Silicones and silicone alternatives

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Why Use Silicones?

The first reference to the use of silicones in cosmetics found by the author was an article published in 1953 [Ref 1]. Further articles rapidly followed as dermatologists evaluated the properties of this new class of materials as protective agents. The first paper to appear in the Journal of the Society of Cosmetic Chemists was in 1955 [Ref 2], which described methods to evaluate the relative cutaneous protection afforded by topical application of silicone fluids. This was followed in 1956 by a paper [Ref 3] describing the chemical structure and physical properties of silicone fluids, silicone esters and dimethicone copolyols. Now silicones are one of the most commonly found group of materials across all product categories.

Silicone fluids are now commonly known as dimethicone, which is the INCI name for a range of fully methylated linear siloxane polymers end blocked with trimethylsiloxy units and with a viscosity ranging from 5cs to over 1 million cs. Silicone esters are dimethyl siloxane polymers of organic fatty acids, for example behenyl dimethicone and cetyl dimethicone. Dimethicone copolyols are now listed by their ratio of ethylene oxide and propylene oxide molecules, for example Bis-PEG/PPG-15/5 dimethicone, which is dimethicone end-blocked with an average of 15 moles of ethylene oxide and 5 moles of propylene oxide.

The first reference found to the use of cyclic dimethyl siloxanes [cyclomethicones] was in a paper presented by Tom Elliot at the 10th I.F.S.C.C. Congress, Australia in 1978, describing more durable make-up based on pigmented water-in-solvent emulsions. Elliot found that the use of volatile cyclomethicone in the oil phase together with the adoption of a water-in-oil emulsion system enabled more durable colour effects to be produced on the skin but stated that the stability of the emulsion system is critical and depends on correct choice of emulsifiers, the ratio of water to volatile solvent and on pigment level.

Following that paper by Elliot more than 200 others have been published in the International Journal of Cosmetic Science. According to Tony O'Lenick [Ref 4] the explosion of silicone technology in the cosmetic industry happened in the early 1990s when organofunctional silicones that possessed the desirable properties of both silicone and organic polymers became available.

Now silicone compounds are used for enhancing skin barrier properties; retaining moisture; wetting colour pigments and improving their durability; protecting hair and imparting smoothness and enhancing skin feel. They are used in deodorants to combine quick drying with velvety feel and they keep water-resistant sunscreens on the skin. They are used as emulsifiers and to add body and texture to emulsions. Low-viscosity dimethicones prevent emulsions from soaping and form a breathable protective film on the skin. Phenyl silicone fluids make skin and hair shiny and supple. High-melting alkyl-modified silicones protect the skin by forming an occlusive film that prevents water loss and regulates the moisture content of the treated area. The film-forming properties of silicone resins and resin elastomer gels make for particularly long-lasting effects in foundations.

A brochure available from **Wacker** describes these attributes in detail and suggests products from its Belsil range of silicone compounds that fulfil these requirements. It also discusses the use of silicones in lipsticks, eye shadows, eye liners and nail enamels as well as for skin and hair care and it contains a selection guide to its extensive portfolio of silicones. **BRB International** claims to be the largest independent producer of silicones in the world and has produced a simple but informative guide to selecting the correct silicone for formulating personal care products and a presentation available as a

download on its personal care product range. That and other articles about silicones can be found on http://www.brb-international.com/silicones/market/personal-care.

According to **Dow Corning** silicones are used to confer either a matte or a shine effect in colour cosmetics. Because of their higher refractive index phenyl silicones help produce glossy films and are used in products such as lipsticks or lip glosses. If a matte effect is desired, as in foundation applications, silicone elastomer dispersions can be used and alkylmethylsiloxanes provide a pleasant feel, a waxy consistency and an increased compatibility with organic ingredients. Because of their low surface tension, good wetting properties and their ability to remove dirt or colour cosmetic residues low molecular weight silicones are used in facial cleansers. **Dow Corning** supplies standard silicones to meet these requirements through its Xiameter brand and publishes a selector guide on-line at https://www.xiameter.com/en/Pages/SelectorGuides.aspx.

Because silicones have been used by the cosmetics industry for so long most of those mentioned so far have become commodity items available from many suppliers and distributors including **A&E Connock; Ashland; Clariant; Elementis; Ele Corporation;, Gelest, Grant Industries, Guangzhou DX Chemical Co**. and the Abil range from **Evonik.** However it is still an area where new materials are constantly being developed, each with its own unique claims.

