systems. These high molecular weight cross-linked silicones brought alternative texture and feel dimensions to skin care and color cosmetic products. They created a mattifying effect upon application on the skin, providing a smooth, soft and even skin appearance. Elastomer powders also provide distinctive aesthetic properties that can range from smooth and silky, to powdery with a dry soft finish.[10] In particular, they were key materials in a new type of application, the so called "skin primer." Silicone-based primers were key to achieving flawless skin. The silicone will fill in fine lines and wrinkles and flatten the skin, resulting in a smooth canvas.[11] Silicone penetration in BB creams, a huge market success starting back in 2009, demonstrates the importance of these materials in skin care innovations.

Silicones have been used in skin care products for more than 50 years and still maintain a very high use level today as Figure 2 demonstrates. Silicones are present in more than 50% of new launched skin care products in 2015.[12]

Figure 2: Silicone usage in skin care, sun care and color cosmetics in 2015[12]



Safe Use of Silicones in Skin Care Products

Silicones are among the most extensively studied materials used in consumer and industrial applications today. Dow assesses the safety of every product commercialized for the Personal Care industry. In addition, more than 1,000 studies have been conducted by silicone manufacturers to assess the safety of silicones relative to workers, consumers, the environment and manufacturing processes.[13, 14] Although silicones are not biodegradable, they are degradable either in the soil for nonvolatiles polydimethylsiloxanes or in the air for the volatiles species such as cyclopentasiloxane[15]. Dimethicone and several derivatives such as alkyldimethicone and hydroxyl propyldimethicone are recognized as being safe for use in cosmetic and medical/pharmaceutical applications.[16]

Some silicone elastomers are used in medical devices such as tubing for extracorporeal circulation or pacemaker leads because of their excellent biocompatibility due to their low chemical reactivity, low surface energy and hydrophobicity. Dimethicone, simethicone and silicone elastomers are also used in several pharmaceutical applications such as excipients, controlled release devices, injection needle siliconisation, silicone antifoam, scar care and silicone tubing.[17]

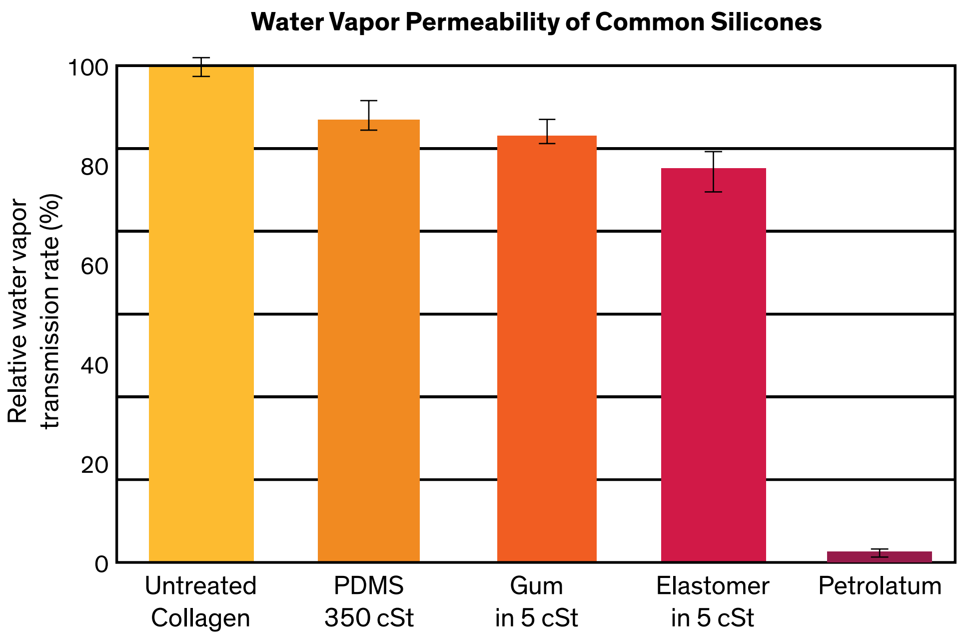
An in-vitro and in-vivo study conducted on cyclopentasiloxane (molecular weight ~ 370 daltons) and dimethicone 350 cSt (molecular weight > 500 daltons) demonstrated that the majority volatilized from the skin in the former case and remained on the surface of the skin for the latter.[18] Silicones are also typically used in antidandruff shampoos as part of scalp care, where they help counteract the negative impact of the antidandruff actives on conditioning.[19] No silicone derivatives are listed in the American Contact Dermatitis Society (ACDS) Core Allergens Series (CAS), or the European Standard (ESS), Extended International Series (EIS) or British Contact Dermatitis Society (BCDS).[20]

