

Silicone Safety and the Cosmetic Industry

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ABSTRACT: *The use of silicones in personal care products continues to expand because of the unique performance attributes they provide and their well-established record of safety. As a result, progressively larger volumes of silicones are being released to the environment, and interest in their life cycle has increased. The present article summarizes relevant fundamental chemical and physical properties of silicones and how these relate to material performance, safety and environmental fate.*

Silicones are ubiquitous in personal care products with good reason. The variety of silicone materials available and their unique performance characteristics make them beneficial for a wide range of cosmetic applications. Decades of scientific research, combined with actual experience in market applications, have provided a large knowledge base relevant to safety and environmental aspects of silicones. The materials science of silicones is also well-developed and has enabled an understanding of the relationship between fundamental physical/chemical properties and bulk material properties. This article attempts to summarize important aspects of these relationships, specifically with respect to safety and environmental considerations associated with personal care products. Linking key performance characteristics at a macro level with underlying chemistry on a molecular scale can provide a deeper and broader foundation for design, formulation and development of personal care products. With structure-property relationships established, a brief summary of current literature relating to environmental aspects of the use of silicones is provided. This should assist in evaluating various claims

made in connection with personal care products containing silicones.

If properly designed and manufactured, silicones are highly biocompatible materials.

Defining Silicones

The term *silicone* covers a vast range of material types—from watery liquids to “fluids” that are stiff enough to walk on; from highly hydrophobic substances to completely water-miscible materials; from soft gels to stretchy elastomers to brittle, glasslike resins. Developed commercially in response to important practical needs¹ by combining the best attributes of flexible organic materials and inert inorganic minerals (quartz), silicones have expanded far beyond where the early pioneers likely imagined they would and into a diverse array of fields, including aerospace, electronics, engineering, health care, medical devices, automotive and maritime industries, construction, food and

beverage and personal care.

One of the most fundamental defining attributes of silicones is a backbone or skeletal structure composed of repeating —Si—O— units (termed siloxane), with organic groups occupying any of the bonding sites on the silicon atom not already occupied by oxygen atoms, as shown in **Figure 1** on Page 812. Various combinations of these building blocks are thus referred to generically as organosiloxanes. The organic groups are often denoted by the letter “R” in shorthand chemical structures and can be selected from a long list of species. Most commonly, the organic fragments are methyl groups (—CH_3 or —Me), hence the frequent appearance of the word fragment methi- in the ingredients list of common personal care products (e.g., dimethicone, cyclomethicone, etc.). Other groups—including vinyl, long chain alkyl, hydroxyl, alkoxy, phenyl, polyether, alkylamine, among others—can also be found in personal care silicones. Silicone materials used in personal care products contain mostly difunctional “D” units, in which each silicon atom is bound to two oxygen atoms and two organic groups. Other —Si—O— framework arrangements are found in silicones for personal care products to a lesser degree. Some hair fixatives contain these silicone resin structures. Resins can contain various combinations of “M,” “D,” “T” and “Q” units. The chemical structures of resins are more complex so they are often simply described as “MQ,” “MDQ,” “MT,” etc. resins. More detailed descriptions of the various structures associated with silicones can be found in numerous books and reviews in the scientific literature.^{2–7}

Relevant History

The early development of silicones was driven by industrial and military needs. However, less than a decade after E.G. Rochow’s 1940 discovery of the

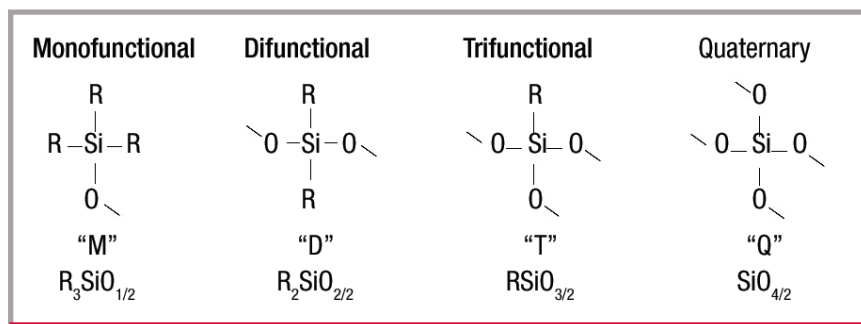


Figure 1. Basic building blocks of siloxanes

direct process that enabled industrial production on a large scale,¹ silicones were already finding important uses in the medical world.⁵ In the late 1950s, silicone was used to produce the first functional and easily sterilized implantable shunt to treat hydrocephalus.⁷ By the late 1960s, interest in silicones for health care applications had grown substantially and scores of applications to address human needs had either been successfully launched or were being actively investigated, providing a rich source of early clinical data on safety and performance. A summary of this early experience appeared in Walter

