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THE EVOLUTION OF SILICONE CHEMISTRY: I. LIPOPHYLIC SILICONES

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Summary

In this article, a general overview of the evolution of lipophylic silicones chemistry is presented. We also report on the advances that have been made in the work carried out to achieve experimental applications of the cosmetic industry. These compounds have an important play role in the development of dermocosmetologic technology, because they knowledge is a key factor influencing the technological and economic development of pharmaceutical formulations.

Riassunto

Nel lavoro viene riportata una panoramica generale dell'evoluzione registratasi nel comparto della chimica dei siliconi lipofili.
Questa categoria di prodotti chimici, arricchitasi di nuovi studi condotti per valutare a pieno le potenzialità del loro uso cosmetico, ha rivelato di rappresentare un punto di riferimento basilare per lo sviluppo tecnologico ed economico anche delle formulazioni farmaceutiche.

INTRODUCTION

PDMS attracted the attention of the cosmetic industry very early due to their unique combination of characteristics. Nevertheless, their inadequate solubility in water and other solvents prevented them from being used on a large scale in cosmetic formulations. Subsequently, syntheses carried out in this field have led to an entire series of modified organo-polysiloxanes utilized in a wide range of products and applications (1-2).

CLASSIFICATION

Below we present an overview encompassing all the derivatives of lipophyllic silicones (3-5) developed up until now, outlined in the following diagram:

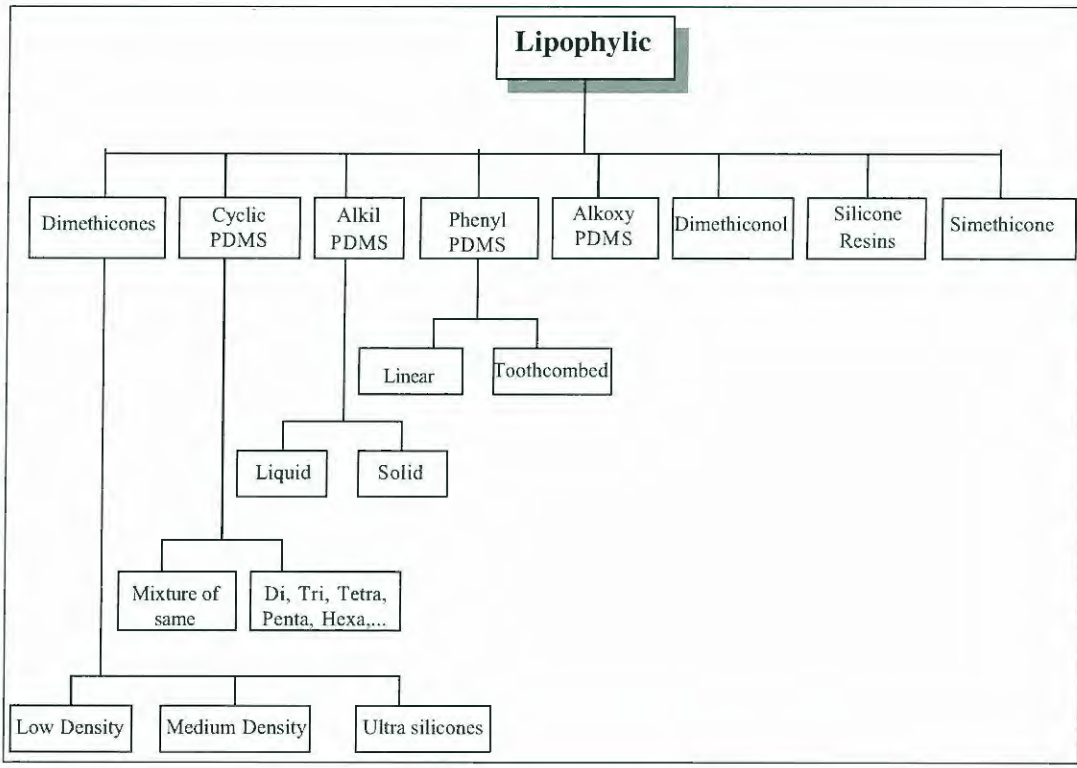

Fig. 1 Classification of lipophyllic silicones

DIMETHICONES

Also termed silicone fluids, these silicones are formed by the linear bonding of siloxane units. Dimethicones of different viscosities are obtained depending on the number of monomeric units making up the PDMS (6), starting from the most basic or dimeral dimethicone with a viscosity of 0.65 cP (having the particularity of being volatile without being cyclic) up to PDMS whose unit numbers range from 4000 to 6000 siloxane bonds, with dimethicones of 1 000 000 cP. From that point on, the denomination changes to silicone elastomers or silicone rubbers. The most commonly used range of viscosities in cosmetic formulations rnns from 0.65 cP to 60 000 cP, which offer the best combination of aesthetic qualities for body care formulations. High-viscosity PDMS offer water repellency in lotions, creams and sunscreen products. The medium- and low-viscosity dimethicones confer better lubricity, softness and spreading to the formulations. The incompatibility of

