Silicones in cosmetics and their impact on the environment

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ABSTRACT

Silicones are generally considered cosmetic ingredients of versatile uses. In contrast to their physiological inertness after dermal use, a growing body of research and evidence focuses on their toxicological impacts, particularly with respect to the environment. The article presents silicones in light of their chemistry and production methods, cosmetic use, degradation and bioaccumulation, and regulatory status. Finally, alternatives in the context of natural cosmetics represent untapped potential due to the widespread use of silicones as cosmetic ingredients.

Keywords: cosmetics, cyclic silicones, safety, silicones, siloxanes

Article category: Professional article

WHAT IS A SILICONE?

Silicone is the commercial name commonly used for polymers composed of **siloxanes**. A silicone is a widely used chemical compound in which silicon atoms (Si) are linked via oxygen atoms (O), forming characteristic silicon oxide bonds (Si–O) (1). Methyl substituted siloxanes are known as polydimethylsiloxanes and they form two main structures: a linear and a cyclic structure (2, 3).

Silicones have different particle sizes and shapes, molecular weights and chemical modifications that contribute to various physicochemical properties, and can be used in many areas of human life, mostly in industrial processes and personal care products (3, 4). It should be emphasised that the chemical structure is related to the characteristic features that directly affect the safety or the risk of their use (4).

PRODUCTION METHODS

There are three methods of silicone synthesis typically used in the chemical industry: the **Grignard method**, the **Rochow method** using silicon reaction with an alkyl chloride and an **addition method** (4). Using these methods, reactive monomers such as methyltrichlorosilane, dimethyldichlorosilane, methylphenyldichlorosilane, diphenyldichlorosilane or phenyltrichlotosilane are prepared. In the next phase, the monomers are subjected to hydrolysis with excess water_at a temperature between 10 and 90°C in organic solvents such as ketones and esters. After the continuous hydrolysis of, for example, dimethyldichlorisilane, a mixture of cyclic and linear hydroxyl-terminated oligosiloxanes is obtained. To obtain linear dimethylsiloxane polymers, the hydrolysate is subjected to the polymerisation or polycondensation process (4).

During the polymerisation process, the hydrolysate is first transformed into a mixture of cyclic monomers, mostly octamethylcyclotetrasiloxane (also known as D4) and decamethylcyclopentasiloxane (also known as D5), after which ring-opening occurs. The result is a mixture of linear polysiloxane and about 15% of cyclic oligomers. The polycondensation process of the linear hydroxyl-terminated oligosiloxanes is used to obtain linear high-molecular weight polymers. The end-product is also a mixture of linear polymers and cyclic oligomers, but with only 2% of cyclic oligomers (4).

SILICONES IN COSMETICS

In the cosmetic industry, silicones and silicone derivatives mainly act as emollients, humectants, surfactants (emulsifiers), and film formers, antifoaming, viscosity-controlling agents, antistatic and binding agents (5). Particularly beneficial in terms of cosmetic use and skin chemical compatibility is their physiological inertness. Silicones are used in hair care products, shower gels, antiperspirants and deodorants, shaving products, decorative cosmetics and skincare products (1).

The most common polydimethylsiloxanes in cosmetic and personal hygiene products that appear under the name of **cyclomethicones** are **octamethylcyclotetrasiloxane** (D4) and **decamethylcyclopentasiloxane** (D5) (Figure 1.).

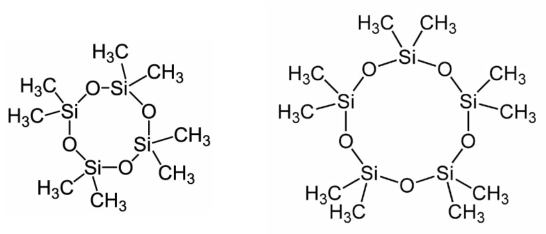

Figure 1: Octamethylcyclotetrasiloxane (D4) and decamethylcyclopentasiloxane (D5).

SILICONES AND THE ENVIRONMENT

The **annual world production** of methylsiloxanes has already reached over 8,000,000–10,000,000 tonnes. Consequently, they have been identified as emerging persistent toxic compounds because of their widespread use, the properties of high volatility and low water solubility. The impact of methylsiloxanes on biota and the ecological environment has become a matter of great concern today (3).

Although silicones have long been considered environmentally neutral, very widespread use is causing serious controversy (5). Recent studies have shown some harmful effects on the health of living beings and they may also cause damage to the environment (2). Thus, appeals to continuously **monitor silicones** in the environment are justified.

