

JOURNAL OF COSMETIC SCIENCE

The Official Journal of the Society of Cosmetic Chemists

*Publishing technical papers on topics of
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SOCIETY OF COSMETIC CHEMISTS

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Overcoming Challenges in Silicone Alternative Solutions in Personal Care

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Accepted for publication November 11, 2024.

Synopsis

Silicones are widely used in cosmetic formulations due to their specific physicochemical properties and resulting strong contributions to the performance on skin and hair. However, restrictions for cyclic silicones put in force by the European Union coupled with increasing consumer demands for cosmetics based on renewable resources and biodegradable ingredients result in cosmetics formulators facing challenges to find silicone alternatives while maintaining product performance levels. In this review, the challenges in finding alternative solutions are described for the three different types of silicones: volatile (cyclic), low molecular weight (linear), and high molecular weight (linear) silicones. While there are replacements for volatile silicones, which match many properties, the substitution of the other two types is more difficult and typically requires the adjustment of the complete formulation. This is shown with several examples.

INTRODUCTION

Silicones (Polydimethylsiloxanes and derivatives) have been used in cosmetics products for decades due to their unique sensory and conditioning properties for both hair and skin applications^{1, 2, 3}. For skincare applications, silicones produce a pleasant “silicone-like” sensory effect. In addition to this, silicones also reduce the soaping or whitening, which is an undesired sensory aspect appearing upon applying skin-care emulsions on skin. For haircare, they contribute to claims like hair shine, combability, or reduced hair breakage.

The distinctive properties of silicones can be explained by molecular characteristics, which are quite different from carbon chemistries. The silicon-oxygen and silicon-carbon bonds are comparatively longer in comparison to the carbon-carbon and carbon-oxygen bonds due to increased steric repulsion owing to a larger silicon (Si) atom. Therefore, for silicones, the bonds have a high degree of freedom, and the molecules have a high flexibility. This unique structure with the Si–O–Si backbone and the hydrophobic side groups results in properties like low surface energy and thus low surface and interfacial tension leading to

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fast spreading on surfaces like skin and hair⁴. Additionally, silicones are very stable over a wide range of temperatures and conditions.

On the other hand, silicones require an energy-intensive process to make⁵. The initial step of this process is the production of silicon metal from mined quartz and various reduction agents in submerged electric arc furnaces. The required reducing gas such as carbon monoxide or hydrogen is produced from fossil materials such as coal or in some cases even biobased materials such as charcoal and woodchips. This production of silicon metal is considered to be the most energy consuming and hence greenhouse gas emitting part of the entire process of making silicone polymers.

In the next step, the silicon metal obtained is then reacted with methyl chloride and further with water to remove the chlorine. That chlorine is then recycled to make methyl chloride. Subsequently, the resulting products are separated into various fractions and then polymerized into silicone polymers.

From an environmental perspective, it is worth noting that silicones are not biodegradable⁶. After several years of evaluation and debate, the European Union has finally restricted⁷ the use of octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5), and dodecamethylcyclohexasiloxane (D6) to a maximum concentration below 0.1% w/w in both leave-on and rinse-off applications. The rationale for this restriction is that D4, D5, and D6 are considered to be substances of very high concern (SVHC) due to their very persistent (vP) and very bioaccumulative (vB) properties. Even if the restriction has been set only for the volatile, cyclic silicones, the decision has an impact on the perception of silicones in cosmetics in general. Furthermore, the regulatory bodies in other regions can also be expected to follow with such bans.

In anticipation of bans for different silicones, and to actively remove cyclic silicones in personal care formulations before the published deadlines (June 6, 2026, for the use of D6 in rinse-off (D4/D5 for use in rinse-off products are already banned since January 31, 2020) and June 6, 2027, in leave-on applications), formulators are looking to substitute them with more natural alternatives. However, a direct replacement of silicones with natural emollients is not trivial due to the unique properties of silicones described above. Therefore, an exact 1:1 replacement by products based on carbon chemistry is currently not possible. Formulators must adapt the entire formulation to match the properties of the formulation with silicones.