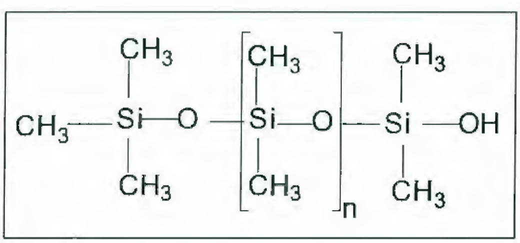

Fig. 2 Chemical structure of PDMS

dimethicones with organic elements and their low surface tension mean that lotions and creams (emulsions in general) will spread in a thin water-repellent film that is not occlusive.
Linear PDMS, traditionally used in emulsions for very dry skin, due to the gloss and stickiness provided by their relatively high refraction index, are sometimes limited in their use by these very factors.

The addition of 0.5-2% linear PDMS by weight is enough to produce a sensation of softness in lotions and skin creams, while 5-10% is needed for a protective barrier. In sunscreens, 1-3% confers water-repellent properties and desvicificante agents, resulting in a formulation that is neither sticky nor greasy. In concentrations below 1%, they act as defoaming agents (7) to prevent the "whitewash" phenomenon in emulsions.
The applications of linear PDMS have been limited by its poor ability to solubilize in the non-polar or oil phase of emulsions. In addition, it is excessively glossy (especially those with a high MW) and is overly sticky when proportions are increased to provide a barrier effect. The work of Vaughan on the phase diagram is therefore of great interest in the light of this problem (8).
Vaughan's work suggests that dimethicones can be solubilized in the non-polar oils commonly used in cosmetics for body care, such as paraffin. Nonetheless, in practice this does not hold true, except for PDMS with a viscosity of under 5 cP, due to the fact that the study of solubility parameters cannot generally predict the solubility of high MW silicones in cosmetic formulations. This effect is the result of the increase in the eutrofia of the mixture of PDMS + maximum-solubility cosolvents. However, this insolubility is not especially problematic regarding its inclusion in topical formulations.
There are numerous parameters that explain the ease of PDMS inclusion in emulsions:

1) The emulsifiers and coemulsifiers normally used to stabilize emulsions can surround the small concentrations of dimethicone employed, even when other oils with solubility parameters and properties different from those of silicone fluids are involved.
2) Most dermocosmetic formulations are viscous enough and therefore, according to Stokes's law, stable enough to accept the inclusion of dimethicones in the usual concen-

trations of formulations. Nevertheless, in less dense emulsions, ruptures can occur, preventable using dimethicone cosolvents. One of the few solvents that generally facilitates the incorporation of PDMS to these fluids or formulations is isopropyl myristate (9-10).

3) Finally, the low intramolecular force (synonymous with high surface activity) in silicone fluids allows, under normal shaking conditions, the reduction of the droplets to a small enough size to considerably increase the active contact surface of the droplets and therefore increase, according to Stokes's law, the dispersiveness of dimethicone in emulsions or formulations in general.

CYCLOMETHICONES

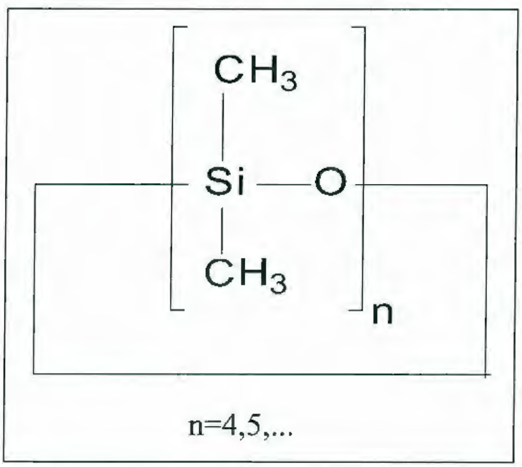

Fig. 3 Cyclomethicones: General chemical structure

These silicones are also known as volatile PDMS or dimethylcyclosiloxanes due to their characteristic of evaporating normally and to a different extent at body temperature depending on the degree of polymerization of the cyclomethicone. These volatile silicones have the advantages but not the drawbacks of silicone and, if only in their applications in O/W cosmetic emulsions, it should be noted that they greatly reduce the viscosity of the oil phase and therefore influence the stability and rheology of the emulsion (11-12).

