

Silicones and silicone alternatives

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Silicones are polymers with alternating silicon and oxygen atoms with various organic radicals attached to the silicon. They are unique compounds both in terms of their chemistry and in their wide range of useful applications. Their properties include low surface tension, high lubricity, enhanced softness, chemical inertness, low toxicity and non-stick properties. For a very short guide to their basic chemistry see SPC February 2012.

Despite recent qualms about the use of cyclic silicones and the antagonism towards all silicones exhibited by natural and organic certification organisations silicones and their derivatives continue to be one of the most commonly used group of materials in hair, skin and sun care products and in colour cosmetics.

A recent survey by the author of ingredient listings of the top 50 brands of anti-ageing skin care products showed dimethicones in 35 products, cyclomethicones in 23 and other silicones, mostly silicone emulsifiers, in 11. A similar exercise looking at sun care, after sun products and facial moisturisers showed that out of 82 products surveyed dimethicones appeared in 44 and cyclomethicones in 17.

Why are silicones such a popular group of materials? It must be because of their versatility. They are a recognised skin protectant and are used extensively in barrier creams and hand creams. They are added to emulsions to inhibit soaping on application; to impart a dry powdery skin feel; to reduce the sensation of greasiness in high oil-content emulsions; to improve dispersion of pigments and metallic oxides and to give shine and smoothness to hair. In addition there are a number of unique silicone emulsifiers that enable the creation of water-in-silicone and water-in-oil + silicone emulsions, which will be described in the February 2013 issue of SPC.

Silicone technology can be used to confer wash-off and transfer resistance to colour cosmetics. Two resins from **Dow Corning** developed for this application are MQ-1640 Flake Resin and MQ-1600 Solid Resin. They are blends of trimethylsiloxysilicate and polypropylsilsesquioxane designed to give a soft flexible film that resists wear and wash-off while also improving the intensity and shine of colour cosmetics. Information from Dow Corning shows the results of flexing and stretching colour cosmetic products that contain about 4% of MQ-1640 and how the film of colour remains homogenous and water-resistant.

Silicones are often used as coatings in pigment technology to aid dispersion and improve application properties, not only for colour cosmetics but also for micronised sunscreens. An example of this application is a recent introduction from **Croda** trade named Solaveil Sensation. It is titanium dioxide treated with hydrated silica and coated with aminopropyl triethoxysilane. Croda claim that this coating avoids the need for silicone-based dispersions and it enables Solaveil Sensation to be dispersed in C12-15 alkyl benzoate, giving the product a light and refreshing skin feel.

Silicone elastomers are used for their unique skin feel of dry smoothness: a recent introduction by **Dow Corning** is EL-9240 Silicone Elastomer Blend, which is a mixture of high molecular weight silicone elastomer in volatile, low viscosity, dimethicone. It is said to provide dry smoothness with a light, silky, non-greasy skin

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feel. It also acts as a thickening agent for water-in-oil and water-in-silicone formulations and silicone fluids and is suitable for cold-processing.

Two other silicone-based materials with thickening properties are Bentone Gels TMF-V and 1002-V from **Elementis Specialities**. Bentone Gel 1002-V is a dispersion of an organically modified hectorite in an ultra pure cyclopentasiloxane [INCI: Cyclopentasiloxane, disteardimonium hectorite, propylene carbonate]. Bentone Gel TMF-V is methyl trimethicone, disteardimonium hectorite and triethyl citrate. They provide thermostable viscosity control of an emulsion's oil phase, impart thixotropic flow, improve application properties and impart a pleasant residual silkiness to the skin.

Chemsil produces silicone-based cosmetic ingredients and has recently introduced a silicone cross-polymer base to be used in the formulation of cold process skin care and cosmetic products. It is trade-named Gelaid CPE [INCI: Cyclopentasiloxane, dimethicone/vinyl dimethicone crosspolymer, hydroxyethyl acrylate/sodium acryloyldimethyl taurate copolymer]. By adding water, esters, oils and actives it is possible to formulate a stable and elegant emulsion with a silky after feel. Gelaid CPE delivers both water and micronised silicone polymer to the skin surface and as the microemulsion breaks on the skin, the silicone polymer droplets coalesce to form a soft flexible film, sealing in hydrating moisture.