However, the Cosmetic Ingredient Review (CIR) Expert Panel concluded that frequently used silicones such as amodimethicone (mostly used as a hair conditioning agent) and dimethicone (mostly used as an antifoaming and skin-conditioning agent) are safe as used in cosmetic products (6). A similar opinion was issued by the Scientific Committee on Consumer Safety (SCCS) for D4 and D5, the main cyclic volatile methylsiloxanes (7), but was later amended and narrowed to hair styling aerosols and sun care spray products (8).

DEGRADATION AND BIOACCUMULATION

Hair care products, body lotions, deodorants and nail polishes are types of personal care products that contain up to 16% **cyclic volatile methylsiloxanes**. Due to a high vapour pressure (0.121 kPa for D4 and 0.021 for D5 at 23 °C) and a high Henry's Law constant value (259 for D4 and 185 for D5), cyclic volatile methylsiloxanes are mostly released into the atmosphere during the use of products (about 90%), while about 10% is discharged into wastewater (9).

They are then transported to the air from water/soil and oxidised by atmospheric hydroxyl radicals ($^{\bullet}OH$). This is considered a major degradation pathway for airborne cyclic volatile methylsiloxanes (10). The final degradation products in the environment are carbon dioxide and silicic acid and/or silica (11).

D4 and **D5** are the most commonly used silicones in cosmetic products. They have a strong adsorbing potential to organic matter in sewage sludge, sediment and soil. The degradation half-life for aerobic sediment is 242 days for D4 and more than 1,200 days for D5 at 24 °C. After they volatilise into the atmosphere, the degradation half-life for both is around 13 days. In addition, studies indicate that silicones can be found in aquatic food webs at many locations, with the highest levels close to sources of emission. D4 and D5 concentrations were found in the blood plasma of fish, birds and mammals, but the oral pathway of exposure is still unknown. It is expected that both substances are available for storage in lipid compartments (11).

According to the ECHA Annex XV Restriction report – Proposal for the restriction of octamethylcyclotetrasiloxane and decamethylcyclopentasiloxane, D4 meets the criteria for identification as a '**persistent, bioaccumulative and toxic**' (PBT) and a '**very persistent very bioaccumulative**' (vPvB) substance, while D5 is classified as a vPvB substance. The toxicity of D4 corresponds to reproduction category 2, and is based on both aquatic and mammalian studies (11).

In the European Union, approximately 4.7 tonnes of D4 and 205 tonnes of D5 are discharged into surface waters a year. It is believed that all emissions originate from the use of wash-off personal care products, and that they contribute to 95% of total emissions of D5 (195 tonnes/year) and 63% of D4 emissions (around 3 tonnes/year). Therefore, wash-off personal care products are considered to have the highest environmental risk for these substances (11).

EVOLUTION OF EXPOSURE CONSCIOUSNESS TO SILOXANES

It has been more than fifty years since silicones were first introduced to beauty products. The awaking interest of scientists about the impact of silicones on the environment is summarised in Figure 2. Special attention is given below to periods IV, V and VI.

Period IV

In period IV (from 1996 to 2000), scientists focused not only on the numerous applications of silicones and their side effects observed in biological samples (e.g. breast implants), but also on degradation pathways, options for silicone monitoring in the environment and on long-term toxicological effects.

New cosmetic formulations were developed with lipophilic and amphiphilic silicones which resulted in improved sensory properties, such as the silky and soft skin feel and smoothness of application on the skin, and desired cosmetic activities, such as good moisturising properties. Silicone manufacturers conducted their own research, in which they found that siloxanes do not present significant environmental risks to living organisms (5).

Period V

During the period from 2001 to 2008, interest in silicone use was at a similar level as in previous years, but more focus was placed on personal care products. Delivery systems for cosmetically active ingredients, e.g. silicone elastomers, were developed. Scientific articles about sources of human exposure to silicones as environmental pollutants were published, and silicones were identified in water, sewage, sediments, soil and air samples. This period saw an increase in awareness of likely human exposure to various siloxanes that have accumulated in the environment (5).

Period VI

In the last decade of silicone research, we have witnessed significant progress in the enhanced monitoring of environmental concentrations and the assessment of spatial migration through the air and bioaccumulation. It was concluded that some volatile silicones can migrate over long distances, as evidenced in analyses of Arctic air. Human exposure to silicones is not only the result of environmental pollution, but also due to the direct release of various personal care products that contain silicones.

WHAT ARE THE ALTERNATIVES?