In general, cyclomethicones are transparent liquids with a viscosity under 5 cP (Vaughan's theory can be applied to them), the only exception being the trimer (D3), which is a crystalline solid that easily evaporates at room temperature (not typically used in cosmetic formulations) (13).

The most commonly used cyclomethicone is the pentamer D5 in general provides better solubility properties. Cycles with more than 6 siloxane bonds (or 6 silica atoms), such as hexamer cyclomethicone, are normally found in commercial preparations in very low concentrations, mixed with the analogous pentamer and do not therefore influence the volatility and solubility ranges of the final product at all. These cyclomethicones, termed INCI for cyclic silicones including hexamethyl disiloxane due to its volatility, are obtained as normal components during the distillation phase in the manufacture of linear silicone polymers (14).

The different types of cyclic silicones (D3, D4, D5, D6, etc.) are separated by fractionated distillation.

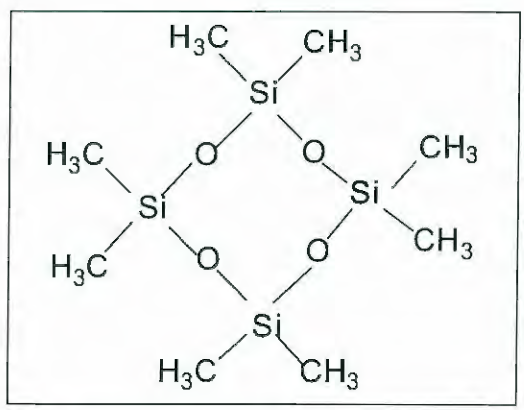

Fig. 4 Chemical structure of tetramer Cyclomethicone

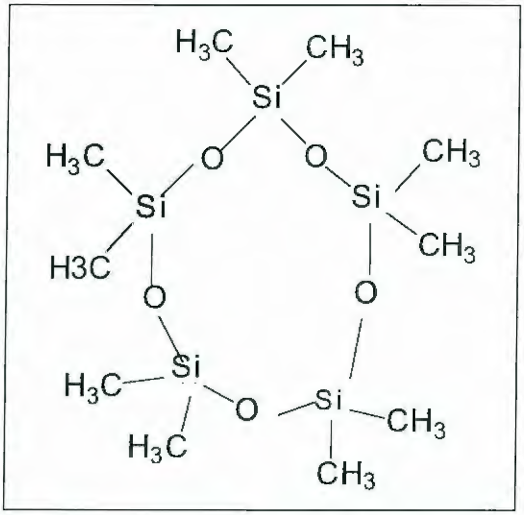

Fig. 5 Chemical structure of pentamer Cyclomethicone

Tetramer and pentamer cyclomethicones are the easiest ones to obtain and are therefore the most commonly used volatile silicones since they also have the best properties at room temperature. In the early history of silicone manufacture, these cyclic dimethicones were doubled and blocked for use in the production of silicone elastomers, such as those used to compact bathtubs. Nowadays, volatile silicones are produced and sold as a mixture of the afore-mentioned molecular types (the most common mixture consists of D5 and traces of D6 in different proportions depending on the desired properties).

Let us now address the general properties of cyclic PDMS that provide them with their great versatility and widespread use in personal care products (15-16):

1) These elements are volatile at room temperature. The lack of a strong intermolecular attraction and of blocking at the ends of the polymer by sizeable groups confers great volatility to these materials with a relatively low MW. Their volatility increases considerably upon contact with body temperature, entirely evaporating without leaving a dry residue. They are therefore used as transitory excipients that are easily spread and easily eliminated with no residue (17).
2) Cyclomethicones have a low vaporization heat in contrast with other volatile ingredients (18). This means that a formulation containing cyclomethicone leaves a dry or "evanescent" feeling, but without producing a cold sensation by absorbing energy from the skin in order to evaporate (19).
3) They have better solubility than dimethicones. They are compatible with most waxes, fatty acids, vegetable oils, fatty esters, mineral oils, glycerine, as well as with non-volatile silicones. Cyclomethicones are better solvents than linear PDMS, as they are soluble in pure alcohol and in both aliphatic and aromatic hydrocarbons. They can be easily emulsified in aqueous systems thanks to their high surface activity or low surface tension. Therefore, diverse cosmetic excipients can be used to easily obtain anhydrous cyclomethicone solutions using emulsifiers agents (20).