There are various ways of combating the visible signs of ageing, one being that of optical blurring or soft focus effect. By transmitting light between microspheres within wrinkles the depth is disguised. **Centerchem Inc.** produces AuraSphere [INCI: Isododecane, adipic acid/neopentyl glycol crosspolymer, lauryl dimethicone, hydrogenated polyisobutene], which is described as an anhydrous complex dispersed in a moisturising gel base. In addition to line blurring and wrinkle filling it imparts long wearing properties, a novel sensory feel and a silicone cushion to products without the use of cyclomethicone.

Over the past decade silicone elastomers have been at the forefront of new materials for skin care because of their unique feel on the skin. They give cushion, slip and a dry powdery skin feel. Gensil-220 RD from **Biogenics** is a silicone-like elastomer gel comprising water, hyaluronic acid and pseudo ceramide with dimethicone and dimethicone/vinyl dimethicone cross polymer. It is free from cyclomethicone and provides a silky soft skin feel as well as a moisturising and barrier repairing effect.

Shin-Etsu Silicones has an extensive range of silicone-based ingredients including elastomers: USG-103 is a silicone elastomer dispersed in cyclopentasiloxane. It is designed as a highly efficient thickening agent for silicone, which maintains its viscosity upon dilution in low molecular weight silicones and can readily suspend powders like titanium dioxide and particles such as glitter. The same company also produces a range of silicone powders that includes KSP-300 [INCI: Diphenyl dimethicone/vinyl diphenyl dimethicone/silsesquioxane crosspolymer]. It has a soft, silky feel and is recommended for creating powder to cream formulations.

NuLastic Silk-E-ID-LSA [INCI: Isododecane, Polysilicone-23] from **Alzo International** is a high molecular weight silicone elastomer reacted with an amino

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functional polyurethane that is said to deliver outstanding emolliancy and to impart transfer resistance to decorative cosmetics.

A property common to most silicones is their hydrophobic character so a silicone elastomer that can blend with up to 75% water and 40% glycerin plus a wide range of polar and non-polar ingredients is of interest. The material is trade-named EL-7040 Hydro Elastomer Blend and is supplied by **Dow Corning**. It is a blend of caprylyl methicone and PEG-12 dimethicone/PPG-20 crosspolymer and it has the ability to incorporate water and polar materials whilst maintaining a viscous gel structure. It may be used to form gelled serums and to deliver water-soluble actives such as ascorbic acid, Aloe barbadensis and caffeine.

A particularly useful property of EL-7040 hydro E is the way it can form clear gels with organic sunscreens such as ethylhexyl methoxycinnamate and ethylhexyl salicylate as well as emollients like C12-15 alkyl benzoate and caprylic/capric triglyceride, which suggests the possibility of clear gelled sunscreens.

Three products introduced silicone technology to hair care in the 1980s: the use of dimethiconol in cyclomethicone as an anti-frizz hair serum; polymethylsiloxanes in 2-in-1 shampoos and amodimethicone as the essential conditioning aid that is still regarded as the benchmark for hair conditioning properties. It is a cationic polymer that is substantive to hair to provide targeted conditioning action; it protects hair from thermal damage and increases colour retention. **A&E Connock** supplies it as a water-dispersible blend with trideceth-12 and cetrimonium chloride

Other materials for hair conditioning are available and **Evonik** offers Abil Soft AF 200 and Abil Soft AF300. Both materials are listed as aminopropyl dimethicone under the INCI system. AF 200 has been optimised for high-performance conditioning from shampoo formulations and AF 300 is designed for application in conditioning rinses. They are said to provide excellent hair conditioning properties with superior hair feel, softness and smoothness and also improve hair manageability and combability.

Also from **Evonik** is Abil ME 45 [INCI: Silicone quaternium-22, polyglyceryl-3 caprate, dipropylene glycol, cocamidopropyl betaine] as a microemulsion that is clearly soluble in water and that can be added to shampoos and conditioners. It claims heat protecting properties and to improve colour fastness and hair conditioning.

Dow Corning CE-8411 Smooth Plus Emulsion is a non-ionic silicone emulsion with amine and polyether functionality designed to add moisturising feel and conditioning benefits to shampoos and conditioners. Its INCI name of Bis-diisopropanolamino-PG-propyl dimethicone/bis-isobutyl PEG-14 copolymer is rather daunting but test results published by Dow Corning show it to impart excellent conditioning to both wet and dry hair along with improved shine and colour protection. It also provides increased smoothness, slipperiness, softness, volume, and flexibility to hair.