The **HallStar Company** offers Hallbrite PSF [INCI: Undecylcrylene dimethicone] as a versatile emollient that delivers an elegant, silky feel to lotions and creams, while providing enhanced substantivity and water-resistance. It is said to have superior organic compatibility and to provide formulations with anti-whitening benefits. It aids in the dispersion of pigments and metal oxides and is ideal for colour cosmetics and sun care applications. Chemsil K-12 from **Innospec Performance Chemicals** is a blend of dimethicone and PEG-10/15 dimethicone crosspolymer to give a self-emulsifying paste of a polyether modified dimethicone gel. It is used to formulate stable W/Si creams without the addition of an emulsifying agent. It is sheer sensitive, to facilitate the dispersion of pigments or other cosmetic ingredients and it enables formulation of unique textures of W/Si emulsions containing up to 90% water.

Makeup preparations in particular have benefitted from silicone chemistry: they have revolutionised the application and longevity of most makeup products, including foundation, eye shadows, blushes, and liquid and pencil eyeliners. They improve spreading on application and impart a luxurious, comfortable feel on skin, keeping the makeup moist and flexible. According to a brochure available from **Wacker** [Ref 5] a perfect foundation is the basis of beauty. It must never dry out the skin, must not wear off and it must look natural. Volatile and low melting point alkyl-modified silicones and low viscosity dimethicones enhance the application of foundations and so ensure a uniform result.

Emulsil S-362 [INCI: Bis-hydroxyethoxypropyl dimethicone] from **Innospec** is a carbinol functional silicone fluid that is lighter and more lubricious than polar silicones. It is intended for use in colour cosmetics and sunscreens based on metallic oxides and claims improved suspension of pigments, salts and sunscreens. Bis-Hydroxyethoxypropyl dimethicone is also available from **Dow Corning** as DC5562 Carbinol Fluid.

SiBrid DE-15 from **Gelest Incorporated** is polydiethylsiloxane and is described as a light emollient with a soft, cushion-like skin feel, imparting excellent slip and spreading properties in skin care and colour cosmetics. It serves as an excellent vehicle for wetting the pigments in W/Si foundations and pressed powders and is said to provide greater compatibility than dimethicone with common cosmetic ingredients. **Gelest** also supplies SiBrid TM-081 [INCI: Caprylyl methicone] that combines the light

dry feel and excellent slip of silicone with organic compatibility. Because of its good pigment wetting properties it is recommended for use in long wearing foundations, lipsticks, and eye shadows.

Diasphere KS-500 [INCI: Polymethylsilsesquioxane] from **Kobo Products** is a microsphere of 4.5µm average particle size that has the ability to scatter light to diminish the look of fine lines and wrinkles on the skin. It imparts finished products with an elegant silky texture and increased payoff, and because of its ball-bearing effect, enhanced slip. **Kobo** also supplies pigments coated with triethoxycaprylylsilane, making them easy to disperse in esters, mineral oils and silicone fluids. Higher pigment loading can be achieved compared to methicone treated pigments and they also have zero hydrogen potential and no residual methanol. Soft-focus and a ball-bearing effect is also provided by DC 9701 Cosmetic Powder [INCI: Dimethicone/vinyl dimethicone crosspolymer, silica] from **Dow Corning**. It is a silicone powder with a silica treated coating that enables the powder to flow freely without agglomeration and it is easy to disperse in different media, even in the presence of pigments.

Pecosil ARS-12 [INC: Lauryl phenylisopropyl dimethicone] from **Phoenix Chemicals** is described as a series of alkyl or alkyl aryl polydimethyl siloxane waxes. It produces waxes of different consistency to modify the feel properties of cosmetic products. This versatile material improves mould release for lipstick, is a bonding agent for hot pour or pressed powder, imparts barrier properties to enhance moisturising in creams and lotions and it provides high gloss to lipsticks and water-resistance in sunscreen products.

