

16. Silicones in Personal Care Applications

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Silicones used in personal care applications are of diversified types, including cyclic, linear, or organo-functional polydimethylsiloxanes (PDMS), as well as silicone elastomer dispersions and resins. This wide range of molecules provides benefits that impact the performance of almost every type of beauty product, conferring attributes such as good spreading, film forming, wash-off resistance, skin feel, volatility and permeability.

The first use of silicone in personal care applications dates back to the 1950s, when a PDMS was incorporated into a commercial formulation to provide skin protection [1].

Since then, the use of silicones has kept increasing, along with the evolution of the knowledge around those materials (see Figure 1). Further to their first success, silicones made another breakthrough in the antiperspirant segment during the 1970s. Low molecular weight cyclosiloxanes were used as volatile carriers for the antiperspirant active, enhancing consumer acceptance of products thanks to the pleasant skin feel they could confer as well as their nonstaining properties [2].

Silicones then made their entry into hair care products. Amino-functional polymers were incorporated into styling mousses and rinse-off conditioners, while fluid or emulsion forms of high molecular weight PDMS were formulated into two-in-one conditioning shampoos. More recently, silicone elastomer dispersions were introduced to the market and gave formulators access to a new sensory dimension in terms of silkiness. Today, silicones find a use in virtually all types of personal care products, in segments as diversified as hair care, hygiene, skin care, sun protection or color cosmetics.

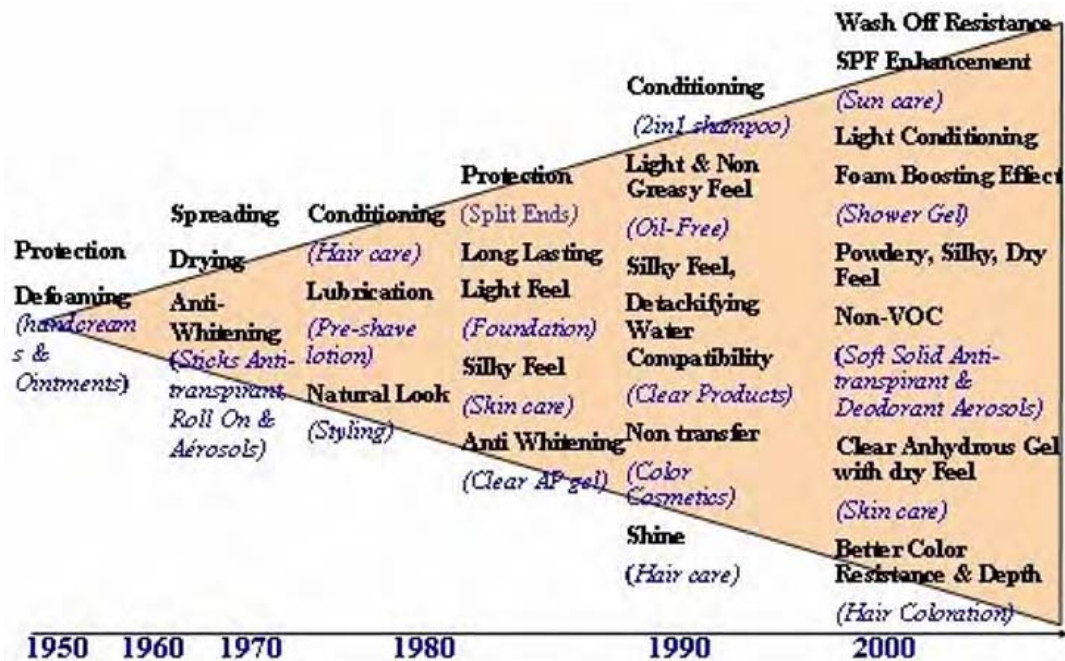


Figure 1. History of silicone uses in personal care.

Types of Silicones Used in Personal Care Applications

The versatility of silicones accounts for their wide use in beauty care products. This diversity stems from the unique set of physicochemical properties of PDMS as well as the variety of polymer types that can be used. Silicones incorporated into personal care products vary in molecular weight, structure or substituents attached to silicon atoms.

The most commonly used silicones are linear PDMS of various viscosities, ranging from the shortest possible chain, hexamethyldisiloxane with a viscosity of 0.65 cSt, to polymers with high degrees of polymerization and viscosities over 10^6 cSt, often called silicone gums. Cyclic PDMS with 4, 5 or 6 dimethylsiloxane units is also widely encountered in formulations. Because of their volatility, low molecular weight linear and cyclic PDMS materials are often referred to as volatile silicones.

