Silicones and Alternatives 2018
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There is no doubt that silicones in all their various structures have played a very important part in cosmetic formulations but in recent years questions have been raised about their safety to humans and their effects on the environment. First, in 2009 cyclotetrasiloxane (D4) was banned in cosmetic products then the use of cyclopentasiloxane (D5) was banned in hair styling aerosols and sun care spray products [Ref 1]. In 2017 environmental concerns led to the European Commission (EC) banning D4 and D5 in rinse-off cosmetic products with 0.1% or more of either substance and the European Chemicals Agency (ECHA) has proposed to extend the restriction to leave on personal care products. In 2018. D4, D5 and D6 are now considered substances of very high concern (SVHC) according to the criteria set out in REACH article 57. Whatever the outcomes from these discussions the cosmetics industry is actively looking for alternatives to cyclomethicone, dimethicone and other silicone materials.

As cosmetic ingredients cyclosiloxanes have very appealing properties; they are clear, tasteless, essentially odourless, non-greasy and non-stinging and are used as conditioners, delivery agents, lubricants and solvents, and they impart a silky and slippery feeling to the touch. The sensorial properties of D5 are mainly due to its exceedingly low surface tension, which is responsible for its excellent spread on this skin and dry and silky feel. Silwax D02 [Ethyl methicone] from **Siltech** can be used to lower the surface tension of low viscosity mineral oils, natural esters and triglycerides, providing a greener alternative to cyclomethicone. From **Surfatech** are the Cosmosurf CE range of poly citrate esters derived from citric acid, natural alcohols and a cross-linking reagent from corn that give the feel of D5 and may be used in sun care products to impart dispersion and film forming properties, water-proofing and SPF boosting. Cosmosurf CE100 and CE100HV are octodecyl citrate cross-polymers and Cosmosurf CE140 and CE140 are stearyl/octodecyl citrate cross-polymers.

Crodamol STS [PPG-3 benzyl ether myristate] from **Croda** is offered as a multifunctional alternative to cyclomethicone and dimethicone. It is readily emulsified yielding highly stable emulsions and offers low skin spreading properties, imparting a dry emollience. It smooths hair cuticles and has a high refractive index, so it imparts shin and gloss to hair. The ether linkages of Crodamol STS increase polarity and improve compatibility with pigments and its benzyl moiety confers better compatibility with sunscreens, sterols and fragrances. Because it is non-volatile it can enhance the stability of silicone emulsions and will not flash off with alcohols in hydroalcoholic systems.

BergaCare FG 5 [INCI: Ethylhexyl palmitate ethylhexyl stearate, hydrogenated olive oil unsaponifiables, caprylic capric triglyceride] from **Berg + Schmidt** is suggested as a replacement for D5 due to its very similar sensory profile. It creates a smooth and silky skin feel, has a high spreadability and penetrates quickly into the skin while being non-tacky. BergaCare FG 5 is based on renewable, readily biodegradable raw materials and is an odourless transparent liquid with low viscosity. Gilsolide C from **Gilas**, is a mix of vegetable components, [INCI: Polyglyceryl-4 oleate, glyceryl olivate, hydrogenated rapeseed alcohol] that imparts dry and silky textures, is an excellent pigment dispersing agent and is offered as a "green" substitute for D5.

In an industry that strives to use natural materials from sustainable sources plant-based functional alternatives for volatile cyclic silicones are of special interest. Gosulin IL from **Gova** is the result of combining fermented alcohol (isoamyl alcohol) with refined coconut oil (lauric/cocoic acid) to give isoamyl cocoate. Gosilin IL is claimed to give a silicone-like feel and, because it is volatile, it adds weightless and low odour spreadability to formulations. It can reduce the oiliness of mineral oil and is a good wetting agent for pigments and titanium dioxide. It has a hair conditioning effect like cyclomethicone and is soluble with dimethicone so can be used to remove waterproof make-up.