Dimethicone comes in a wide range of differing viscosities. **KCC Beauty** supplies it under three different trade names as SeraSense SF 60K, SeraSense 30K and SeraSense 12.5K. Each is described as a high viscosity fluid, which makes it highly substantive, with low spreading qualities, which is good for pigment adhesion as well as providing a non-greasy skin feel. **KCC** also markets SeraSense SA 31 [INCI: Glucamidopropyl aminopropyl dimethicone], which is a diamino-functional silicone polymer designed for extra substantivity and conditioning ability for use in a wide variety of leave on and rinse-off conditioners and in serums for coloured or dry damaged hair. SF1555 from **Momentive Performance Materials** is Bis-phenylpropyl dimethicone, which is a clear, high refractive index phenyl modified silicone fluid with low viscosity, low volatility and with good organic compatibility. It may be used as a non-greasy emollient in antiperspirants, colour cosmetics and skin and sun care products and is particularly suitable for clear or low residue antiperspirants.

Why Not Use Silicones?

When over an extended period of time silicones have established their versatility, safety and usefulness in cosmetics why now is there a backlash against them? Much of it is because of internet misinformation, which blames silicones in personal care for every misfortune possible, from causing acne to being toxic to the user. The other problem, also widely reported on the internet, is concern about the environment. These issues are discussed at length by the Global Silicones Council, a not-for-profit, international organisation whose stated mission it is to promote the safe use and prudent product stewardship of silicones worldwide. It is comprised of the Silicones Environmental, Health and Safety Council of North America (SEHSC), Centre Européen des Silicones (CES) in Europe and the Silicone Industry Association of Japan (SIAJ) and further information is available on its web site http://www.siliconesinfo.com.

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The Global Silicones Council reports that silicones are among the most extensively studied materials in consumer and industrial use today. More than 1,000 studies have been conducted to assess the safety of silicones for workers, consumers, the environment and manufacturing processes. The results of this continued research and testing demonstrate the safety of silicones in diverse and important applications when used properly.

The cosmetics industry relies heavily on safety assessments by the Cosmetics Ingredient Review [CIR] panel of experts, which in a 78 page report published in 2011, concluded that cyclomethicone, cyclotetrasiloxane, cyclopentasiloxane, cyclohexasiloxane and cycloheptasiloxane are safe as cosmetic ingredients in the practices of use and concentration as described in this safety assessment. The safety of numerous other silicones has been examined by the CIR including dimethicone, amodimethicone, various alkyl methicones and silicone esters and all were found safe as used in cosmetic products in a report dated 2003.

In Europe the Scientific Committee on Consumer Safety (SCCS) performs a similar function to the CIR and in 2010 it published the opinion that cyclomethicone (D4 and D5) does not pose a risk for human health when used in cosmetic products. Despite the detailed examinations described by the CIR, Environment Canada cast doubts on their safety by suggesting that D4 and D5 may pose a risk to humans and to the environment. However in late October 2011 the Canadian Board of Review released the following statement: “The Board conducted a scientifically rigorous review of all the relevant scientific information related to our mandate. Taking into account that information, the Board has concluded that Siloxane D5 does not pose a danger to the environment or its biological diversity. Furthermore, the Board concluded that, based on the information presented, Siloxane D5 will not pose a danger to the environment or its biological diversity in the future”

In England and Wales the Environment Agency has published an intention to file a restriction order, which has been added to ECHA's registry of current restriction intentions. It reads “The siloxanes octamethylcyclotetrasiloxane (D4) and decamethylcyclopentasiloxane (D5), used in the personal care industry, have been proposed by the UK, which expects to submit the intention on 16 January 2015. The restriction concerns their use in wash-off personal care products and states that these must not contain more than 0.1% of D4, or more than 0.1% of D5, in the EU.

In fact D4 has largely been phased out of cosmetic use so if this restriction order is activated it is D5 for which a replacement is required. Tony O’Lenick of **Siltech** summarised the attributes that would require consideration for a satisfactory alternative as viscosity, surface tension reduction, flammability, its effects on skin and its cost. A major attraction of D5 is the way it imparts a dry skin feel. This is not due to its volatility, which is negligible at skin temperatures, but to its low surface tension [Ref 6]. A similar effect can be obtained by mixing alkyl silicones with natural oils, for example behenyl dimethicone is soluble in soybean oil and reaches a critical micelle concentration at about 4%, at which point it gels the oil. This gel has a low surface tension and imparts a dry skin feel while dramatically reducing the silicone content of the oil phase.