One of the 10 recommendations for patients with sensitive skin is to preferably use facial foundations that are powders or creams or, if of the liquid type, are based on silicone derivatives such as cyclomethicone or dimethicone.[21]

Silicone Are Permeable Materials

When applied to the skin, silicones form water vapor permeable films on the surface due to their relatively open and flexible chemical structure.[3] However, misconceptions about silicones still exist. Because of their hydrophobicity, silicones are often compared with hydrocarbons. In order to clarify the question about the occlusivity of silicones, an in-vivo study was performed to show the hydration effects of three common silicone excipients and three water-in-(oil-plus-silicone) systems containing them.[2, 22] In- vitro water vapor permeability, transepidermal water loss (TEWL) and stratum corneum hydration values were compared between the pure silicones, formulations thereof and petrolatum. Petrolatum is known as an occlusive agent with moisturizing properties.[23] For the in-vitro screening study, candidates were coated onto a collagen sheet and fixed on a Payne cup device containing water. The ability of water to evaporate outside of the cup through the coating in controlled temperature and humidity conditions was assessed and converted into water vapor transmission rate (WVTR) values. Figure 3 shows the corresponding results.

Figure 3: In-vitro occlusivity screening results



The in-vivo study assessed the effects of the same three silicones on corneometry and transepidermal water loss (TEWL) performance. In addition to the neat silicones, corresponding formulated systems consisting of each silicone in a water-in-oil emulsion were included. The measurements were performed on 26 young female panelists' forearms. After a baseline measurement and a single application of the product, measurements were performed at three time points: 15 minutes after application, 4 hours after application and after dry wiping.

TEWL results (Figure 4) suggested an overall similar trend across time points, with increased effects after 15 minutes, as one would logically expect. The observed TEWL decreases for the silicone materials were not significantly different from the untreated skin control zone and were significantly lower than those of petrolatum. The petrolatum results were expected and have been described in the scientific literature.[23]

As a conclusion, both in-vitro and in-vivo results confirmed the nonocclusive behavior of the commonly used silicones considered. This was further confirmed by capacitance measurements.[3, 22]

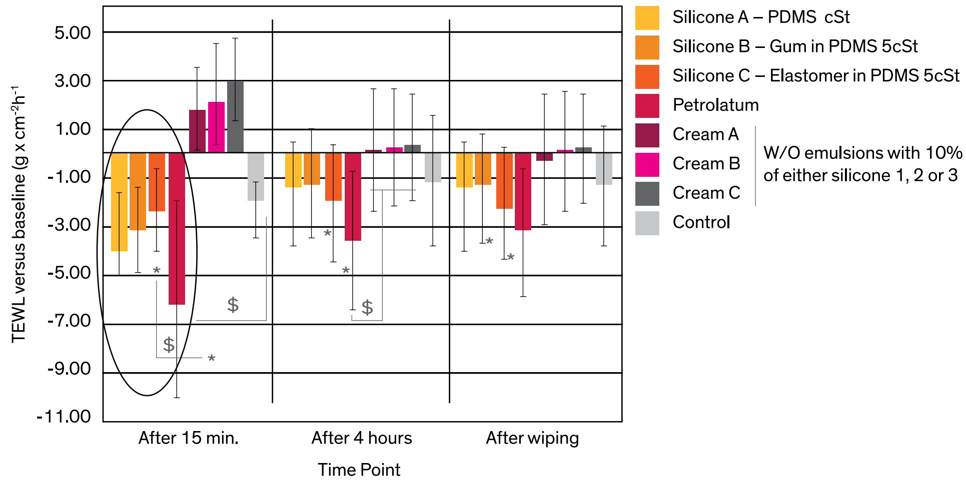
Silicone Benefits in Skin Care Products

Silicones are recognized as multifunctional ingredients in a variety of skin care products. With their unique set of chemical and physical properties, these highly versatile materials can bring a wide array of benefits in skin care products:[24]

- Sensory and texture enhancers
- Emolliency and high spreadability
- Transient to long lasting effect
- Wash off and transfer resistant
- Nonocclusive to semipermeable
- SPF enhancement
- Protection
- Cleansing

The next paragraphs will review in more detail their use, not only as sensory enhancers, but also film formers for long lasting wash off resistance, protection and skin tightening as well as how they can help to increase formulation efficiency via emulsification or as delivery vehicles or even provide optical effects such as soft focus. In short, silicones can play major roles whether in facial care, body care, color cosmetics or sun care.