The entire class of silicones, i.e., polydimethylsiloxanes and derivatives, contains products with different ingredient chemistries. Cyclic siloxanes, namely D4, D5, and D6, are comparatively lighter in feel (to other silicones) and volatile. Out of these, especially D5 is still widely used in skincare, color cosmetics, and hair oil applications. The INCI for cyclic silicones found in cosmetic market products is cyclomethicone. Likewise, linear “polymerized” polydimethylsiloxanes with a generic chemical structure of $R_3Si\{O-SiR_2\}_n-O-SiR_3$, also widely used in cosmetics, have the INCI name dimethicone. Depending on the degree of polymerization (n), one obtains different dimethicones with different properties. Indeed, dimethicones from 1 cSt to several thousand cSt are used in different personal care applications. In terms of their properties, lighter dimethicones (1–350 cSt) are emollients while heavier ones are gums (>1,000 cSt). The generic INCI of dimethicone for all these different compounds with different properties can be somewhat misleading. In hair care, two other variants are used: Dimethiconol—same backbone and methyl groups as dimethicones but equipped with terminal hydroxygroups, or

amodimethicone, which are dimethicones containing a cationic sidechain. In addition to those and cyclic silicones, silicone elastomers are used. However, they constitute a very small share of the personal care market products and therefore will not be discussed in this paper. Figure 1 shows the molecular structures of the different silicone emollient types and some emollients based on carbon chemistry, which are often used in cosmetics.