Hydrogenated olive oil is a principal ingredient in Solivia-FX from **Solice Biotech**. It is combined with squalane unsaponifiables from olive oil and hydrogenated castor oil to provide an emollient to replace silicone and mineral oils. It finds application in anti-frizz haircare products and skin hydration formulations where it imparts a long-lasting smoothing and moisturising film without stickiness. Anti-frizz properties are also claimed for Frizzblend Max from **Innospec**. It is a moisture-activated amine modified silicone fluid, propoxytetramethyl piperidinyl dimethicone with cyclopentasiloxane, that gives frizz control plus shine and conditioning at use levels of 2.5% - 10%. Frizzblend MAX-CF is cyclomethicone-free, being a combination of propoxytetramethyl piperidinyl dimethicone, dimethicone and isododecane.

Sollivia-FX from **Sollice Biotech** is a combination of hydrogenated olive oil, unsaponifiable squalane from olive oil and hydrogenated castor oil offered as an alternative to silicone in anti-frizz hair products. Plantasens Olive LD [INCI: Hydrogenated ethylhexyl olivate, hydrogenated olive oil unsaponifiables] from **CRM International** offers conditioning properties in hair care applications very similar to silicones and can be easily incorporated in a shampoo up to 1% while maintaining a good viscosity and it is possible to formulate clear compositions.

Olive oil makes an appearance in Sensolene from **Hallstar** as ethylhexyl olivate, which is offered as a fast-absorbing, multi-functional lipid emollient that gives a silicone-like texture while enhancing the barrier function of the skin. It is polar so can help solubilise crystalline UV filters while providing a lighter touch to formulations. **Tri-K** uses olive oil to create Fision EcoSil [INCI: Hydrogenated ethylhexyl olivate, hydrogenated olive oil unsaponifiables] as a botanically derived alternative to silicones. It creates an even protective film on the skin leaving it feeling smooth and moisturised and can help reduce greasiness and tackiness in a formulation. Hemisqualane is a plant-derived non-polar C15 hydrocarbon made via fermentation of sugar cane and offered by **Aprinnova** as an alternative to petroleum-based paraffins and silicone ingredients. In makeup, it facilitates a smooth and even application for lipsticks and foundations. It also demonstrates excellent cleansing properties for makeup removal, including waterproof formulations like mascaras.

BASF Care Creations suggests four of its emollient materials as silicone replacements: Cetiol 4 All [Dipropylheptyl carbonate] is offered as primary emollient to replace dimethicone and suitable for creating interesting textures, Cetiol Ultimate is a mixture of undecane and tridecane resulting in a fast-spreading volatile material suitable for replacing D5 in a wide range of applications from ultra-thin oil-in-water formulations to clear sun protection formulations, smooth dry body oils and very light facial foundations. Cetiol CC [Dicaprylyl carbonate] is offered as a pigment dispersant and solvent for organic sunscreens and Cetiol Sensoft [Propylheptyl caprylate] is recommended as a silicone replacement in products for babies and those with sensitive skin.

The **Innovation Company** offers Dedraflow products based on hydrogenated polyisobutene as emollients with a wide range of sensorial perceptions and that have the same volatility and texture as silicones. They are photostable and inert and have higher negative zeta potential values to enhance skin penetration and not form a seal on the skin from actives. Different grades of Dedraflow are uniquely matched to the common silicone profiles of D4, D5 and dimethicones. Another series of silicone replacement materials from the **Innovation Company** are the Creaester ET esters of ethyl alcohol or sodium ethylate and fatty acids derived from sunflower, macadamia, meadowfoam and canola oils. These vegetable oils are rich in essential fatty acids and therefore have a strong compatibility with the skin.

Despite the problems over cyclosiloxanes, other silicones continue to offer unique and valuable properties to cosmetic products. KSP-441 [Polysilicone-22] from **Shin-Etsu Chemical Co.** is a hybrid silicone powder that combines the softness of a silicone rubber with the smoothness of a silicone resin. KSP-441 is alkyl modified and has outstanding oil absorption properties that make it of interest in sweat-proof makeup and it provides a soft-focus effect, resulting in a smooth and natural look. KSP-441 has an average particle size of 12 microns and true specific gravity 0.92. **Shin-Etsu** also offers two silicone gels comprising dimethicone/vinyl dimethicone crosspolymer with dimethicone. They have a 3-dimentional cross-linked structure that diffuses light, providing a soft-focus effect. Tospearl Microspheres from **Momentive** are a series of micro-fine spherical cross-linked siloxane particles, INCI: Polymethylsilsesquioxane. Each grade has a specific particle size that can result in improved lubricity of skin lotions and lipsticks, a reduction of powder agglomeration in pressed powders and provide soft-focus effects.