Useful combinations in this respect are liquid alcohols and ethoxylates or propoxylates of fatty alcohol; several different esters can also be used (benzoates, adipates, palmitates, etc.). The same cyclomethicones are excellent cosolvents of dimethicones with a high MW (21).

4) Characteristics derived from their silicone nature. They tend to reduce the viscosity of the products to which they are incorporated, that is, facilitating the formation of a film that flows easily, surrounding or engulfing the particles or components of a formulation and thereby easing its spreadability on the skin.

As components in a formulation they contribute, due once again to their high degree of spreadability, a silky feeling and emollient properties to products for skin care. In contrast to linear PDMS, the soft, sticky feeling is obtained without greasiness. Like dimethicones, they ha-range of concentrations used to control sedimentation. A non-volatile content of 10-20% is appropriate, providing a solution that is clear, easy to spread and non-irritating.

Upon rubbing, the low friction and low evaporation heat of the volatile component assure a texture that is dry, non-cooling, silky and softening. The residual film is water repellent and long-lasting. Silicone gum has also been shown to confer substantiveness to certain compounds. Preliminary findings indicate a positive effect on certain chemical sunscreens (29), mineral oil and isopropyl myristate. Research has revealed that PABA derivatives are 50-100% more resistant to wash-off when these megasilicones are incorporated to them (30).

SILICONE RESINS

These branched silicones have generally a high molecular weight, the same characteristics as the silicone gum and the identical application in topical products, as well as substantiveness and water repellency. When these trimethylsiloxylicates are combined with linear PDMS, they therefore provide a liquid that is easy to work with. This dimethicone/trimethylsiloxylicate mixture can be emulsified, acting as a barrier to water, which aids in preventing other emollients from dissipating from products for skin protection. They provide emollient properties with low viscosity, leaving a soft, dry film. The combined use of phenyl and methyl groups in silicone resins decreases fragility, but increase in stability and improve in thermal behaviour. In short, silicone resins consist of copolymers of siloxane units (wherein a -CH group is substituted for a phenyl group), trimethylsiloxane and methylphenylsiloxane, in which the methyl and phenyl groups are bonded to the same silica atom. Pure phenyl silicones tend to be fragile, and glossy, with a low melting point, and therefore inappropriate for technical uses, although they are notably resistant to oxidation. Resins are therefore very complex polymers with a reticular structure with three-dimensional crossed bonds.

SIMETHICONES

The simethicones are PDMS in emulsion or dispersion with pyrogenic silica. These emulsions can use a non-ionic element as an emulsifier and the diluting media can be water to hydrocarbonated solvents. These emulsions are easy to incorporate and possess the characteristic of chemical inertness and the high surface activity of the group, as well as considerable defoaming power, to the point where they are measured in milligrams for each kilo and a half to be defoamed. They work well in alkaline and acid media.