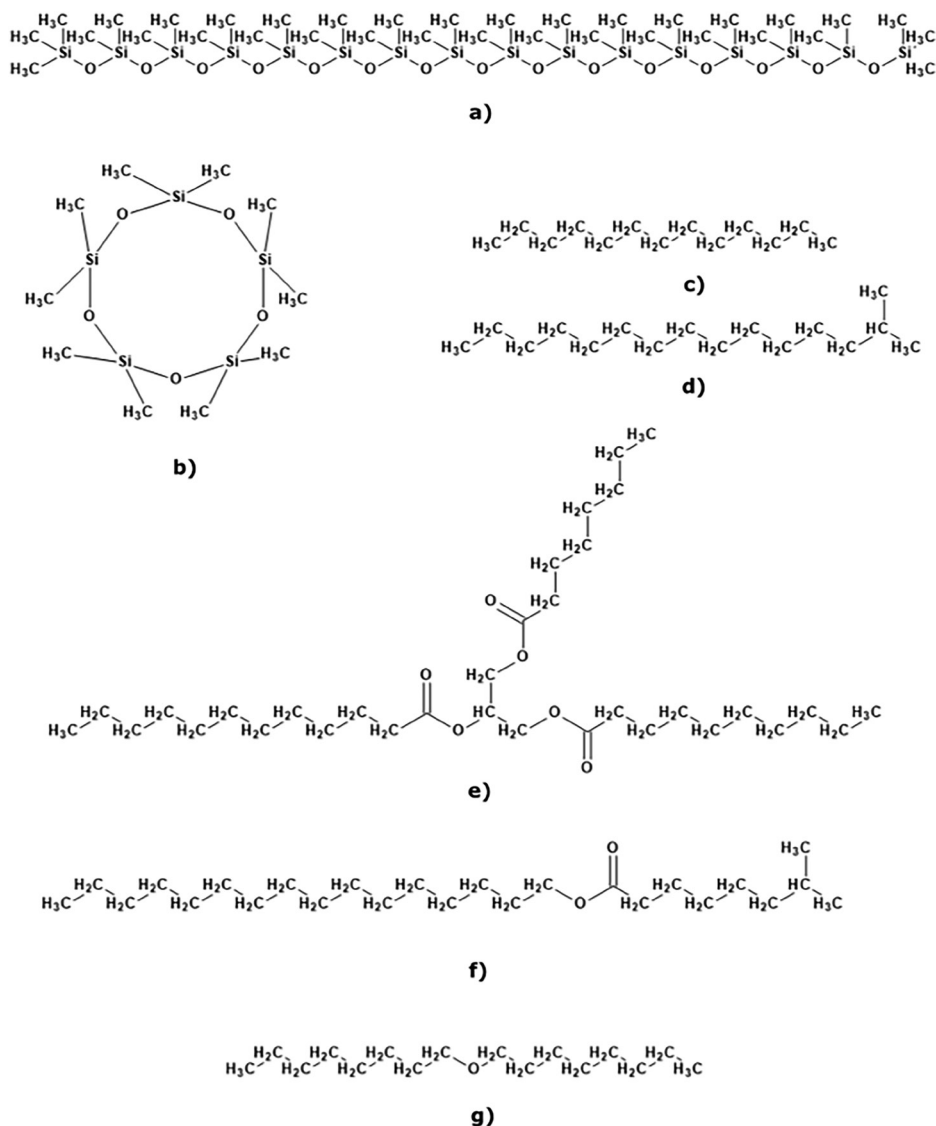


Figure 1. Representations of silicone versus natural emollients used in personal care cosmetics. a) simple snapshot representation of a linear “polymerized” polydimethylsiloxanes commercially known as dimethicone. The degree of branching and polymerization determines the product viscosity and sensory properties of the dimethicone, b) cyclopentasiloxane (D5), c) hydrocarbon-based tridecane, d) hydrocarbon based isohexadecane, e) a triglyceride, f) an ester, g) an ether-based emollient. Other emollients are guerbet alcohols or mixtures between these different classes.

In the next sections, we show approaches to explore natural-based alternatives to the following silicones:

- Volatile (cyclic) silicones.
- Low molecular weight silicones.
- High molecular weight silicones.

CHALLENGES AND ATTEMPTS IN REPLACING VOLATILE (CYCLIC) SILICONES

The special property of cyclic silicones is their volatility, which makes these silicones feel extremely light on skin. They are used extensively in leave-on applications ranging from face care, sun care, color cosmetics, hair care, and particularly often in antiperspirants and deodorants. Volatile silicones provide a light skin feel that remains after their quick evaporation. Moreover, they are excellent solvents for all other silicones used in cosmetics.

When replacing volatile silicones in cosmetic formulations, several approaches are undertaken. Currently, the most common approach is to replace them with hydrocarbons. Their polarities and viscosities are similar to silicones, and they are available in a large variety of characteristics. In case high volatility is important, low boiling hydrocarbons like isododecane or undecane are the preferred choice. The usability of these hydrocarbons as silicone alternatives was proven for a facial foundation: A tinted day care fluid was formulated with an ultra-fast-spreading emollient mixture (undecane and tridecane). It was shown that this formulation could match the properties of the silicone containing formulation for mechanical smear resistance, rain resistance, gloss kinetics, blemish coverage, and color homogeneity⁸. In case more substantivity is required, many other options are available, like isoheptadecane, C15–C19 alkanes, (hemi-)squalane⁹, or petrolatum liquidum¹⁰. These are only some of the most frequently used examples among an abundance of options available. Hydrocarbons can be used from fossil and bio-based sources as well¹¹.

Although hydrocarbons offer a large flexibility to the formulator, they still miss some of the desired sensorial aspects of silicones. Therefore, hydrocarbons can be mixed with a sensorial agent. In these mixtures, often volatile hydrocarbons are used to mimic the volatility of silicones, and the sensorial aspect is covered by a non-volatile ester such as diheptylsuccinate. By adjusting the mixing ratio, the viscosity can be set to similar ranges as known from dimethicones. Volatile hydrocarbons are also used by silicone polymer producers when they must replace cyclomethicone solvents for these polymers. In all these approaches, ingredient suppliers try to match the performance of silicones as closely as possible to reduce the efforts needed by the formulator.

Additionally, another approach worth mentioning is the replacement of unwanted cyclic silicones with linear dimethicones. On the one hand, this approach is affecting the full formulation only to a minor extent, making it easier for formulators, but on the other hand, it does not eliminate silicones completely and should only be seen as an intermediate solution.

Beyond this ingredient-driven replacement, one could also revise the formulation from the beginning to replace silicones. This attempt can be found in formulation areas where silicones played a major role in the past, like anti-perspirants or deodorants formulations. In these cases, the simple replacement by another ingredient influences so many aspects of the formulation that a total revision is needed. For example, ester emollients like isopropylpalmitate or propylheptylcaprylate, or ether types of molecules like PPG-15

stearyl ether or PPG-14 butyl ether are used together with hydrocarbons, depending on the most important needs of the formulator (including costs and sensorial aspects).

