

Silicones and silicone alternatives

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John Woodruff

When silicones were first offered as ingredients for cosmetic products about 50m years ago they were the inert dimethicones or so-called silicone oils. Their principal function was as replacement materials for hydrocarbon oils and for imparting water-resistance to barrier creams. Their molecular weight is controlled by the number of O-Si groups in the molecule, and their viscosity ranges from 0.65cst to 1,000,000cst. The higher molecular weight dimethicones are often mixed with cyclomethicones to form so-called silicone gums, which have wide applications in hair care.

Silicones are polymers that include silicon together with carbon, hydrogen, oxygen, and sometimes other chemical elements. By a process termed hydrosilylation it is possible to form a Si-H bond, which can then be reacted with a terminal double bond, resulting in a stable Si-C bond. This gives rise to important groups of silicone compounds including alkyl silicones, fluoro silicones, PEG/PPG products and copolymer resins by a process known as functionalisation. These materials may then be derivatised to provide esters, phosphate esters sulfosuccinates, sorbitan esters, sulphates and carboxylates.

Modified silicones include the addition of perfluoro groups to increase spreading properties and of alkyl groups to improve substantivity and wet combing and to impart a velvety feel in skin creams. Aryl and phenyl groups give added gloss to hair and improve organic compatibility and polyether and glucoside groups provide emulsifiers, conditioning properties and foam boosting activity.

Silicone waxes are of interest to formulators. Their melting point depends on their molecular structure and varies from a soft gel to a high melting point wax. When incorporated into emulsions they lower the surface tension of the oil phase and thus improve its spreading properties and they can also be added to shampoos to add conditioning properties.

Silicones are driving innovation in personal care and allowing product differentiation based on performance. That statement was made by Claudius Schwarzwald, Centre Européen des Silicones, at In-Cosmetics 2006 and it is hard to imagine cosmetic compositions without them.

Current developments in silicone technology include combining basic silicone structures with organic moieties to create new hybrid materials. This is providing silicone resin gels and powders, new hyper-branched structures and materials such as silicone-polyethers for thermal protection of hair and thermoplastic silicone elastomers as film formers and fixatives. Future developments are expected to provide silicone-based delivery systems for bioactive compounds for controlled release, biologically active silicone compounds and enzymatic silicon-carbon bond formation.

One group of silicone compounds that found wide-spread acceptance were the cyclomethicones with D4, cyclotetrasiloxane, and D5 or cyclopentasiloxane proving the most useful. Because cyclomethicones are volatile they require careful handling but once incorporated in an emulsion they improve its spreading properties, eliminate soaping and give a dry, silky skin feel. Unfortunately the use of cyclomethicones was queried by Canadian authorities and then under REACH and there was a real risk that its use in cosmetic products would be banned.

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This spurred many ingredient suppliers to find alternative non-silicone materials that could be substituted for D4/D5 but in late October 2011 the Canadian Board of Review for Cyclopentasiloxane in the Environment 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” On receipt of this statement the CTPA placed on its web site its own statement: “This reaffirms the position of the European cosmetics industry that the option of no regulatory action for the siloxanes, in the EU under REACH, is the most appropriate”

Dow Corning is a name synonymous with silicone technology and it offers an outstanding range of materials for cosmetics and personal care products. Its own statement on the matter reads “Based on more than 300 scientific studies, Dow Corning continues to believe that products containing D4 and D5 are safe for human health and the environment when used in accordance with accepted health and safety principles”.

During the period of uncertainty leading up to these pronouncements many ingredient suppliers have been looking into their portfolio of materials to identify possible alternatives and formulators most probably have not been including D4/D5 into new formulations. In addition products made to Ecocert or Soil Association standards for natural and organic cosmetics cannot include silicone materials so there remains a market for alternatives. The properties of D4/D5 that need to be considered when seeking replacements are their volatility and extremely low surface tension, which substantially contributes to their sensorial properties.

Because the use of D4 was the first cyclomethicone to be queried and the more likely to be banned D5 has become the more popular and it is the one for which other materials are being offered as replacements. LuxVeil 5 from **Arch Personal Care** is a mixture of isododecane and PPG-3 myristyl ether neoheptanoate with a low viscosity and high volatility profile. It is claimed to deliver the same feel and performance as cyclopentasiloxane, quickly evaporating from the skin, leaving a soft, luxurious skin feel.