References

1) **Smith AL. (1991)** Introduction to Silicones. *Chem. Anal.* **112,** 3-19
2) **Ruiz MªA, Hernández A, Llacer J.M. and Gallardo V. (1998)** The development of silicon chemistry: History, General Characteristics and applications. *Cosmetic & Toil.*, **113,** 57-65
3) **Wendel SR, Disapio AJ. (1983)** Organofunctional silicones for personal care applications. *Cosmetic & Toil.*, **98,** 103-106
4) **DOW CORNING (1990)** Unique formulas for success. A guide to formulating with silicones
5) **Israeli Y, Philippart JL, Lemaire J. (1992)** Photooxidation of Polydimethylsiloxane Oils.1. Effect of Silicon Hydride Groups. *Polym Degrad Stabil,* **36,** 179-185
6) **Gallardo V, Hernández A, Parera A. and Ruiz MªA. (1999)** The effect of preparation technique on droplet size in silicone emulsion. *J. Cosmet. Sci.,* **50,** 9-14,
7) **Brecevic L, Bosankilibarda I, Strajnar F. (1994)** Mechanism of Antifoaming Action of Simethicone. *J. Appl Toxicol,* **14,** 207-211
8) **Vaughan CD. (1985)** Using Solubility Parameters in Cosmetics Formulations. *J. Soc. Cosmet. Chem.,* **36,** 319-333
9) **Voigt R, Bornschein N. (1982)** Tratado de Técnología Farmacéutica, Ed. Acribia, Zaragoza, p. 393-398
10) **Smid-Kobar J, Kristl J, Srcic S. (1986)** Polydimethylsiloxane oil in ointments. *Pharm. J. of Slovenia,* **37,** 86-90
11) **Israeli Y, Lacoste J, Cavezzan J, Lemaire J. (1993)** Photooxidation of Polydimethylsiloxane Oils.3. Effect of Dimethylene Groups. *Polym Degrad Stabil,* **42,** 267-279
12) **Gallardo V, Montoya R. and Ruiz MªA. (2001)** Study of silicone vehicles for *Aloe vera. J. Cosmet. Sci.* **52,** 255-263
13) **Deryaguin BV, Karasev VV, Lavygin IA, Skrokhodov II, Khronova ENA. (1992)** Boundary Viscosity of Polydimethylsiloxane Liquids and Their Binary-Mixtures (Reprinted from Special Discussions of the faraday Society). *Prog Surf Sci,* **40,** 322-328
14) **He XW, Widmaier JM, Herz JE, Meyer GC. (1992)** Polydimethylsiloxane Poly (Methyl Methacrylate) Interpenetrating Polymer Networks.2. *Synthesis and Properties. Polymer,* **33,** 866-971
15) **Wendel SR. (1987)** Uses of silicones in cosmetics and toiletries. Dow Corning-Europa
16) **DOW CORNING (1990)** Using Silicones in Topical Products. *Drug Pharm. Sci* (Top Drug Delivery Formulations), **42,** 389-409
17) **Ruiz MA, Hernandez A, Parera A, Gallardo V. (1995)** Dimethylsiloxane polymers: Vaporization rate test/freezing temperatures. *J. Soc. Cosmet. Chem.* **46,**175-180
18) **Christou G, Tran C, Young C. (1991)** Gas-Liquid Critical-Temperatures of Binary-Mixtures Containing a low-Molecular-Weight polydimethysiloxane of Hexaethyldisiloxane Fluid Phase. *Equilibria,* **62,** 153-162
19) **Baquerizo I, Gallardo V, Parera A, Ruiz MªA. (1998)** Evaporation-freezing and rheological behavior of silicone. *J. Soc. Cosmet. Chem.* **49,** 89-100
20) **Willemin C. (1992)** Paramètre de Solubilité: Charactersation et sèlection des silicones. *Parfums Cosmet. Arômes,* **102,** 57-63

21) **Disapio AJ, Starch MS. (1981)** New silicones emulsifier technology. *Cosmetic & Toil.*, **96,** 55-57
22) **Wolf P, Yarosh DB, Kripke ML. (1993)** Effects of Sunscreens and a DNA Excision-Repair Enzyme on Ultraviolet Radiation-Induced Inflammation, Immune Suppression, and Cyclobutane Pyrimidine Dimer Formation in Mice. *J. Invest. Dermatol.*, **101,** 523-527
23) **Hernandez A, Gallardo V, Parera A, Ruiz MªA. (1996)** Stability and Optimization of silicone-based sunscreen formulations. *J. Soc. Cosmet. Chem.* **47,** 377-386,
24) **Pons L, Parra JL. (1995)** Ciencia Cosmética. Consejo General de Colegios Oficiales de Farmacéuticos. Madrid 1995. pag. 333.
25) **Sharaf MA, Mark JE, Alghazal AR. (1993)** Effect of Chain-Length Distributions on the Elastomeric Properties of Polydimethylsiloxane Networks Having High Functionality Cross-Links. *Abstracts of papers of the American Chemical Society,* **205,** 25-30
26) **Sharaf MA, Mark JE, Alhosani ZY. (1993)** Regular Bimodal Polydimethylsiloxane Networks-Elastomeric Properties of the Tetrafunctional Networks (propiedades de los elastómeros de siliconas). *Eur Polym J.*, **29,** 809-817
27) **Roidl J. (1986)** Soportes volátiles para sustancias activas. Conferencia 101 simposio de la *GK, Boletín* **n.1 22**-1209-05 (Múnich 1986)
28) **Disapio AJ, Fridd P. (1988)** Dimethicone Copolyols para aplicaciones en cosmética y artículos de tocador. Preprints IFSCC London, *DOW CORNING bulletin* **n.1 22**-12114A-05
29) **Ruiz MA, Zouaki J, Gallardo V. (2002)** Latex as a sunscreen carrier in a silicone vehicle. *Int. J. Cosmetic Sci.* **24,** 235-239,
30) **Baquerizo I, Gallardo V, Parera A, Ruiz MªA. (1999)** Development, Formulation, and Effectiveness Testing of a silicone-based barrier-type hand cream. *Drug Develop. and Ind. Pharm.* **25,** 1259-1265,

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