In hair oil formulations, large quantities (70–95%) of cyclic D5 are used to dissolve high molecular weight, high-viscous dimethiconol or other silicones. Due to the high volatility of D5, this is an elegant way to treat the hair with small amounts of these heavier silicones, avoiding hair that feels and looks greasy. In addition to this, the high molecular weight silicones act as rheology modifiers, i.e., to thicken the flow behavior of the final product. Viscous hair oil formulations are needed for consumers to apply the product more easily and to avoid the aspiration of the hair oil by the consumer. Therefore, to react to the imminent D5 ban, substituting cyclic silicones requires alternative solutions to dissolve high molecular weight silicones. Besides very low molecular weight dimethicones, volatile hydrocarbons (e.g. (iso)dodecane, undecane, tridecane, isohexadecane) can be used as solvents giving similar properties. Another silicone alternative option is replacing them with lighter emollients like dicaprylyl carbonate, coco-caprate, or dicaprylyl ether in hair oil sprays.

CHALLENGES AND ATTEMPTS IN REPLACING LOW MOLECULAR WEIGHT (LINEAR) SILICONES

Dimethicones are utilized in skin care applications for two primary reasons. Firstly, they serve as conventional emollients that impart the desired sensory profile to the formulation, resulting in a pleasant, waxy, slippery, and light silicone-like skin feel. In this regard, lighter dimethicones with viscosities ranging from 1 to 50 cSt are employed as sensory-inducing emollients, and they are typically incorporated in significant quantities.

The second function of silicones is to act as anti-soaping or anti-whitening agents. Certain ingredients widely used in cosmetics, such as fatty alcohols or biopolymers, can enhance a whitening effect when the emulsion is rubbed on the skin due to foaming. This undesired effect is perceived as unpleasant by consumers. However, by incorporating a small amount of a silicone into the formulation, the whitening effect can be eliminated. It is important to note that the quantity required to achieve the anti-whitening or anti-soaping effect is significantly lower than what would be used with a conventional emollient. Including larger amounts of heavier dimethicones in skin-care emulsions can result in a greasy and sticky sensory feel.

With growing consumer awareness for sustainability aspects, and brands preparing for potential regulatory bans on all types of silicones, a dimethicone-free trend is rapidly gaining momentum. Formulators are faced with the challenging task of finding natural and high-performing alternatives to dimethicones, often working within tight timeframes.

In the present section, light dimethicones that are commonly used in skincare for their sensory benefits will be the focus. The initial step in this process involves identifying natural-based emollients or mixtures that can match the sensory and physicochemical performance properties of dimethicone at the emollient level. This can be achieved by combining emollients with different properties, such as varying polarities, spreading values, viscosity, and sensory characteristics. By doing so, formulators can attain a good level of flexibility in terms of potential replacements.

However, it is worth noting that the process of selecting the appropriate emollient and determining the ideal ratio to mimic the performance of dimethicone can be quite daunting. The intricate nature of this decision-making process adds an additional layer of complexity to the formulation development journey.

Assume that a formulator has narrowed down the potential replacements to only a few candidates based on their experience, supply, and cost guidelines. However, in reality, the number of potential options could be significantly higher. It is unlikely that any single emollient among these candidates on its own would be a perfect match to dimethicones. The number of potential binary or ternary mixtures that could match the performance of dimethicones can easily become very large. It is important to note that no formulator would explore all possible candidates, as it would be extremely time-consuming and expensive. However, it is highly likely that the ideal natural-based candidate to replace dimethicones is present within these possible mixtures. Therefore, it is evident that one needs an alternative method to capture potential candidates.

An effective approach to overcome this challenge is to leverage digitization, scientific modeling, and the benefits derived from enhanced computing power. One such option is Emollient Maestro¹², a digital service that can be utilized to identify natural-based candidates as replacements for a wide range of synthetic silicones, including D5 and dimethicones with viscosities ranging from 1 to 200 cSt, mineral oils, and hydrocarbon-based emollients such as isododecane, isohexadecane, squalene, and many more.

The algorithm powering Emollient Maestro employs prediction and optimization models that theoretically explore all possible emollient combinations and then return the best ones that match a given synthetic dimethicone benchmark. This service offers a highly efficient, quick, and cost-effective solution for formulators to identify potential replacements for dimethicones and other synthetic emollients.