A rather more complicated mixture of isododecane, hydrogenated polydecane and Bis-behenyl/isostearyl/phytostearyl dimerdillnoleyl dimmer dillinoate under the trade name Lipo SFS-5 is offered by **Lipo**. It is claimed to provide the same performance characteristics as cyclopentasiloxane but without the drying and whitening effects on application and it will also mask the whitening effect of antiperspirants on skin and clothing.

It is unlikely that either of these materials will gain acceptance by Ecocert so the simpler expedient of using Neolight 180P from **Kokyo Alcohol Kogyo** may be preferable. This is isostearyl neopentanoate, which is claimed to be a dry and non-oily emollient, with low viscosity and low solidification point. It has good affinity to powders, resists hydrolysis due to its neo-structure and may be used as a sensorial replacement of cyclopentasiloxane.

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BRB International offers low viscosity dimethicones with excellent spreading, easy rub-out and lubrication properties together with unique volatility characteristics as alternatives to cyclomethicones. **A&E Connock** suggests the use of its Hexamethyldisiloxane V0.65, which has many properties similar to D5 as regards volatility, sensorial properties and suppression of soaping up of emulsions.

Dermal Esters from **Alzo International** is a mixture of isodecyl isononoate and ethylhexyl isononoate with quick drying properties and a similar skin feel to D5. Alzo also suggests its Beantree [INCI: Methylheptyl isostearate], which is a low molecular weight double branched ester with a dry skin feel that is EcoCert approved to replace silicones in natural products.

With Ecocert approval DUB Zenoat from **Stearinerie Dubois** is propanediol dicaprylate and is entirely derived from vegetable and renewable raw materials. It is a colourless and odourless ester with excellent spreading properties and a non greasy, satin-smooth feel. It also has very good solubilising properties making it a vegetable alternative to cyclomethicones, isohexadecane, and liquid paraffin and propylene glycol esters.

Stearinerie Dubois also supply isodecyl neopentanoate under the trade name DUB VCI 10 and describe it as the lightest ester in the Dubois range. It has a very low viscosity and excellent spreading properties thanks to its very short and branched chains, which allows a good miscibility with silicones, especially dimethicones and silicone elastomers. The same material is available from **Lubrizol** as Schercemol 105 Ester and Lubrizol have an extensive range of esters, some of which may be considered if seeking to replace cyclomethicone or dimethicone in formulations. Of particular interest may be neopentyl glycol diethylhexanoate, diisopropyl sebacate and diisopropyl adipate, used alone or in combination.

Inolex provide two variations of a mixture of neopentyl glycol diheptanoate and isododecane that mimic the properties of volatile silicone emollients in personal care products. They are trade named Lexfeel D4 and Lexfeel D5 and are described as highly purified, light dry fluids. **Sasol** has Parafol 12-97 [INCI: Dodecane] and Parafol 14-97 [INCI: Tetradecane] described as naturally derived hydrocarbons with a very light skin feel. From **Floritech** there is Floramac 10 [INCI: Ethyl macadamiate], which is another offering suggested as a suitable substitute for D4/D5. It is a dry emollient derived from macadamia nut oil, which provides skin feel similar to many silicones and silicone derivatives. Floramac 10 is plant-derived, non-volatile, and unlike many synthetics it has broad coupling and solubility characteristics. Its slip and spreadability characteristics are similar to isopropyl myristate and isopropyl palmitate and it is a good solvent for organic sunscreens.

Essa Technologies markets an ester based on olive oil named Essachem [INCI: Octyldodecyl olivate], which although lacking the volatility of D4/D5, it has similar light and fast spreading properties and imparts a soft smooth after feel on skin. Also based on olive oil, Softolive from **Soliance** is a mixture of hydrogenated ethylhexyl olivate and hydrogenated olive oil unsaponifiables. It is described as a highly stable olive-based emollient with an elegant, dry skin feel, which is of interest if seeking a replacement for a fluid dimethicone.

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Active Shine Amazon from **Chemyunion** is described as a natural sensory modifier for hair and is a vegetable source alternative to silicone as it provides a similar feel and properties to hair [INCI: Orbignya speciosa (Babassu palm) kernel oil, Astrocaryum murumuru (palm) seed butter]. **Creations Couleurs** has a range of materials under the heading Dedraflow 5X based on hydrogenated polyisobutene that are designed to replace D4/D5 in cosmetic and personal care products. They are said to have the same skin feel as cyclomethicone and their volatility profile is very similar and it is claimed that they can be used to replace cyclomethicone without any further modifications in the formulation to deliver the same feel and performance.