Figure 4: Transepidermal water-loss results



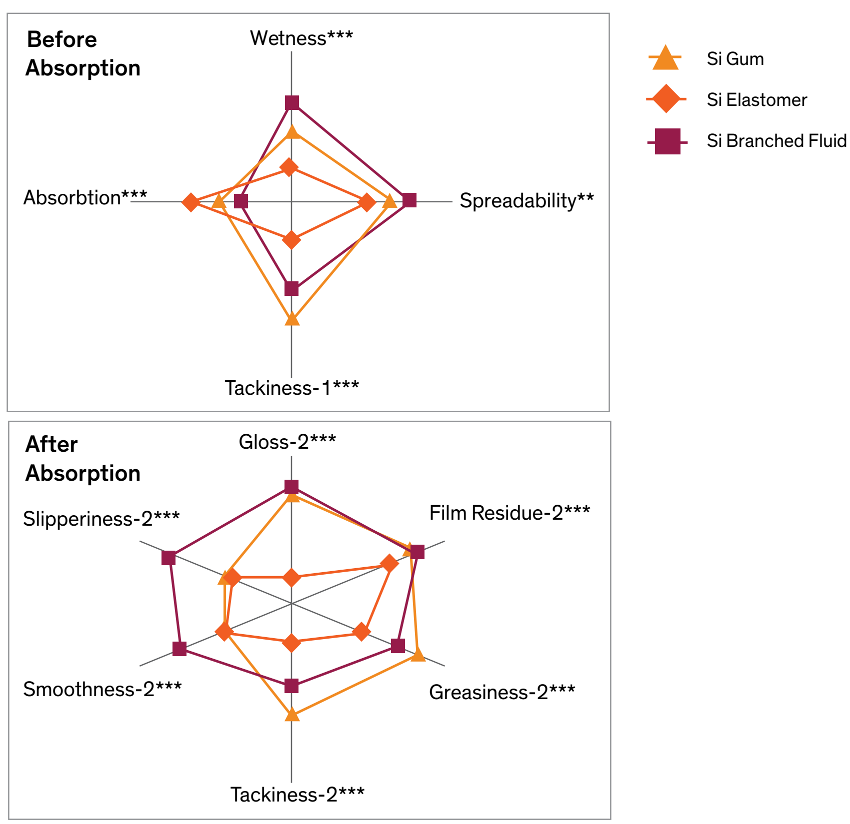
Sensory enhancers

Although skin feel has always been a key aesthetic parameter, consumers increasingly select skin care products on a more complete sensory experience encompassing product texture, appearance and feel. Silicones have been well known for the distinctive skin feel they impart,[8] but their effects are much broader, especially from the high molecular weight species such as silicone gums and silicone elastomers.

Figure 5 illustrates the difference in sensory profile of three high molecular silicones.

Linear silicone gum (Dimethicone or Dimethiconol), branched silicone Polydimethylsiloxane (PDMS) (Dimethicone/Vinyl Dimethicone Crosspolymer) and cross linked PDMS (Dimethicone Crosspolymer), also known as silicone elastomers, were diluted in dimethicone 2cSt and evaluated for their sensory profile before and after absorption.

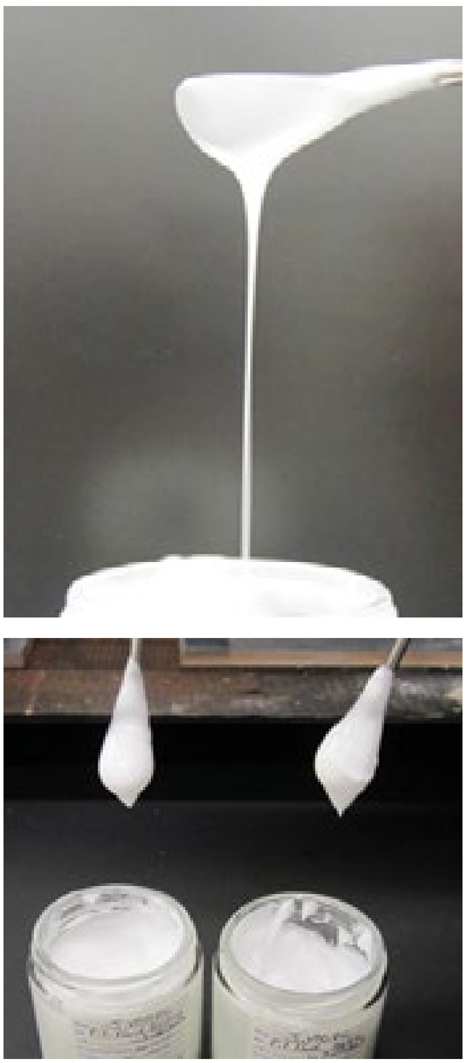
Figure 5: Sensory profiles of different high molecular silicone polymers delivered from dimethicone 2 cSt.