Silicones, particularly cyclomethicones, have very specific characteristics, depending on the total composition of a cosmetic product. It is hard to find just one substitute that matches all of a cyclomethicone's properties, but there are some alternatives already used in cosmetic products. Particularly limited are those permitted for use in cosmetics that follow the concept of natural cosmetics, i.e. cosmetics that are based on **ingredients of natural origin**. Those alternatives include, for example, vegetable oils, squalene, isoamyl laurate, dicaprylyl carbonate, dicaprylyl ether, polycitronellol, undecane, etc.

Nevertheless, alternatives for silicones do exist, but are generally more costly and/or less available. **This is where the manufacturers and suppliers of cosmetic ingredients may find untapped potential.**

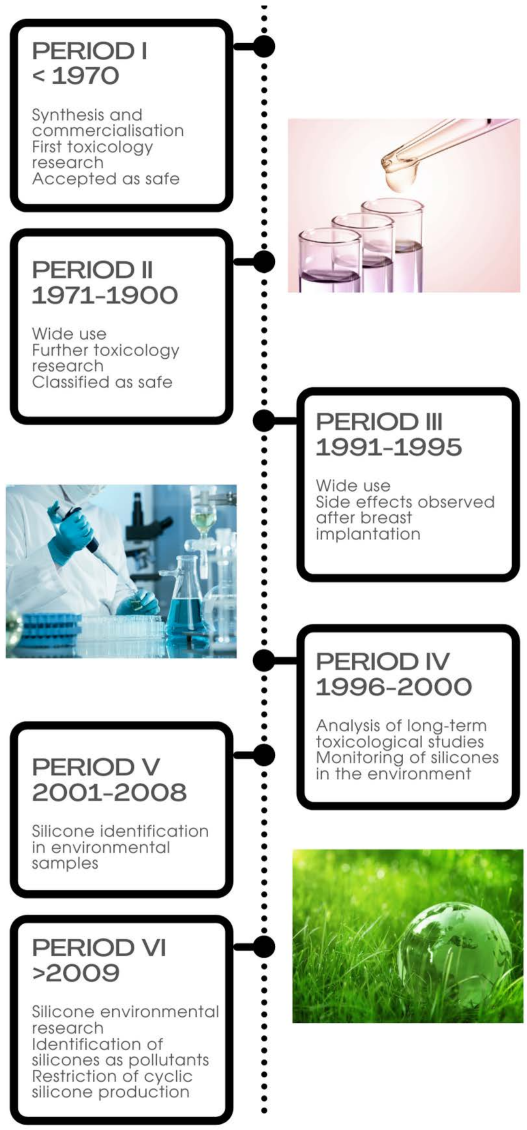

Figure 2: Milestones in the history of silicones and human awareness of their environmental issues (adopted from 5).

CONCLUSION

There is increased awareness of the likely direct or indirect toxicity of volatile methylsiloxanes to various organs. In regions such as Canada, the USA and Europe, **risk assessment procedures** have been defined that may lead to the introduction of new regulations to control their usage (12). Because some of silicones (i.e. cyclosiloxanes) have been identified as 'persistent, bioaccumulative and toxic' or 'very persistent very bioaccumulative' substances, they are regulated in the European Union by the European chemical regulation framework called REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals) (11). However, the silicone industry believes that the decision for such categorisation is not supported by available scientific evidence (13).

Wash-off cosmetic products containing D6 and leave-on cosmetic products containing D4, D5 and D6 with concentrations equal to or greater than 0.1% by weight of each of these substances were limited in accordance with the ECHA's proposal (European Chemicals Agency). Additionally, in May 2019, D4 was added to Annex II of the European Union Cosmetic Regulation 1223/2009, which means that D4 may not be added intentionally to cosmetic formulations sold in the European Union (14).

Although linear silicones may have similar 'persistent, bioaccumulative and toxic' or 'very persistent very bioaccumulative' behaviour as cyclic silicones, more studies must be conducted to classify them and restrict their use in cosmetic products, if needed (5). Nevertheless, precautionary principles seem to be reasonable based on their indisputable widespread presence.

Finally, we live in a world with truly extensive silicone production for the needs of the pharmaceutical, medical and food industries and, last but not least, the cosmetic industry. More than 50% of all new cosmetics launched in the last 10 years contain at least one type of a silicone (15). It is therefore essential to **monitor the release** of these substances into the environment, **conduct independent scientific research** and be more aware of the possibilities of environmental and ecological risks.

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