Not content with suppliers claims Jennifer Allen of **Cornelius Technical, Quality and Regulatory Department** undertook her own investigation to compare the principal properties of cyclopentasiloxane with suggested alternatives. Parameters tested were spreadability, slip, dry feel, skin penetration and after feel. Each material performed well in at least one test and it was determined that **BASF's** Luvitol Lite [Hydrogenated polyisobutene]. is a close match to cyclopentasiloxane for slip and dry skin feel and is also quite close in regards to after feel. A combination of Pelemol 89 [INCI Ethylhexyl isononanoate] and Jeesilc PS-PTLV [INCI: Phenyl trimethicone, Bis-vinyl dimethicone/dimethicone copolymer] from **Jeen**, performed the best in the spreadability coefficient test plus the mixture gave very close results in the after feel test and is the closest match for skin penetration with good dry feel properties. The full report is available from jja@cornelius.co.uk

As may be expected, some of the larger suppliers have made their own studies into silicone replacements and have published suggested alternatives. **Cognis** have published a brochure [Ref 1] on the subject and suggest short chain esters, carbonates and ethers that offer the lightness of cyclic silicone in silicone-free leave-on products. Of these Cetiol C5 [INCI: Coco-caprylate] is said to be the nearest alternative to D5. It is said to match the sensorial profile of cyclomethicone; comes from 100 % natural, renewable feedstock, has good skin compatibility and good wetting ability for powders.

Cetiol CC [INCI: Dicaprylyl carbonate] is offered as a dry emollient and is claimed to provide a dry, velvety and smooth skin feel similar to some silicones. It is a good solvent for UV filters and shows improved make-up remover efficacy in facial cleansing lotions. Photomicrographs show superior dispersion of micronised titanium dioxide in emulsions compared to D5. Other suggestions are Sensoft [INCI: Propylheptyl caprylate] for its luxurious, silky and velvety skin feel and Cetiol OE [INCI: Dicaprylyl ether] for its light, silky skin feel and is especially suitable for antiperspirant applications because of its stability at extremes of pH.

Even companies that are primarily silicone suppliers have looked at possible D5 replacements. **Siltech** suggest **Silwax DO2** [INCI: Ethyl methicone] that can be used in conjunction with a vegetable oil and only 2% to 4% changes the feel of the vegetable oil to give a dry silky emolliancy remarkably similar to cyclomethicone. If no silicones can be used then Siltech offers a range of natural polymers based on citrate polyesters, which can be used as silicone replacements giving similar spread slip feel and gloss. One example is Cosmosurf 150 [INCI: Octyl dodecyl citrate crosspolymer], which is alcohol soluble, and described as a multi-domain ester.

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Dow Corning suggests investigating the properties of a linear volatile dimethicone with viscosity of 2cs to replace the volatile and sensory properties of D4 and D5 or dimethicones up to 20cs for their sensorial properties. Newly launched by Dow Corning is DC CB 1502 Gum Organic Blend, a mixture of C11-13 isoparaffin, isohexadecane, dimethiconol and dimethicone that is specifically designed for anhydrous hair serums where volatility is crucial and when cyclomethicones are to be avoided.

Silicones also find applications in body washes, shampoos and hair conditioners and the Cognis brochure has many ideas to provide the sensory or conditioning performance that consumers expect and require from such products if they are to be successful replacements.

However efficacious materials are in their own right if they are to be viewed as possible alternatives to achieve a particular effect in a formulation none are likely to be direct replacements in existing formulations. Their introduction as substitutes is going to require an in-depth study of the entire formulation. Volatile siloxanes have been the principal silicone materials of concern and the emphasis has been on their replacement. Meanwhile mainstream cosmetic products have continued to use the most suitable materials available for a particular purpose, and in very many cases this has meant the use of silicone-based materials.

The safety of silicone compounds is well established and the CTFA CIR [REF 2] report states that silicone compounds do not readily cross membrane barriers and are not absorbed through the skin. They are not metabolised by the body or by micro-organisms and are relatively innocuous when administered orally or parentally.