Although the difference between these 3 silicone materials is only in their structure configuration, the resulting sensory profile is very different, and these differences are also observed in both o/w and w/o systems at concentration as low as 5% of the dispersion.

The branched silicone PDMS also impacts the texture of formulations by giving a stringy texture as illustrated in Picture 1.

Picture 1: Stringy texture provided by the branched silicone polymer (top) in comparison with creams with silicone gums and silicone elastomers.



Sensory clues: As explained previously, silicones cannot moisturize the skin as they are water vapor permeable, but they can give the perception to the consumer that the formulation helps to moisturize the skin and this at very low level.

A cream containing 1.2% of a very high molecular weight PDMS delivered under emulsion form was perceived to be more moisturizing by 19 panelists among 22 when compared to the same formulation without the material.

In a similar test, a cream containing 0.6% of the branched silicone polymer was perceived to be more moisturizing by 23 panelists among 28 when compared to the same formulation without the silicone polymer.

By allowing the incorporation of water within its gel structure, a PEG modified elastomer allows the creation of formulations with more wetness and refreshing feel compared to first generation silicone elastomers while keeping the unique smooth powdery feel.[25]

Film formers

Long lasting performance for color cosmetic and wash off resistance in sun care are important needs and are growing today in facial care as well providing benefits such as skin protection against pollution, long lasting moisturization and an anti-aging effect.

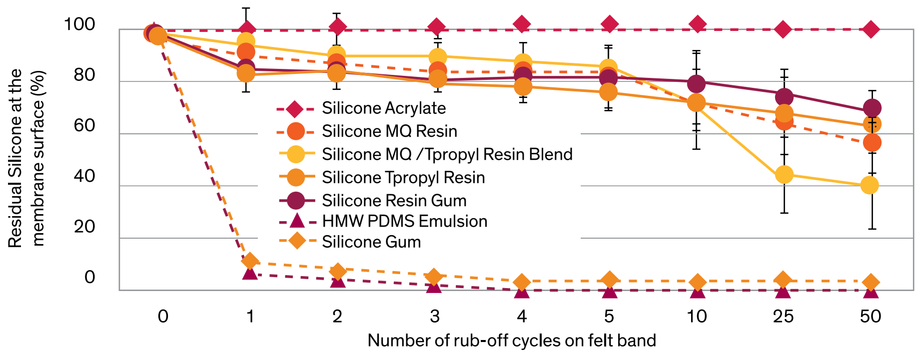
The use of film formers is very high in the color cosmetic segment, with 75% of the new product launches contained a film formers in 2014. Among these film formers, silicone film formers represented around 16%, mainly silicone resins and silicone acrylates.[26]

Silicone film formers are permeable to water vapor but have excellent water repellency and good sebum repellency, more so than organic film formers.

They also have been optimized for improved flexibility, an important parameter for comfort of wear and film integrity. Their resistance to rub off is excellent in comparison with silicone gums as illustrated in Figure 6.[27]

Figure 6: Resistance to rub-off of a film coated on collagen.

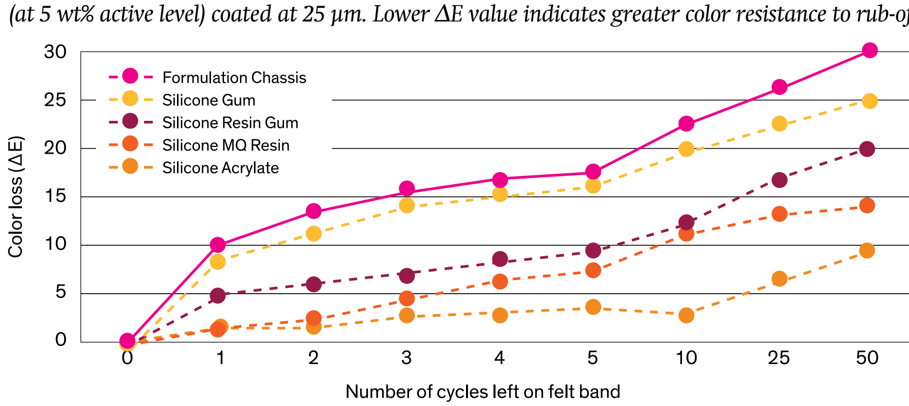
Resistance measured by XRF after friction cycles using washability tester/felt band. Neat film-formers (diluted at 20 wt% active level in a solvent carrier) coated on collagen (50 µm). Higher % value indicates greater resistance to rub-off.