Figure 2 illustrates the emollient-level performance profiles of dimethicone 5 cSt, which is commonly used in skin care emulsions for its sensory benefits, and an optimized natural-based emollient mixture of dicaprylyl carbonate, dicaprylyl ether, and undecane/tridecane (ratio 1.7:3.2:1) obtained from Emollient Maestro. The left panel in Figure 2 shows an overlapping physico-chemical profile of the silicone (which was experimentally measured) versus the natural-based emollient mixture (which was predicted). In this panel, various properties that formulators consider when selecting a new ingredient, i.e., viscosity,

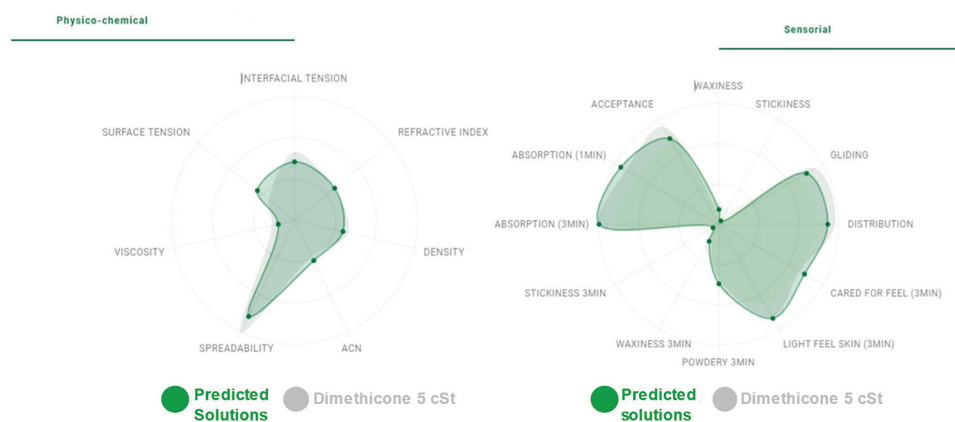


Figure 2. Physico-chemical (left) and monadic sensory (right) comparisons between dimethicone 5 cSt (experimentally measured) and a natural-based emollient combination recommended by Emollient Maestro (prediction), exhibiting a good agreement at the emollient level.

spreading value, density, refractive index, surface tension, interfacial tension (polarity), and equivalent alkane carbon number are compared.

The right panel of Figure 2 shows an overlapping sensory profile of the silicone versus the natural-based emollient mixture. The sensory profile of dimethicone was assessed using trained panelists and is represented on a monadic scale, while the sensory profile of the natural-based emollient was theoretically estimated using Emollient Maestro. It is worth noting that Figure 2 demonstrates a good agreement between both the physico-chemical and sensory profiles of dimethicone 5 cSt and the natural-based emollient mixture proposed by Emollient Maestro.

As previously discussed, the unique structures of dimethicones mean that they are used in personal care formulations for a secondary reason, namely as anti-whitening agents. Therefore, removing dimethicones can lead to a strong undesired whitening effect on the skin upon application. This is caused by the formation of foam due to the presence of ingredients such as fatty alcohols and biopolymers, which are present in significant quantities in cosmetic emulsions. Small amounts of dimethicones can reduce the foaming and significantly reduce the whitening effect.

By utilizing solutions from Emollient Maestro and adjusting selected galenic ingredients, formulators can develop a truly silicone-free skin care formulation with the same performance. Through experimentation with various combinations in a reference formulation, the following combinations can prove to be effective. Firstly, using mono- and diglyceride-based waxes as an alternative to fatty alcohols offers advantages in minimizing whitening effects. In addition, incorporating biopolymers such as alginate, when cross-linked with CaCl_2 , can produce particles that further reduce the whitening effect while providing a pleasant and non-sticky feel on the skin.

Furthermore, it is crucial to carefully select emulsifiers that have a neutral sensory impact. This means opting for emulsifiers that do not dictate or negatively influence the sensory characteristics of the final formulation. By choosing emulsifiers with a neutral sensory profile, the desired sensory attributes of the silicone-free formulation are maintained.

By employing these strategies and combinations, formulators can successfully develop a silicone-free skin care formulation that meets the desired sensory and performance criteria.