Changing the structure and going from linear species to network or cross-linked systems leads to silicone resins and silicone elastomer dispersions. Such resins contain a number of T or Q units in a three-dimensional structure resulting from the hydrolysis/condensation of the corresponding initial silane monomers. Silicone elastomer dispersions are cross-linked gels that can be prepared through a hydrosilylation reaction. The reaction involves low levels of catalyst, usually platinum derivatives, and is generally run into an adequate solvent. SiH-containing silicone polymers are reacted with di-vinyl materials to link independent silicone chains. If the reaction is carried out in cyclic PDMS as the solvent, it leads to the formation of a swollen and loosely-reticulated network or a silicone elastomer dispersion.

Substitution of methyl with other groups allows significant modification of PDMS properties, accessing other benefits. Most common are linear alkyl, phenyl, polyether or aminoalkyl groups. This leads respectively to silicone waxes (if alkyl groups of sufficient length are grafted onto the backbone), water dispersible polymers or substantive polymers.

All these materials can be prepared by hydrosilylation, through the addition of various molecules bearing a vinyl group on a SiH-containing silicone polymer. Another route to such polymers involves the manufacturing of specific chlorosilanes to generate functional polymers after hydrolysis.

Silicone Benefits in Beauty Care Products

In skin care, a fundamental aspect is the “feel” provided, or how the product is perceived on skin upon and after application. Silicones convey a very differentiated feel to cosmetics, described as smooth, velvety, nongreasy and nontacky [3]. They can also help diminish the tackiness induced by other raw materials present in the formulation. They are appreciated by formulators because of their film-forming properties, providing substantivity, wash-off resistance and protection. PDMS materials have been found to be noncomedogenic and nonacnegenic, meaning they are not expected to encourage undesired skin pore clogging or acne [4]. Their antifoam characteristics also help reduce the so-called “soaping effect,” an undesired foaming phenomenon observed in skin creams formulated with soap-based emulsifiers.

Sun care products are devoted to protecting and reducing damage to skin induced by UV radiation. Here, the formulator's goal is to create on skin a film of UV-protective actives as homogeneous and as resistant to water removal as possible, even after a swim. Low molecular weight silicones like cyclics are included in sun care formulas to improve spreading [3-4-5]. Because of their hydrophobicity, PDMS and in particular high molecular weight polymers, have demonstrated substantivity. In such formulations, the active can be made more resistant to wash-off. This helps maintain the level of sun protection of the formulated product after application on skin. In addition to wash-off resistance, alkylmethylsiloxanes have also been shown to enhance the sun protection factor (SPF) of products containing either organic or inorganic sunscreens.

In color cosmetics, silicones are used to confer either a matte or a shine effect [6]. Phenyl silicones, because of their higher refractive index, help produce glossy films. This accounts for their use in products such as lipsticks or lip glosses, where shine is sought after. On the contrary, if a matte effect is desired, as in foundation applications, silicone elastomer dispersions can be used, possibly because of their effect on light scattering.

Alkylmethylsiloxanes are also appreciated because of their ability to provide, together with a pleasant feel, a waxy consistency and an increased compatibility with organic ingredients commonly used in such formulations [7]. Low molecular weight silicones are used in facial cleansers because of their low surface tension, good wetting properties and ability to remove dirt or color cosmetic residues, while delivering a dry and nongreasy feel [8].

Hair conditioning relates to softness, volume, body, sheen, feel and fly-away control [7]. This also includes hair protection from daily aggressions such as chemical treatments, combing or drying. Silicones are most often used in hair care because they can provide these conditioning benefits, consequently becoming key ingredients in shampoo or after-shampoo products.

High molecular weight PDMS as well as aminoalkyl copolymers (also called amodimethicones) can deposit on hair and are particularly efficient in making hair easier to comb [1]. In the case of PDMS, a thin film is formed, bringing gloss and soft feel to the hair shaft [9]. When amodimethicones are exposed to an aqueous environment, some nitrogen atoms will quaternize and bear a positive charge. Because of its keratinic nature, the hair shaft bears a global negative charge when wet, especially if it is damaged. This generates an electrostatic interaction thought to promote deposition and anchorage of the polymer, thus enhancing conditioning.

Other types of silicones are used in hair care. Volatile silicones can be incorporated to reduce drying time in some rinse-off applications like shampoos [10], thus limiting the need for hair dryers and the resulting heat damage to the hair shaft. Silicone resins have been proven to enhance hair volume [11], while silicone polyethers are used in hair styling products to help confer optimized form to hair [12].