This resistance to rub off has been validated in foundations shown in Figure 7 and lipsticks formulations

Figure 7: Evaluates resistance to rub-off of a foundation coated on a skin-mimicking substrate.

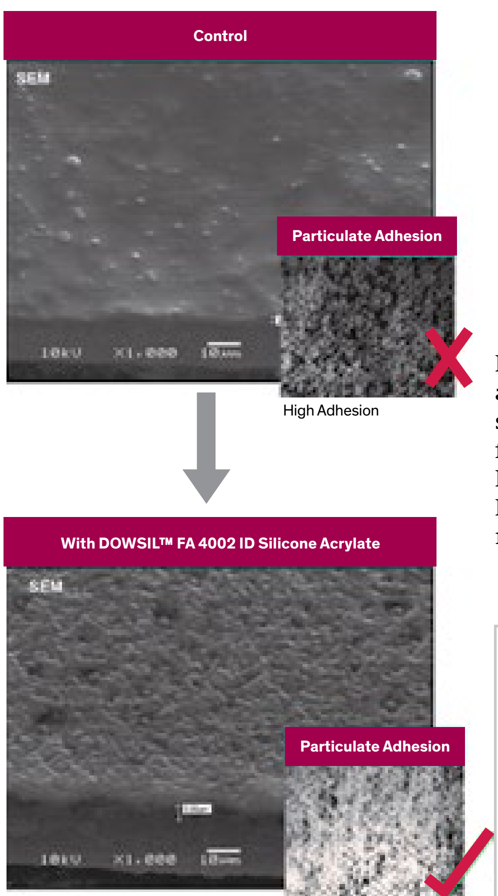
Color resistance is measured by colorimetry after friction cycles on a felt band. Liquid foundations (at 5 wt% active level) coated at 25 µm. Lower ΔE value indicates greater color resistance to rub-off.



Additionally, silicone film formers provide benefits beyond long lasting wear and comfort. By adjusting the silicone acrylates film-former interaction with the rest of the formulation ingredients, it is possible to generate surface micro roughness upon evaporation of the volatile ingredients. Carbon black is used to represent pollution particles. The comparison with the formulation control (no silicone acrylate) together with the SEM picture illustrating the micro roughness can be seen in Figure 8. Effects were observed in a variety of formulations chassis (oil-in-water, water-in-oil, hydrogel) at a ~2% active level.[22]

Silicone acrylates and silicone resins also have the ability to tighten the skin when delivered from very simple gel formulations. At 3% addition level both technologies provide a tightening perception while still being comfortable as measured by panelists as well as with instrumental methods such as the cutometer.[28]

Figure 8: SEM picture showing the difference in surface micro roughness and the corresponding carbon black adhesion for formulation control and with 2% addition level silicone acrylate



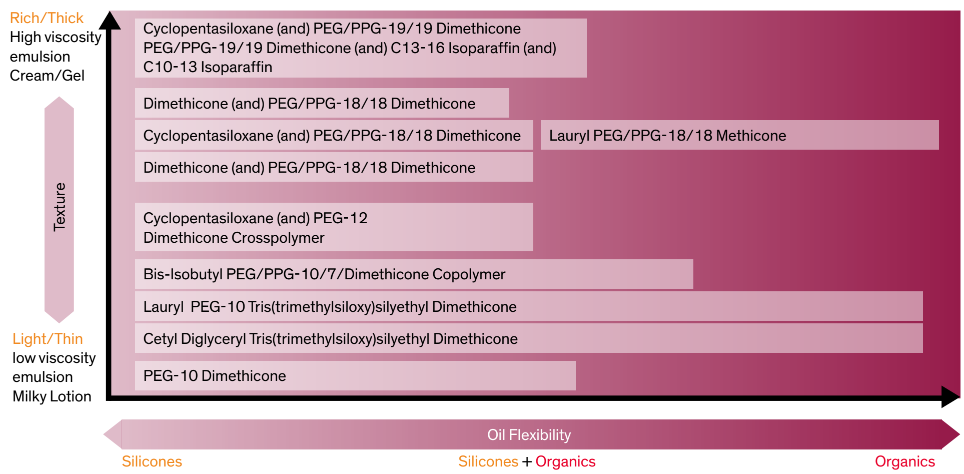
In-vitro testing on 60-micron coating on collagen (internal test)