The effectiveness of this approach has been tested on a benchmark day care face cream¹³ that would typically contain 10% of dimethicone 5 cSt, commonly found in the market. Figure 3 depicts a sensory comparison between the formulation containing dimethicone 5 cSt and the formulation containing emollient mixtures predicted by Emollient Maestro. The results of the comparison revealed that the natural-based formulations exhibited an almost identical sensory profile during application of the day care face cream as the one containing dimethicone. This rigorous evaluation process allows an estimation of the sensory attributes of the silicone-free formulation in a standardized manner, ensuring reliable and consistent results.

A standardized assessment allows an objective estimation and comparison of the whitening effects of the formulations, providing valuable insights into the performance of the natural-based alternative. The results indicate that both the formulation containing dimethicone 5 cSt and the natural-based alternative effectively minimize the whitening effect typically associated with the absence of dimethicone.

Day Care Face Cream

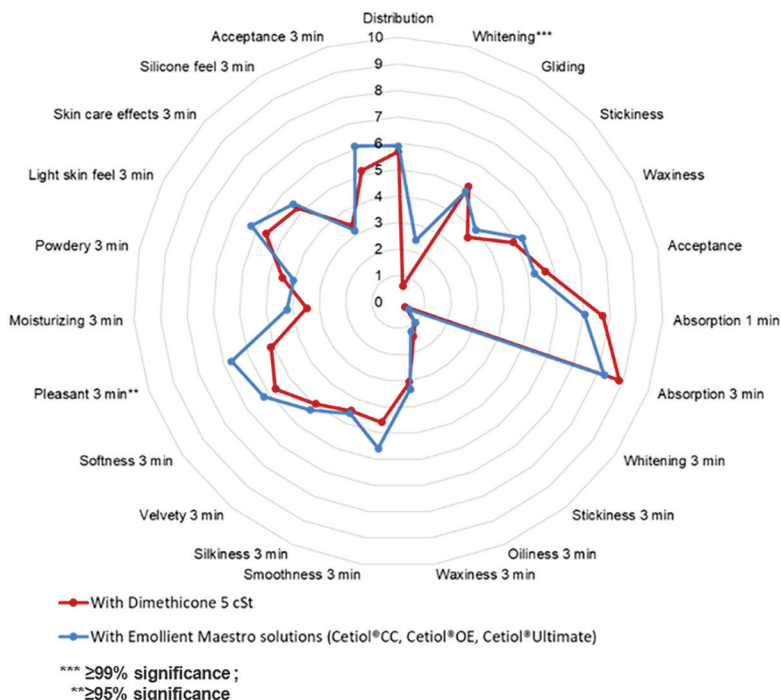


Figure 3. Monadic (formulation level) sensory comparison between the 100% natural-based day care face cream formulation and one containing Dimethicone 5 cSt.

In conclusion, digital methodologies combined with formulation development can be effective in creating true dimethicone-free and biodegradable formulations. This empowers formulators to concentrate their resources on exploring the combination of galenic ingredients that could result in a silicone-free product.

CHALLENGES AND ATTEMPTS IN REPLACING HIGH MOLECULAR WEIGHT (LINEAR) SILICONES

For hair care formulations (shampoos, conditioners, hair oils), high molecular weight silicones are used (see above). Their substitution is even more challenging because their performance is a result of the described silicone specific properties like low surface energy and their high molecular weight. Therefore, all alternative ingredients so far on the market will not be able to cover all performance aspects of these silicones. The challenge to deposit conditioning substances on hair from shampoos is the same for silicones as for alternative solutions. In classical shampoos based on anionic surfactants (sulfate surfactants, especially sodium laureth sulfate), cationic polymers have been used since the 1970s to co-deposit them on the hair. This is achieved via so called co-acervates, which phase separate upon dilution when the shampoo treated hair is rinsed^{14,15}. The same mechanism can be used to deposit alternatives to silicones on the hair. Among the alternatives to silicones, natural oils¹⁶ like coconut oil, shea butter, argan oil, etc. are often used. To incorporate such natural