Polysilicone-22 is supplied from **DSM** as Parsol-FX and is described as the first polymeric UV-B filter consisting of chromophores attached to a silicone backbone. This enables SPF day care or sunscreen formulations that leave a dry, silky touch on the skin. When added to rinse-off and leave-on hair products Parsol-FX is said to deliver multiple benefits including prevention of colour fading, gloss enhancement and improved conditioning.

Silicone elastomers such as Belsil EG 1 and Belsil REG 102 from **Wacker** improve spreadability and exhibit pronounced shear-thinning attributes. They are solid at rest but convert to a liquid state in response to shear stress, allowing for quick spreading on the skin. Such gels generally contain dimethicone/vinyl dimethicone crosspolymer with cyclopentasiloxane as a liquid component, which evaporates upon application to leave the elastomer. With the move away from cyclosiloxanes alternative materials with silicone elastomer-like properties are sought.

Silsoft EAU from **Momentive** is an innovative structuring agent comprised of a proprietary hydrophobic silicone copolymer bound to a hydrophilic water-swellable network. Silsoft EAU microgel's ability to swell and de-swell allows for the creation of a wide range of textures with a water-fresh feel. It is claimed to be an excellent oil-in-water emulsifier that offers outstanding pigment dispersing for brush and beauty sponge application of foundations, CC creams and other colour cosmetic products, [INCI: Polysilicone-34, isononyl isononanoate, aqua].

Gaining the bronze award for best functional ingredient, In-Cosmetics 2017, Siligel from **IFF/Lucas Meyer** is a natural gelling agent providing a silicone-like skin feel with hydrating properties and a high resistance to electrolytes. It is a mixture of xanthan gum, lecithin, sclerotium gum and pullulan; it is easy-to-process and can be used as a thickening, stabilising, co-emulsifying and suspending agent. ACB Bio-Water Bamboo from **Active Concepts** is a fermented bamboo extract which delivers a silicone elastomer-like skin feel plus moisturising and skin softening benefits without exposing skin to osmotic stress. To address moisture depletion with eco-appeal, ACB Bio-Water Bamboo [INCI: Lactobacillus/Arundinaria gigantea ferment filtrate, Leuconostoc/radish root ferment filtrate] acts as a protective, conditioning agent for natural cosmetic formulations as it enhances epidermal slip and skin, hair and formula aesthetics.

Possibly spurred on by the banning of more than 0.1% D5 in wash-off products replacing other silicones in hair products is a very active area. Oleoflex FG-100 from **Applechem** is a honey-like non-greasy gel, consisting of natural oils and a synthetic polymer [INCI: Helianthus annuus (sunflower) seed oil, Carthamus tincorius (safflower) seed oil, styrene/butadiene copolymer]. It has a 2-dimensional micro-sponge polymer network that forms a flexible and invisible vegetable oil film. It is

claimed to enhance and extend the benefits of natural oils in hair care formulations, to smooth and restore damaged hair cuticles and to protect and reduce hair damage from shampooing, combing, and styling.

Emosmart and Emogreen are readily biodegradable, fluid, inert oils designed as silicone replacements in hair care by **Seppic**. They are alkanes of differing carbon chain lengths from C13-15 to C21-28 and increasing in viscosity. By careful selection they can replace D5, dimethicone and phenyl trimethicone in shampoos, conditioners and hair styling products. Active Shine Amazon 3R from **Chemyunion** is supplied as a replacement for phenyl trimethicone. It is claimed to be a synergistic combination of Orbignya speciosa kernel oil and Astrocaryum murumuru seed butter that offers benefits such as hair shine, manageability, detangling and softness.

Ref 1 SCCS/1549/15; OPINION ON decamethylcyclopentasiloxane (cyclopentasiloxane, D5) in cosmetic products, Final version of 29 July 2016

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