Formulation efficiency

The majority of skin care products are emulsified systems, mainly o/w but w/o are also popular especially in foundations, BB creams and in a lesser extend sun care. W/O systems provide benefits such as wash off resistance, substantivity, improved barrier properties, emolliency, moisturisation and in some cases, can influence the penetration of actives. Water-in-oil and water-in-silicone emulsifiers have existed since the mid 1980s and versus their organic counterpart, they are typically liquid at room temperature, do not require waxes for stabilization (cold process) and can accommodate a high level of silicone oils and water for a weightless feel and their use level can be as low as 1.5%. Since the introduction of silicone water in oil emulsifiers 30 years ago, many variants have been developed, increasing significantly the flexibility in the oil phase and water phase compositions such as the addition of natural oils, pigments, organic and physical sunscreens, humectants and actives.[29] Figure 9 illustrates the broad range of w/o silicone emulsifiers available today, covering a broad range of oil phases and textures (solid to liquid).

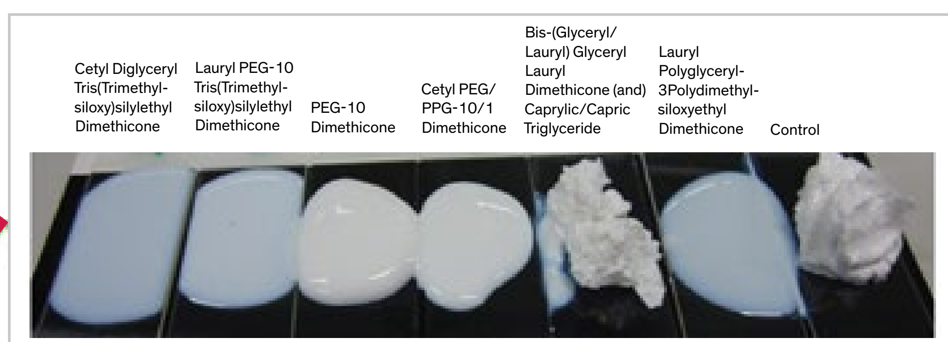
Foundations and BB creams are one product category where w/s silicone emulsifiers have been very popular as they increase the spreading, the color uniformity and help to disperse and stabilize pigments in low viscosity systems. They allow the emulsification of high level of volatile silicone, a carrier of choice in these type of products for imparting a very light feel and also being nonocclusive.[29]

Figure 9: Mapping of DOWSIL™ brand Emulsifiers – Emulsion texture versus type of oil phase



In order to address some concerns around the PEG functionalities, a silicone emulsifier with glyceryl functionalities was developed (Cetyl Diglyceryl Tris(trimethysiloxy)silylethyl Dimethicone).[30] This new emulsifier not only performs well where the PEG versions were used but has also been found to improve the performance of color cosmetic and sunscreen formulations especially regarding pigments and physical sunscreens dispersion as illustrated in Picture 2.

Picture 2



Silicone can also have benefits for the delivery of actives. Silicone elastomers in particular are one possibility for entrapment delivery systems that can demonstrate different release for vitamins and fragrances. [31]