The Alternatives

Until the controversy over cyclomethicones began they were often used as solvents and carriers for high molecular weight dimethicone and dimethiconal. Various alternatives are now being suggested; **Wacker** launched Belsil GB2050 in October 2014, which is a mixture of dimethicone and dimethiconol with a Brookfield viscosity of 8,000 – 10,000 mPa*s that can be readily diluted with cyclopentasiloxane, disiloxane, C9-13 isoparaffin and low viscosity dimethicones. Primarily for use in

hair conditioning products it is also finding application in skin care and colour cosmetics. Disiloxane is available from **Wacker** as Belsil DM 0.65 and is a suitable substitute for D5 in most applications. Wacker has also produced a D5-free W/Si emulsifier blend trade-named Belsil WO5000 [INCI: Dimethicone, caprylyl dimethicone ethoxyglucoside] that is non-ionic, mild and gentle and shows excellent solubility in all kinds of silicone oils. It is said to be suitable for fluid emulsions with good pigment dispersion, imparting an extremely soft, smooth, velvet skin feel. **Biosynthis** combines coconut alkanes with dimethiconol as Vegelite Si-1517, a silicone gum without D5.

To avoid silicones altogether it is necessary to look at some of the very light esters available such as Crodamol SFX [INCI: PPG-3 benzyl ether ethylhexanoate] from **Croda.** It is said to disperse mica, reduce tack and impart slip and lubricity to hair fibres with a similar sensory profile to D5 and to be better than D5 as a solvent for organic sunscreens. In tests all nine of its rub-out sensory attributes were statistically similar to D5. Also from **Croda**, Crodamol STS [INCI: PPG-3 benzyl ether myristate] is offered as a multifunctional alternative to silicone with similar characteristics such as feel and shine boosting benefits. It is easily emulsified, reduces tack of other emollients and has good pigment wetting properties. The third emollient from Croda to be offered as an alternative to silicones is Arlamol LST [INCI: PPG-3 isostearyl methyl ether]. It has good pigment wetting properties, spreads over the skin quickly to provide a light, dry skin feel and is particularly recommended for makeup applications.

The LexFeel N Series from **Inolex** is a range of 100% natural and sustainable emollients that have the sensory feel of cyclomethicone and dimethicone. They are Ecocertified and readily biodegradable and offered as alternatives to silicone fluids for improving skin-feel and for enhancing shine and texture in hair care products. All six materials in the Lexfeel N range are based on combinations of diheptyl succinate and capryloyl glycerin/sebacic acid copolymer of varying ratios and they can be substituted for D5 and for dimethicones of viscosities ranging from 5cs to 360cs. Other materials from **Inolex** include Lexfeel Shine [INCI: Propylene glycol dibenzoate], which is suggested as a substitute for phenyl trimethicone. Lexfeel Natural [INCI: Heptyl undecylenate] derived from castor oil is an extremely light and dry emollient suitable for natural products and Lexfeel 700 [INCI: Polyester-4] is an emollient, humectant, pigment dispersant, and dye solubiliser used in lipstick, lip gloss and other colour cosmetics.

Alternatives to esters are hydrocarbons and hydrogenated hydrocarbons: Smart5 from **IMCD** was engineered to be as close as possible to volatile D5 and is offered as a direct replacement. It is said to be perfect for makeup as well as providing a very elegant feel on skin and hair and water resistance in sun care. It evaporates in a similar way to volatile silicones and is a combination of isododecane with hydrogenated tetradecenyl/methylpentadecene. The Dedraflow range from **The Innovation Company** offers five volatile grades based on mixtures of hydrogenated polyisobutene with other hydrogenated hydrocarbons. They have been designed to replace cyclomethicone and have the same skin feel and a similar volatility profile and can be used to replace cyclomethicone without further modification to the formulation while delivering the same feel and performance as before.

Dr Straetmans offers three materials of low viscosity with good spreading properties, pleasant skin feel and excellent skin compatibility. Dermofeel MCT [INCI: Tricaprylin] can be incorporated as an oil component in natural cosmetic formulations due to its pleasant silicone-like skin feel and fast absorption. Dermofeel BGC [INCI: Butylene glycol dicaprylate/dicaprate] is for use in baby care, decorative and sun care cosmetics, especially those with a high SPF as it is a very good solvent for

UV-filters. Also a good solvent for UV-filters is Dermofeel TC-7 [INCI: Triheptanoin]; it is a non-greasy oil component of natural origin used in W/O- and O/W emulsions.