In antiperspirants, which typically contain aluminum salts as the active, low molecular weight cyclic silicones are used as carriers, thanks to their volatility and noncooling perception, which leads to a dry feel. They also help prevent salt transfer and cloth staining, a problem associated with mineral oil based products. These cyclic silicones have allowed the development of new product forms such as roll-ons, providing alternatives to CFC-based aerosol formulations [7].

In hygiene applications, the amount of foam is an important parameter, as a shower gel

producing a generous foam will be better perceived by the consumer [8]. Due to their amphiphilic nature, silicone polyethers can impact the water-air interface of the foam structure, resulting in an increase in volume or a stabilization of the foam generated by the cleansing surfactants of the formulation. Some of those polymers also have been shown to reduce the eye irritancy that can be produced by such anionic surfactants.

Silicones and Skin Feel

One of the main reasons skin care formulators incorporate silicones in their formulations is the unique skin feel that silicones confer to cosmetics, which is often described as smooth, silky, elegant or luxurious. Silicones combine an array of properties (low coefficient of friction, liquid at high molecular weight, low surface tension) that impart a perceptively positive feel on skin [13].

Skin feel is a complex phenomenon affected by many variables, so it is difficult to characterize theoretically. A common way to assess sensory properties for a product is to perform sensory panel tests, where a set of trained panelists assess and characterize sensory parameters. Such evaluations confirmed that parameters such as stickiness, gloss, residue, tackiness, oiliness, greasiness and waxiness were almost never cited by panelists evaluating low molecular weight polydimethylsiloxanes, while spreadability and smoothness were often mentioned [13].

Skin feel is impacted by silicone structure. Increasing the length of the chain leads to silicone gums, which have been characterized as giving a velvety feel. Cross-linked silicone elastomer dispersions exhibit a further differentiated feel, which can be described as silky or powdery.

Volatility of Silicones

Low molecular weight silicones are characterized by their high volatility, which influences sensory properties. These materials leave no residue on skin, providing a light feel, which is dependent on the relative volatilities of the silicones considered. Because of their low heat of evaporation (when expressed per gram), they do not need significant heat from the skin to evaporate and consequently do not create the strong cooling effect experienced with water or ethanol-based formulations (see Table 1). This property is particularly sought after in many applications such as antiperspirants, where low molecular weight silicones provide a differentiated dry effect upon use.

Table 1. Heat of Vaporization for Some Volatile Fluids Used in Cosmetics

| <i>Fluid</i> | <i>Heat of vaporization kJ/kg</i> |
|-----------------------|---------------------------------------|
| PDMS, cyclic (DP = 4) | 172 |
| PDMS, cyclic (DP = 5) | 157 |
| Hexamethyldisiloxane | 192 |
| Ethanol | 840 |
| Water | 2257 |

Permeability of Silicones

PDMS polymers exhibit high permeability to gases. A noteworthy particularity is that this permeability is rather independent of their degree of polymerization, contrary to hydrocarbons (mineral oil vs. petrolatum). Neither does structure type (e.g., linear polymers vs. three-dimensional networks) significantly impact permeability. Table 2 gives comparative data for different families of silicones.

Table 2. Permeability Data for Some Volatile Fluids Used in Cosmetics

| <i>Fluid</i> | <i>Water vapor permeability</i> <i>g/m²/h</i> |
|----------------------------|---|
| PDMS, cyclic (DP = 5) | 155.7 |
| PDMS, linear (12,500 cSt) | 107.4 |
| Silicone gum | 148.6 |
| Silicone resin | 110.5 |
| Mineral oil | 98.0 |
| Alkylmethylsiloxane (C30+) | 1.4 |
| Petrolatum | 1.3 |

Permeability is linked to both solubility and diffusion coefficient. Silicones are permeable because they have a relatively high solubility for a number of gases and also exhibit high gas diffusion rates compared to other common polymers. This last characteristic stems from their low intermolecular forces [14].

This behavior is of particular interest for skin creams as it means a silicone film will let water vapor from the dermis and epidermis evaporate and so let the skin “breathe.” In personal care, this property is called “nonocclusivity” and is desirable for products such as body lotions, which are applied to large areas.

However, occlusivity can be increased by substituting methyl groups along the siloxane backbone by longer alkyl groups, thus retaining skin hydration and plasticisation. Surprisingly, aesthetic properties are retained to a great extent [7-14]. Controlled moisturization can be obtained by varying the grafted alkyl group length or the degree of substitution on the polysiloxane chain [14].

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