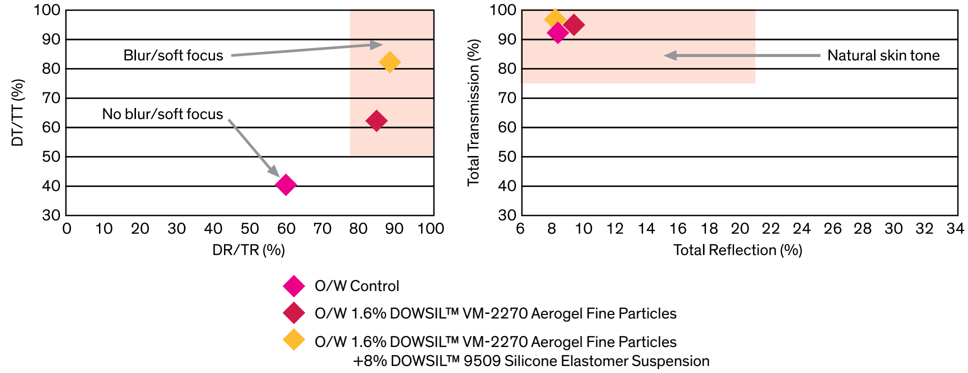
A more recent study has shown the stabilization of vitamin C in a glycerin in silicone system using a combination of silicone emulsifiers and silicone elastomers.[32] Stability studies under different conditions demonstrated that the vitamin C degradation was very limited and Franz diffusion cell methods indicated that the vitamin C was delivered to the skin, concentrated in the uppermost layers, which may act as a reservoir that progressively feeds the lower layers of the epidermis, sites of action for vitamin C . A skin model based on melanocyte-containing pigmented reconstituted human epidermis was used to assess the effect of vitamin C on reducing skin pigment with results showing that an anhydrous silicone system containing 5% vitamin C induced a 34% inhibition of melanin synthesis compared to the control, an untreated skin model. Due to the presence of silicone elastomer, faster absorption, reduced greasiness and glossiness were observed compared to a simple glycerin system, making this formulation more consumer friendly.

Optical effects

With growing consumer demand for products that mask the visible effects of aging, personal care and cosmetics formulators have capitalized on a range of solutions. These cover a broad range of cosmetic powders, including those based on silicone elastomers powders, suspensions, aerogels and their combinations. By using in-vitro screening methods (visual resolution chart and UV-Vis spectrometry with an integrating sphere) and in-vivo validation test methods (image analysis device), several materials were shown to provide soft focus and wrinkle masking performance.

By combining silica aerogel (particle size: 5-15 microns) and a suspension of elastomer powders, increased diffuse transmission (DT) and diffuse reflection (DR) of the light were obtained while keeping a maximum Total Transmission (TT) for the oil-in-water containing the silicone actives vs. the control, as illustrated in Figure 10.

Figure 10: Quantification with a UV-Vis spectrometer of diffused transmission, diffused reflection, total transmission and reflection of the oil-in-water formulation containing the silica silylate alone or combined with the dimethicone/vinyl dimethicone crosspolymer and C12-14 pareth-12 versus the control formulation



These in-vitro results were confirmed in-vivo using image analysis on the crow's feet area of panelists and then ranked by evaluators. The wrinkle masking effect was observed up to one hour after product application. In the case of the combination of silica aerogel and silicone resin wax, the wrinkle masking effect was observed up to 6 hours.[33]

Conclusions

Silicones used in beauty care applications have very unique chemical structures and physical properties such as gas permeability, low surface tension and high stability, which translate into water vapor and oxygen permeability, safe use and unique sensory characteristics, such as easy spreading and smooth feel on hair and skin.

In skin care, silicones can provide the following benefits: sensory enhancement for a consumer perceivable difference, film forming properties for long lasting formulations, skin protection and skin tightening and optical effects to help mask wrinkles. At the bench chemist level, they allow the development of innovative formulations for foundations and sun care products, permitting the delivery of actives while maintaining very good sensory profiles. They are valuable additives across all products for face care, colour cosmetics, sun care and antiperspirant/ deodorant applications.

For more information on silicones in skin care applications, please visit Dow's website: **consumer.dow.com**.