The list of silicone compounds in current use appears almost endless and it is difficult to suggest what may be the most suitable for any particular product category.

Exsymol lists twenty-four silanols, which are organic derivatives of silicone, rich in hydroxyl functions and synthesised in the presence of different radicals. They possess unique biological properties, enhanced or modulated by the presence of these radicals. Examples are silanediol salicylate; dimethylsilanol hyaluronate, silanetriol trehalose ether and polysilicone 3, which has an affinity for keratin-type proteins and improves cutaneous moisture levels and stimulates hair and nail growth.

Biosil Technologies Inc. lists thirty-nine silicone compounds for cosmetics and personal care including fourteen speciality compounds. For hair care there are five ingredients formed by the reaction of a silicone and an amino acid such as dimethiconol panthenol, trade-named Biosil Basics DL-30. It is a water dispersible silicone formed by reacting DL-panthenol with a highly reactive silicone. Other examples are dimethiconol arginine, dimethiconol methionine and dimethiconol cysteine. Cysteine, with its thiol group, is able to create disulfide bridges and dimethiconol cysteine increases hair volume and provides excellent conditioning for damaged hair. There are other silicone compounds for skin care, sun protection products and decorative cosmetics [Ref 3].

A&E Connock lists even more silicone mixtures and compounds and its web site has an interesting article, which although a little out of date, it explains why silicones are such popular additives to cosmetic applications [Ref 4]. Unlike the majority of suppliers A&E Connock sells materials by their INCI designations and they are

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obtained from carefully selected manufacturers worldwide. Its web site lists all silicones of major interest including dimethicones with viscosities from 1cs to 1,000,000; phenyl trimethicone with its outstanding glossing properties and polysilicone-18 cetyl phosphate that is used in conditioners to protect hair colour and in sprays for thermal protection.

Silicone materials are of particular importance in hair conditioning; **Clariant** offers Silcare Silicone SEA [INCI: Trideceth-9 amodimethicone, trideceth-12]. It is a self-emulsifying aminosiloxane that is soluble in water and at 2% in alcohol. It can give clear solutions in shampoos and conditioners and is particularly recommended for use in colour protection compositions. Amodimethicones may also be used in skin care and **Clariant** suggests Silcare Silicone WSI [INCI: Amodimethicone glycerocarbamate]. It is a PEG-free emulsifier with an HLB of approximately 5 that forms water-in-oil (w/o) and water-in-silicone (w/Si) emulsions with a dry, smooth and emollient skin feel.

Silicone emulsifiers impart a feel that will be very difficult to mimic using non-silicone materials. **Grant Industries** offers Gransurf 67 [INCI: PEG-10 dimethicone] with an HLB value of 4.5. It is designed for use in w/o and w/Si emulsion systems where a silicone gel or oil is present in the oil phase. Gransurf 90 [INCI: Cetyl PEG/PPG-10/1 dimethicone] with a HLB value of 5 is designed for cold process w/o and w/Si formulations. Gransurf 90 features a broad compatibility profile with UV-filters due to its branched hydrocarbon C16 chains and its polymeric structure results in heat stability up to 60°C and freeze stability down to - 25°C.

Biosil claims that Biosil Basics I-90 [INCI: Cetyl PEG/PPG-10/1 dimethicone] is an alkyl silicone polyether that is specifically engineered to provide the low HLB necessary to produce water in oil emulsions. **Dow Corning** suggests DC ES-5226 DM and DC ES-5227 DM Formulation Aids, which are dispersions of PEG/PPG-18/18 dimethicone in either volatile 2cs volatile or non-volatile 5cs dimethicones as primary water in silicone emulsifiers.

Evonik acquired the Degussa range of silicone materials, which includes the well-known Aerosil silica silylates and the Abil range of silicone conditioning aids, silicone fluids, alkyl silicone waxes and silicone emulsifiers. Abil UV Quat 50 [INCI: Polysilicone19] is a silicone conditioning agent that provides hair fibres with UV protection and protects colour against fading and damage from UV radiation. Abil WE 09 is a mixture of polyglyceryl-4 isostearate; cetyl PEG/PPG-10/1 dimethicone and hexyl laurate and is an emulsifier for w/o creams and lotions with excellent heat and freeze/thaw stability that is recommended for sun protection preparations with a high content of organic and/or physical UV filters.