Noll's book *Chemistry and Technology of Silicone*,² which described applications in the areas of medicine, pharmaceuticals and cosmetics. In the decades since, research, development and product applications have only expanded. Throughout its history, the combination of silicone's unique properties has proven to be exceptionally useful in a wide variety of medical, health care and personal care materials for human use. In the personal care field, low-viscosity fluids have been used in deodorant and hair care formulations since the 1970s. Medium- to high-viscosity fluids are found in numerous products such as

skin creams, hair shampoos, conditioners and styling products, while elastomers and resins find uses in color cosmetics and hair styling products, to name a few.^{8,9} The various performance characteristics of silicones are derived from their molecular attributes including backbone flexibility, low intermolecular interactions and large distances between molecules, the nature of the organic side groups, and the stability of the various bonds between atoms in the molecules. In this article, these are explored further in relation to the human safety aspects of silicones. In general, careful design at the molecular level gives rise to the material attributes that are important to performance in personal care such as degree of hydrophobicity/hydrophilicity, permeability, spreadability and optical properties.

Human Safety

One of the clear conclusions drawn from decades of human use and controlled scientific studies, along with ongoing regulatory scrutiny, is that if properly designed and manufactured, silicones are highly biocompatible

materials. Biocompatibility as defined by a number of researchers is “the ability of a material to perform with an appropriate host response in a specific situation.”^{10, 11} Clearly, long-term implantation poses different challenges than a topical application and, therefore, understanding the attributes of silicone *as they relate to a specific use* is critical. Skin sensitization, allergic response, eye irritation and toxicity are likely to be more relevant to cosmetics applications than immune response in, for example, a subcutaneous implant. However, the inherent characteristics of the silicone material being used are fundamentally important regardless of their end use.

Relationships between molecular structure and physical properties are important to understand for almost any material, and silicone is no exception. Decades of investigation on silicones have produced a large body of knowledge that is relevant to safety, including physical form and deformation behavior, chemical inertness/stability and biocompatibility/impact on a cellular level.

Physical form and deformation behavior: Most silicones used in personal care are either flowable liquids or soft elastomers. Silicone polymers have low glass transition temperatures, meaning they still flow at temperatures well below those typically experienced by humans. Silicone gels and reinforced elastomers useful in personal care applications are not physically “stiff” enough to cause tissue injury, even in situations involving significant stresses such as vigorous rubbing. These attributes arise from the extreme flexibility of the siloxane backbone, and large distances and low attractive forces between polymer chains.¹²

Chemical inertness/stability: The linkages between Si, O, C and H atoms in organosiloxanes are highly stable. Chemical transformations are possible but require extremely reactive agents (strong acid or base, high energy radiation, high temperatures, etc.) to be carried out. This means that conditions found in normal personal care applications are not severe enough to cause any significant chemical reaction or degradation. Silicones degrade at different

rates over time depending upon specific conditions found in the environment forming innocuous by-products (see the **Environmental Safety** section), but the time frame and chemistry of those transformations are not relevant to human exposure in personal care applications.

Biocompatibility/impact at the cellular level: Cosmetics and personal care product manufacturers conduct appropriate biocompatibility testing guided by the demands of end use performance and by requirements of the International Organization for Standardization, the US Food and Drug Administration and United States Pharmacopoeia and others. Generally speaking, satisfactory performance requires acceptably low impact in biologically relevant in vitro or in vivo test environments. At the heart of acceptable behavior is the impact of the material at the cellular level. The chemical stability and low toxicity of silicones is a major contributing factor to their biocompatibility. An abundance of peer-reviewed biological impact data is available for silicone raw materials, as well as finished

silicones. An excellent entry point into this literature is through Silicones Environmental Health and Safety Council (SEHSC) publications.¹³ The Siloxane Research Program has been conducting studies and publishing data on the safety of silicones since 1994. From a practical perspective, purity is also a consideration.⁶ Carefully manufactured silicones produced in clean facilities under strictly controlled conditions do not contain contaminants that could adversely affect biocompatibility.¹⁴ If not carefully excluded, non-silicone materials commonly found in a manufacturing environment such as solvents, lubricating materials, caustic materials, etc., could contaminate silicones and create issues ranging from mild irritation to toxic or allergic responses.

Environmental Safety

A large body of literature exists concerning the environmental fate and effects of siloxanes, a significant portion being directly relevant to personal care applications. Recent reports,¹⁵ reviews^{16–18} and book chapters^{9, 19} provide summaries of and/or numerous references to the primary literature. The field is still being actively researched as evidenced by recent publications.^{20–24} Various regulatory agencies located in North America and Europe continue to weigh evidence and consider appropriate responses with industry groups providing input to the process.^{25, 26} This section attempts to provide a brief summary based upon currently available information, along with some key lead references.