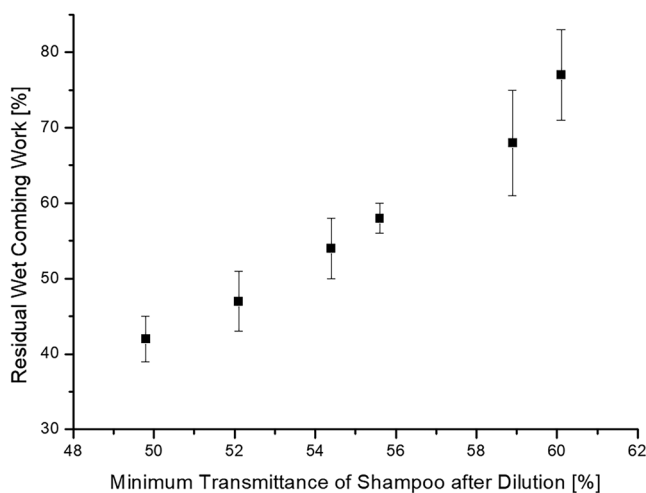


Figure 4. Residual wet combing work versus minimum transmittance of the investigated shampoo.

oils and other emollients into shampoos can be as challenging as for high molecular weight silicones. An elegant vehicle to tackle this challenge is the use of (micro)emulsions. One example is a microemulsion based on a light emollient showing good conditioning performance¹⁷. It could be shown that the amount of phase separation occurring by dilution (measured as minimum transmittance) correlates well with the conditioning effect of wet hair (measured as residual wet combing work, which is the relation of the combing work after shampoo treatment to the combing work before treatment) (Figure 4). The more precipitation occurs (less transmittance), the better the conditioning effect (lower residual combing work).

Another alternative launched more recently is a mixture of polycitronellols in volatile hydrocarbons¹⁸. The authors report improved wet and dry hair conditioning and anti-hair breakage compared to some light emollients including D5. Another product is based on hydrogenated polyfarnesene, a high viscous biobased ingredient claimed to be similar to dimethiconol in combing, gloss, and gliding when applied from a rinse-off hair mask¹⁹.

Further alternatives can be found in the area of wax dispersions. The use of ethylene glycol distearate as pearlizing and opacifying wax in surfactant-based formulations is well known in the industry. Opacifying wax dispersions generally consist of smaller particles that can be deposited on the hair surface using the coacervate mechanism described earlier. With this deposition, the wax particles can also offer hair care benefits like improved wet or dry conditioning²⁰. A recently launched wax dispersion is based on hydrogenated vegetable oil as a wax component. This product combines pearlshine appearance with excellent hair care properties, particularly in hair breakage protection. This was shown in different shampoos in comparison to placebo formulations²¹. Specific results are given in Figure 5 for two surfactant chassis, one comprising of sodium coco-sulfate and coco-glucoside and the other based on sodium cocoyl glutamate and coco-glucoside.

With the performance benefits shown for these wax dispersions, major excellent hair care properties of silicone-based shampoos like conditioning or hair breakage protection can be reached without silicones. However, as for skincare formulation, a simple drop-in

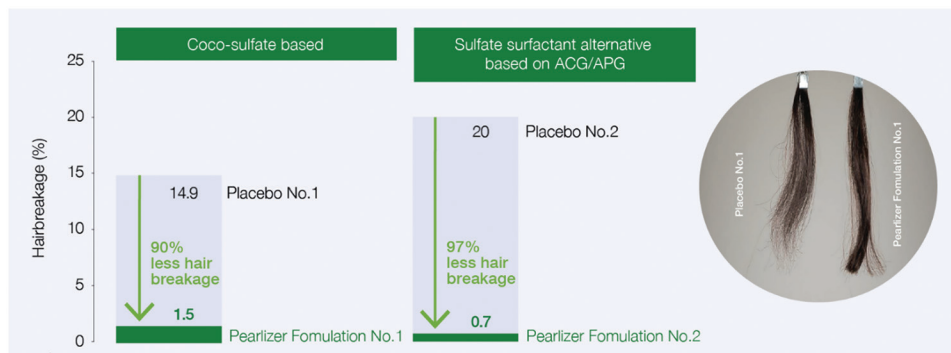


Figure 5. Hair breakage protection results of a pearlizing wax dispersion in two shampoo formulations.

replacement is not possible. Again, the formulation must be adapted, and for high performance, a combination of the different alternatives must be considered, also to fine-tune for the specific product positioning and claims.

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