References

1. www.dowcorning.com/content/publishedlit/Chapter1_silicone-chemistryintroduction.pdf
2. K. De Paepe A. Sieg M. Le Meur b . Rogiers ; Silicones as Nonocclusive Topical Agents; Skin Pharmacol Physiol 2014;27:164–171
3. I.Van Reeth, A.Wilson; Understanding factors which influence the permeability of silicone and their derivatives; Cosmetic & Toiletries July 1994; 109; 87-92
4. James E.Fulton, JR.; Comedogenicity and irritancy of commonly used ingredients in skin care products; j. Soc.Cosmet. Chem. (November/December 1989; 40; 321-333
5. M.Lanzet; Comedogenic effect of cosmetic raw materials; Cosmetic & Toiletries February 1986; Vol 101; 63-72
6. Z.D.Draelos; New treatments for restoring impaired epidermal barrier permeability: Skin barrier repair creams; Clinics in Dermatology (2012); 30; 345-348.
7. Silicone hand cream from Revlon, Revlon Inc, 1956
8. B.Brewster, A Century of Change: The Language of Raw Materials, Cosmetic & Toiletries August 2006, 121(8), 37-66.
9. R.Lochhead, M.Lochhead; Transfer-resistant Lipstick; Cosmetic and Toiletries, January/February 2015; Vol.130, No1, 18-29.
10. (P.Tsolis, P.Marinelli; Silicone Elastomer Technologies for feel and Performance; Cosmetic & Toiletries January& February 2015; Vol.130; No1; 36-39.
11. E.Byron, The Wall Street Journal, September 18, 2008
12. Mintel GNPD Data base, 26th January 2016
13. http://www.silicones.eu
14. http://www.siliconesinfo.com
15. http://www.silicones.eu/sustainability-environment/silicones-in-the-environment
16. Cosmetic Ingredient review Dimethicone and others silicones: International Journal of Toxicology, 22 (Suppl.2): 11-35, 2003; ISSN: 1091-5818 Print/1092-874 Onlibe; DOI: 1-.1080/10915810390294854.
17. A.Colas; Silicones in Pharmaceutical applications, Dow Corning publication, Form No 51-993A-01)
18. K.P.Plotzke, J.M.McMahon, B.G.Hubeell, R.G.Meeks; Dermal Absorption of Siloxanes: Development of an In vitro Model System and Comparison to In Vivo Studies; Poster presented at the 19th IFSCC Congress, Sydney 22-25 October 1996.
19. Cosmetic acceptance of anti-dandruff shampoo,Journal of Investigative Dermatology,Symposium Proceedings.10:3 December 2005,page 201-204.
20. J.Lee, E.Warshaw, M.J.Zirwas; Allergens in the American Contact Dermatitis Society Core Series; Clinics in Dermatology (2011), 29, 266-271
21. Z.D.Draelos; Sensitive Skin: Perceptions, Evaluation, and Treatment; American Journal of Contact Dermatic, Vol 8, No2 (June), 1997 pp 76-78.
22. JL. Garaud, A.Sieg, M.Le Meur, H.Baillet, I.Van Reeth, S.Massé ; Silicones as innocuous materials to keep natural moisture balance and protect skin against particle pollution ; SOFW-Journal, 140, December 2014, pp. 26-34.
23. D.S. Morison; Petrolatum: A useful classic Cosmetics & Toiletries 1996; Vol. 111,.59-65, 69.
24. Van Reeth I: Silicones – a key ingredient ingredient in cosmetic and toiletry formulations; in Barel AO, Paye M, Maibach HI (eds): Handbook of Cosmetic Science and Technology, ed 3. London,Informa Healthcare, 2009, pp 371–380.
25. I.Van Reeth, X.R.Bao, K.Dib, R.Haller; A hydrophilic Silicone Elastomer for Broader Formulating Flexibility; Cosmetic & Toiletries November 2012, Vol.127, No.11, 802- 806
26. Mintel GNPD October 2015.
27. M.Eeman; I.Van Reeth; Silicone film-formers: New approaches for measuring film barrier properties; Poster at IFSCC congress, Paris 27-30 October 2014.
28. I. Vervier, C. Bougaran, I. Van Reeth, J. Yang; Benefits of Silicone Film Formers as Skin Tightening and Firming Agents, poster at IFSCC conference, Zurich 22-23 Septembre 2015
29. I. Van Reeth; X.r.Bao; Y.Kaneta; C.Delvalle; B.Sillard-Durand; Silicone emulsifiers and formulation technique for Stable, Aesthetic products; Cosmetic & toiletries October 2011; Vol 126, No10, 720-730
30. C.Delvalle; C.Scavuzzo, A.Delaunay, A.Sawayama; S.Tamura; T.Souda; S.Hori, New formulations possibilities with a Water-in-oil Silicone Emulsifier suitable for PEG-free Systems; Dow Conring publication ref 27-1463A-01, 2014
31. J.Newton; S.Postiaux; C.Stoller; V.Verhelst, S.Lin; M.Starch; Silicone Elastomer Delivery Systems ; Cosmetic and toiletries December 2005; vol 119, 12; 24- 31
32. M Eeman, R Bao, I Van Reeth; Specialty silicones for skin lightening products, Personal Care Asia Pacific November 2014, 15:6 ; 84-86
33. A-M. Vincent; M. K. Tomalia; , G. Tonet; L.Canfield; In-vitro and In-vivo Test Methods to Demonstrate the Soft Focus effect of Silicone in an Oil-in-water emulsion. Platform presentation, IFSCC congress Paris, October 27th – 30th 2014.
34. Abrutyn, E.S., Bahr, B.C., Fuson, S.M.; Overview of the Antiperspirant Market;Technology and Trends; DCI Magazine; August 1992.

30023848 Form No. 27-1624-01 C