Volatile silicones: Volatile silicones are employed in a wide variety of personal care applications, including underarm deodorants, hair products and cosmetics, often as a diluent or delivery vehicle. The vast majority (> 90%) of these volatile silicones end up in the atmosphere as a consequence of direct evaporation. The consensus appears to be that these materials have average atmospheric lifetimes ranging from ~9 to ~30 days depending upon the specific compound and are transformed ultimately into silicon dioxide, water and carbon dioxide through photo-induced oxidation involving hydroxyl radicals.^{16, 21, 22} As discussed, silicones are stable under conditions typically experienced by humans; however, these hydroxyl

radicals are extremely reactive species and initiate the degradation of silicones via well-described pathways.²⁷

Reliable measurements of volatile siloxane concentrations in the atmosphere have been limited until recently. McLachlan et al. described a method for capturing and quantifying airborne D5 and compared measured levels (0.3–9 ng/m³) with predictive models, emphasizing that measured D5 levels are approximately 10⁸ times lower than the “no observable adverse effect level (NOAEL)” of 435 mg/m³ for exposure of mammals via inhalation reported in the UK risk assessment.²² Genauldi et al., reported atmospheric levels of several linear (L3 – L5; range = below detection limit–0.66 ng/m³) and cyclic (D3 – D6; range = below detection limit–280 ng/m³) volatile siloxanes at 20 sampling sites around the world and compared those with modeled values.²¹ These levels are also at least 10⁵ times lower than the NOAEL reported for a similar series.²⁸ Both reports support the claim that volatile siloxanes are subject to long-range atmospheric transport.

The small fraction of volatile siloxanes from personal care products that partition to the condensed phase generally are deposited in sanitary sewer streams destined for wastewater treatment plants after being washed off.⁹ A small portion of these siloxanes passes through these plants and are released into surface waters, which has generated great interest in determining their actual concentrations, persistence and bioaccumulation potential. Recent publications have reported improved analytical methods for capture and quantitation²⁰ and, separately, measurement of volatile siloxanes in sediment near wastewater treatment plant outfall, nearby zooplankton and various fish and mammals.²³ Levels found in zooplankton and mammals were less than the method detection limit (sub part-per-billion). Bioaccumulation in the livers of fish ranged from part-per-billion to part-per-million levels and varied depending upon whether the fish were from lakes near a populated area versus remote areas with less impact from human activity. Given these levels, the question of toxicity to fish arises. Two recent lab studies²⁹ involving exposure of rainbow trout to the maximum possible aqueous concentrations of D5

(saturation limit) found no observable effects. SEHSC's summary assessment of ecological effects submitted to Environment Canada³⁰ provides additional information, supporting a claim of "no effect" along with references to relevant peer-reviewed literature. Research into potential environmental effects of volatile siloxanes continues as regulatory agencies work to develop appropriate responses.³¹

Semi-volatile/non-volatile methylsiloxanes and polyether-modified silicones: Due to their lack of volatility, most of these silicone materials from personal care products wind up in sanitary systems after being washed off. Upon processing through wastewater treatment facilities, the majority of these silicones remain bound to solids that settle out.⁹ This sludge, in turn, is primarily landfilled or used in surface soil treatment. A minor portion is incinerated, converting any silicone into silicon dioxide, water and carbon dioxide. Even less is discharged to surface waters. The fate of these silicones in sludge, soil and water has been extensively investigated.¹⁶ In general, complete degradation occurs in soil where silicones are exposed to reactive conditions, while minimal degradation occurs in landfilled sludge. The small amounts of these silicones that are discharged to surface water eventually wind up in soil or sediment,^{16, 22} where well-described degradation processes ultimately produce innocuous silicon dioxide, water and carbon dioxide.

Organofunctional siloxanes: Organofunctional siloxanes found in personal care products represent a much smaller portion of total siloxanes entering the environment.⁹ The processes acting on these materials depend upon the nature of the functional group(s) present. More hydrolytically stable materials (e.g., long chain hydrocarbon or aminoalkyl siloxanes) typically contain only low levels of functional group; therefore, they are expected to follow the same degradation pathways experienced by methyl siloxanes. Alcohol-functional siloxanes are much less stable with respect to water exposure and degrade primarily via hydrolysis mechanisms. The ultimate products in both cases are again silicon dioxide, water and carbon dioxide.

Summary / Conclusions

Clear relationships exist between the

fundamental molecular attributes of silicones and their performance characteristics in personal care products. Material properties responsible for the benign nature of silicones when human exposure is concerned are directly linked to these molecular attributes, as are more qualitative properties such as spreadability, breathability, skin feel, wash-off resistance and shine. While silicones are stable under conditions typical for human exposure from personal care products, under more reactive conditions and over longer time scales such as those found in soils and atmosphere, degradation occurs via well-described pathways. Interest in the environmental fate of volatile siloxanes has recently increased. Government agencies working to assess potential environmental impact are examining emerging information from new and ongoing scientific investigations. As full participants in the scientific debate, industry groups claim there is compelling evidence that siloxanes are nontoxic in the environment.

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