There are materials from natural sources that are offered as silicone alternatives. One such is Gosulin IL from **Gova**. It is a mixture of isoamyl laurate and isoamyl cocoate manufactured from sugar and coconut oil that has a very low viscosity and very similar characteristics to D5. It is miscible with dimethicone and improves the application characteristics of emulsions with high oil and wax content and of body butters. It is also said to be a good pigment dispersant including micronized titanium dioxide and is a solvent for organic sunscreens, making it of particular interest for high SPF sun care products. Isoamyl laurate is supplied by **Dr Straetmans** as Dermofeel Sensolv and is also recommended for sun care products because of its pigment dispersing properties allied to its good solvent characteristics.

Alban Muller has Lipolami [INCI: Silybum marianum ethyl ester], which has a light silicon-like touch and it contains over 50% linoleic acid, the most important of the omega-6 family of essential fatty acids. It has an extremely low surface tension, which ensures rapid spreading, small droplet size in emulsions and good pigment wetting and dispersing properties. **Stearinerie Dubois** claims that Dub Zenoat [INCI: Propanediol dicaprylate] can be positioned as a natural alternative to cyclomethicones due to its similar sensory profile and it can also be used as a substitute for synthetic ingredients like dicaprylyl carbonate and isohexadecane. It is an excellent solubiliser for organic sunscreeens and dispersing aid for pigments, which makes it useful in formulations for sun care, makeup and skincare.

Biosynthis offers Vegelight1215 Fluid [INCI: Coconut alkanes] as an Ecocertified alternative to D5 with a very similar viscosity and refractive index and nearly identical sensorial properties. **Biosynthis** also combines coconut alkanes with dilinoleic acid/propanediol copolymer as Viscoplastic Green 350 HVL offered an additive for creams and lotions and with dimethicone/vinyldimethicone crosspolymer as Vegelights Si 113 and 146, which have a long lasting powdery touch. Vegelight 1214 LC is a mixture of coconut alkanes with coco caprylate/caprate that has a very similar feel to D5 and is a good pigment wetting and dispersing agent, particularly suitable for preparing BB creams. Vegelight WSI is a W/O emulsifier also designed especially for BB creams [INCI: Coconut alkanes, polyglyceryl-3 polyricinoleate, disteardimonium hectorite].

Daikon Seed Extract from **Natural Plant Products Inc**.is a natural emollient derived from the seeds of *Raphanus sativus*. Comprising a mixture of C18, C20, and C22 fatty acids, it is extremely light-coloured and odourless. It offers a delicate slip with good absorption and presents a sensory profile more closely associated with esters and silicone emollients. Tests show that Daikon Seed Extract improves dry comb, reduces hair breakage on repeat combing and boosts hair shine, outperforming phenyl trimethicone.

While the majority of silicone alternatives are aimed at replacing volatile and low viscosity silicones Softbutters from **Greentech** are a range of plant derived products specifically developed to replace silicone gums and elastomers. Soft Butters deliver a superior emulsion structure and enhanced viscosity. They are available in apricot, argan, avocado, baobab, camellia, cotton, evening primrose, inca inchi, olive, peach kernel, sweet almond that comprise the named oil with its hydrogenated counterpart. Dermofeel Viscolid [INCI: Hydrogenated vegetable oil] from **Dr Straetmans** is a natural oil thickener supplied in a powder format with a melting point of approx. 60°C. It is used to convert liquid oils into soft, creamy textures. The thickening effect is based on a delicate network of fine lipid

crystals that, upon contact with the skin, melt and form a liquid phase with the sensorial profile of the oil mixture used.

Global 4075 from **Global Seven** is offered as a naturally derived ingredient to thicken vegetable and other oils in anhydrous systems. It is a mixture of glyceryl isostearate and caprylic/capric glycerides and it is mixed with sodium stearate before being combined with the other anhydrous components and it is possible to create products ranging from flowable gels to hard sticks. **Alban Muller** presents Ecogel as a patented optimised combination of ingredients of natural origin derived from a green process. It is a mixture of lysophospholipids, xanthan gum, sclerotium gum and pullulan and is claimed to be the first natural phospholipid-based gelling/emulsifying agent available to create natural gels and creams with an ultra-soft and light skin feel.

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Ref 5 Simply Beautiful: a Guide to Silicones for the Cosmetics Industry published by Wacker Chemie AG

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