Abil T Quat from **Evonick** [INCI: Silicone quaternium-22] is a good example of the use of silicone technology for hair care. It is a conditioning agent that provides easy detangling, smooth wet comb and superior feel. It also protects hair against breakage and shows a strong reduction of combing forces, imparts heat protection properties and gives improved color wash-fastness for dyed hair.

Chemsil are silicone suppliers based in California and selected from their range of materials is a water soluble silicone material trade named Emulsil S-391 [INCI: PEG-3 Dimethicone] designed to be used in hand sanitizers to provide a nice skin feel after

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use by reducing the skin 'drying feel' from the alcohol base. For adding cationic silicone conditioning from clear shampoos Chemsil suggest Microsil HAF-HV [INCI: Propxytetramethyl Piperdiny Dimethicone, Trideceth-6, C11-15 Pareth-7]. **Bluestar Silicones** has its Mirasil range of silicones for the personal care industry, which includes dimethicones, cyclomethicones and amodimethicones as well as a number of silicone gums.

The silicone materials available from **Dow Corning** are too numerous to count; new to our industry is DC MQ-1640 Flake is a blend of trimethylsiloxysilicate and polypropylsilsesquioxane resin that forms flexible, durable films, which feel comfortable on the skin and impart excellent resistance to transfer, wash-off and rub-off. This assists the development of long-lasting, long-wearing, smudge-proof cosmetic products.

Another new material from Dow Corning is CE-7080 Smart Style [INCI: Silicone quaternium-16/glycidoxy dimethicone crosspolymer, undeceth-11, undeceth-5], which is described as an innovative amino silicone elastomer emulsion that has been designed for use in leave-in conditioners and hair styling applications such as mousses, hair sprays, creams and gels, combining hair conditioning and hair styling benefits in a single product.

Siltech develops, manufactures and markets a full line of organo-functional silicone compounds and related specialties for specific customer applications. Its expertise includes organo-modified silicone surfactants and silicone polymers, including a full line of cationic, quaternary and di-functional silicones, as well as a number of reactive silicones. Siltech appreciates that the understanding of the underlying properties of the increasing number of organo-functional silicones has become more difficult and selecting the correct silicones can be daunting. To address this problem Siltech has developed a system called Select-a-Sil. It is based upon the principle that in order to be functional, silicone compounds must be formulator friendly.

Selecting the proper silicone for a particular formulation starts with identifying the specific attributes that are desired. Once the attributes are defined, other formulation issues such as solvent type, concentrations and interaction between ingredients need to be determined. In order to facilitate these selections, Siltech provides a number of "kits" that allow for rapid screening of silicones by application and kits for wetting and emulsification allow the user to quickly screen the effects of a given material in the finished formulation [REF 5].

Silicones are not the preserve of the primary names in this field. Other companies use them to good effect in specialised offerings such as GranPowder PSQ-Pt [INCI: Polymethylsilsesquioxane, Platinum] from **Grant Industries**. It is a powder made from colloidal platinum and polymethylsilsesquioxane that allows for the preparation of oil-based liquid or solid applications that deliver colloidal platinum. Colloidal platinum has anti-aging properties and enhances the skin's natural defence against photo and chemical attacks. Granpowder PSQ-Pt is said to release the colloidal platinum through the contact of skin sebum and other available mediums.

Biogenics produce **Gensil-210L** the principal ingredients of which are dimethicone, dimethicone/vinyl dimethicone crosspolymer, sodium hyaluronate and hydroxypropyl bispalmitamide MEA in aqua/glycol. Biogenics describe Gensil-210 as a silicone

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elastomer with a silky soft skin feel. It contains water, hyaluronic acid and a pseudo ceramide to bring a moisturising and repairing effect to formulations. At 5% in an o/w emulsion, it has been shown to significantly increase skin moisturising and to decrease TEWL.

Personally, with a few exceptions, the author believes that silicone compounds and cosmetic and personal care products are too closely combined for them to be replaced by (currently) non-existent alternatives.

Ref 1 Silicone alternatives for personal care; Cognis-BASF, 2011

Ref 2 Silicone and silicone compounds etc; The Cosmetic Ingredient Review; published by the CTFA.

Ref 3 <http://www.biosiltech.com>

Ref 4 http://www.connock.co.uk/articles_silicones.htm

Ref 5 <http://www.siltechpersonalcare.com/>

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www.creative-developments.co.uk