Microsil Volume from **Chemsil Silicones Inc.** is a highly functional cationic complex developed as a hair conditioning additive [INCI: Propoxytetramethyl piperdiny dimethicone, cetrimonium chloride, trideceth-6, C11-C15 parath-7]. When used at 5-10% it increases the hair volume by 23%, creating fuller hair and body. It can be used in cream conditioners and rinses as well as in clear hair care products and additional

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benefits are enhanced hair shine, anti-static control and hair softness. Also from **Chemsil**, Shineblend 9710 is a mixture of cyclopentasiloxane, cyclotetrasiloxane and dimethicone specially formulated as a feather light, non-greasy hair spray that will leave all hair types with luminous shine.

Bluestar Silicones recommends Mirasil Bright [INCI: C15-18 alkane, diphenyl dimethicone, isodecyl neopentanoate] for brightening hair and for protecting hair styles under conditions of high humidity. **Bluestar** also supplies Mirasil ADMH B100 [INCI: C15-18 alkane, propoxytetramethylpiperidinyl dimethicone, isodecyl neopentanoate] for protecting hair against colour fade and other problems caused by solar radiation. It has antioxidant properties and is also effective in protecting dyed hair against loss of colour caused by washing and from thermal damage.

The foregoing are a representative example of the diverse use to which silicone compounds are put in cosmetic and personal care products. For various reasons formulators are looking at alternative materials but it is important to know the effects that are being sought and it is possible that more than one chemical will be needed as a replacement in an existing formula. Cyclomethicone fluids are responsible for imparting the superior aesthetics consumers have come to expect skin care, hair care, and decorative products to possess but it is cyclomethicones that are causing the most concern so in some cases it is not necessary to avoid silicones completely but only cyclotetrasiloxane (D4) and cyclopentasiloxane (D5).

Single component materials proposed as substitutes for D4/D5 include Cetiol C5 from **BASF Care Creations**. It is coco-caprylate and appears to share the principal properties of skin feel and pigment wetting as cyclomethicone. Neolight 100P from **Kokyo Alcohol Kogyo** is isodecyl neopentanoate; a low viscosity ester with a light dry texture comparable to D5. Neolight 180P from the same supplier is isostearyl neopentanoate and is suggested as a possible replacement for dimethicone. **Croda** produce Crodamol SFX [INCI: PPG-3 benzyl ether ethylhexanoate] as an alternative to volatile silicones. It disperses mica, solubilises organic sunscreens, reduces tack and imparts slip and lubricity to hair fibres.

LuxVeil5 from **Arch/Lonza** is a good example of a blend of materials created to replace D4 and D5 in cosmetic products. It is a mixture of isododecane and PPG-3 myristyl ether neoheptanoate. Extensive testing by Arch shows it to compare favourably with D5 across the complete spectrum of properties that have made D5 such a popular cosmetic ingredient. This includes its volatility, its refractive index, viscosity, surface tension and pigment wetting properties. Sensory testing showed that LuxVeil 5 outperformed cyclopentasiloxane in glide, smoothness, softness and moisturising on the skin and there was no perceivable difference between it and D5 in silkiness and overall raw material preference.

Other blends suggested as silicone replacements are Lexfeel D4 and D5 from **Inolex**. They are mixtures of neopentyl glycol diheptanoate and isododecane that are described as light, dry fluids that mimic the properties of volatile silicone emollients in personal care products. The Lexfeel N range from **Inolex** comprises diheptyl succinate and capryloyl glycerin/sebacic acid copolymer in varying proportions that have the sensory feel of cyclomethicone and dimethicone. They are ecocertified and

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readily biodegradable and are suggested as suitable alternatives to silicone fluids for improving skin-feel, as well as enhancing shine and texture in hair care products.

In a talk at Formulate 2012 by Steve Blech, **Gemro Products**, he proposed using materials from **Koda Corporation** as suitable substitutes for silicones. Polymatrix 12 has a cross-linked structure to give cushion, slip and structure. Polymatrix 12 is a mixture of water, polyacrylate-10, sodium acrylic acid/MA copolymer, caprylyl glycol and 1,2 hexanediol that is said to be alcohol and pH tolerant, to have an elastomeric structure for cushion and to act as a moisture reservoir for the skin.

Sensient Laboratories supplies Covacryl MV [INCI: Sodium polyacrylate] claiming a silicone elastomer effect with a velvet touch and powdery skin feel. MV60 has a matt finish and MV40 imparts a satin finish. They are non-tacky and recommended for water-based gels and emulsions.

The workhorse of silicone compounds is dimethicone in all its various viscosities. It has barrier and skin protecting functions; emollient and moisturising properties and adds to skin feel. Various materials are proposed as replacements including Oligogoline from **Biotech Marine**. It is an aqueous solution of Chondrus crispus (Carrageenan) extract with a high content of polysaccharides. These form a protective film on the skin and the skin feel is said to be comparative to dimethicone. It has biological benefits when applied to the skin and it also imparts gloss and shine plus smoothness to the cuticle when used in hair products.

Kodanol D from **Koda Corporation** is based on sodium acrylic acid/MA copolymer, caprylyl glycol and 1,2 hexanediol plus water and glycerin and is claimed to have a similar texture to linear dimethicones yet is water-soluble. Dedraflows are a range of ingredients based around hydrogenated polyisobutenes from **The Innovation Company**. They vary from very volatile grades without residue to extremely viscous grades with substantial residue.

Unfortunately many possible alternatives to silicones are petroleum-based so will not qualify for Ecocert approval. One that has gained certification is Dermofeel Sensolve [INCI: Isoamyl laurate] from **Dr. Straetmans**. Its low viscosity and surface tension contribute to its silicone-like sensorial profile and its good solvent and dispersion properties suggest its use in sun care products and colour cosmetics. DayMoist CLR [INCI: Hydrolysed corn starch, beta vulgaris (beet) root extract] from **Chemisches Laboratorium Dr. Kurt Richter** is an Ecocert approved complex of natural plant derived extracts that is suggested as a replacement for silicones in skin and hair care applications.

Another alternative with Ecocert approval is Vegelight 1214 [INCI: Vegetable hydrocarbons] from **Biosynthesis**. Described as a bio-degradable non-polar volatile oil with emollient properties it promotes a pleasant skin feel that is soft and non-greasy. Its spreading power and sensorial properties are similar to cyclomethicones and it is an excellent solvent for silicone gums and elastomers. **Northstar Lipids** has an increasing technical focus to its natural oil activities and offers Crambe Abyssinica Seed Oil as a natural oil of high lubricity; high stability and silky skin feel, similar in many respects to a silicone.

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An Ecocert approved mixture of ingredients of natural origin that imparts a silicone-like protective barrier on skin and hair is Natpure Feel-M Eco from **Sensient Laboratories**. Derived from coconut oil it is described as an optimised combination of esters and fatty alcohols [INCI: Isopropyl palmitate, isostearyl isostearate, octyldodecanol, octyldodecyl myristate] with hydrophobic film-forming properties. **Alban Muller** provides Lipolami Milk Thistle as a dry soft-touch oil of natural origin comprising a blend of esters obtained from milk thistle oil. Its INCI designation is Silybum marianum ethyl ester and it provides silky and light textures, has excellent spreading properties and decreases the whitening soapy effect of emulsions.

Floramac 10 [INCI: Ethyl macadamiate] from **Floritech** is described as a dry emollient derived from Macadamia nut oil that provides skin feel similar to many silicones and silicone derivatives. It is plant-derived; non-volatile and has slip and spreadability making it ideally suited for any application where a clear, natural, dry emollient is desired. Essachem O from **ESSA Technologies** is octyldodecyl olivate, and is Ecocert certified. It has a fast initial spread; is fast absorbing and offers a light non-greasy emolliancy. It is recommended for dispersing pigments and inorganic sunscreens and is also suitable for hair conditioning to provide lubrication without a heavy or greasy feel.

Many of the alternative systems described are aimed at replacing silicones in skin care, sun care and decorative cosmetic products but a significant proportion of silicone usage is in hair conditioning. EcoSmooth Silk Conditioning Polymer [INCI: Ethylene/octene copolymer, ethylene/sodium acrylate copolymer] from **Dow Personal Care** is a non-cationic polyolefin copolymer dispersed in water with an acrylic-based polymer dispersant. In a series of comparative performance tests, EcoSmooth Silk was shown to provide equivalent conditioning performance to silicone in two-in-one shampoos.

Ashland Care Specialties suggested a silicone-free conditioning system created by combining Zenix 4617 [INCI: Oleth-5 phosphate] with N-Hance cationic guar derivatives, which provides clear conditioning systems with silicone-like performance. Various degrees of conditioning may be achieved, depending on the cationic guar derivative selected and these systems do not require emulsifiers or suspending agents traditionally used to stabilise silicone-based shampoo formulations. Ashland compared its silicone-free conditioning systems with combinations of silicone and cationic guar and found that, in areas such as detangling and hair feel, performance is virtually the same

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