

# **Silicones as Alternatives to Hydrocarbons in Personal Care Formulations**

**Alfred J. DiSapio  
Dow Corning U.S.A.**

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## Abstract

The use of silicones in personal care products has been expanding rapidly. A significant portion of this increased use has been in place of hydrocarbons. For at least 15 years, silicones have been incorporated into personal care products as a partial replacement or improvement additive for several classes of organic compounds traditionally used as ingredients in cosmetics and toiletries. This movement from hydrocarbons to silicones has been ongoing, driven by several market forces, and at an increasing rate.

Most of the hydrocarbons affected were from categories of fatty chemicals, including the esters, acids, and alcohols. Cost differential has been narrowing as the volume of silicone used increases and the demand for greater purity has added cost to some organics. When the added value of sensory and functional benefits is considered, the balance of total value is frequently in favor of silicones.

The flexible functional and sensory capabilities of silicones make them an interesting candidate for the reduction of organic materials in cosmetic and toiletry formulations. This presentation provides a useful comparison between silicones and several of the hydrocarbon classes of materials from sensory, functional, and environmental perspectives. In addition, formulation examples from various personal care product segments illustrate how silicones can help meet increasingly stringent marketplace needs.

## Introduction

Over the past 15 years, silicones have been evaluated and used as substitutes or enhancements for several classes of organic materials. Various organic ingredients such as esters, alcohols, and fatty compounds have been affected by silicone technology. Some replacement has occurred in the following product segments:

<b>Segment</b>	<b>Material Replaced by Silicones</b>
Antiperspirant	Ester
Deodorant	Ethanol
Sunscreen	Mineral oil
Color cosmetics	Ethanol, mineral spirits
Fragrance	Ethanol
Skin care	Mineral oil, esters, fatty compounds

Recently, the group of materials described by the Cosmetic, Toiletry and Fragrance Association (CTFA) as hydrocarbons has been the focus of more active re-

placement efforts. The CTFA describes these materials as a group of compounds containing only carbon and hydrogen, mostly derived from petroleum. As a rule, they are chemically inert and may contain aliphatic, alicyclic, and aromatic compounds.<sup>1</sup> Pressure to replace hydrocarbons in personal care products is growing as a result of several factors, including:

- A demand for improved functional performance, such as moisturization
- Interest in the enhanced therapeutic value offered by protective and non-comedogenic products
- Regulatory issues, such as volatile organic compound (VOC) restrictions
- A shift in sensory preferences on the part of consumers
- Consumer attitudes, including concern over petroleum derivatives
- Availability and understanding of alternative materials

## The Emergence of Oil-Free Products

Mineral oil, a petroleum distillate, is a ubiquitous cosmetic and toiletry ingredient from the hydrocarbon class. It is widely used as an emollient and unctuous vehicle. The CTFA describes mineral oil as a mixture of saturated hydrocarbons, which is highly refined to minimize aromatics, metals, and other impurities. The material is further described as having a molecular weight range between 220 and 530 and a viscosity range between 3 and 100 cSt at 40°C.<sup>1</sup> The lower molecular weight distillates have the CTFA nomenclature of mineral spirits and have been used as solvents in a variety of makeup products.

Mineral oil was previously on the periphery of the trend toward replacement of organic materials. It is widely used, and an extensive knowledge base has been developed with respect to formulating it into oil-in-water emulsions, the most common skin care product form. However, two recent market developments have focused interest on the replacement of mineral oil: changes in sensory needs and consumer environmental concerns.

First, sensory perceptions of oiliness and greasiness have become increasingly significant consumer-perceived parameters. Consumers have been conditioned to appreciate light, dry, silky-feeling products with minimal perceptible residue. This preference change has resulted in the emergence of an "oil-free" product category. An examination of the products in the foundation and cleanser categories launched in the U.S. in 1990 and 1991 not only reveals expanding silicone use, but suggests that silicones are being used in oil-free products to perform some of the functions typically attributed to mineral oil, such as emolliency. Table I summarizes these product launches.

**Table I. A summary of foundation and cleanser products introduced in 1990 and 1991.**

	Advertised as oil-free	Not advertised as oil-free
No. containing mineral oil	2 (10%)	44 (51%)
No. containing silicone	11 (58%)	26 (30%)
Total no. of products	19	86

As might be expected, 51% of the products not advertised as oil-free contain mineral oil. Surprisingly, a small number (10%) of those advertised as oil-free still contain some mineral oil. It is also clear from these data that the percentage of products using silicones in oil-free categories has almost doubled from 30% in the non-oil-free category to 58% in those advertised as oil-free.

Reinforcement for this change and the reasons behind it came from a consumer focus group study conducted in Germany, France, and the United Kingdom, which shed additional perspective on the concept of oil-free.<sup>2</sup> In all three countries, the concept of oil-free/non-

greasy was positive for most skin care products, with a strong preference for the "non-greasy" terminology. The desire for non-greasy products appeared to reflect consumer interests in benefits such as:

- An ability to absorb or rub in quickly
- No residue or pore clogging effect
- A non-sticky feel
- No skin shine

## Environmental Trends

The second marketplace force is the ongoing consumer concern about the environment. The impact of this issue on mineral oil use in cosmetics and toiletries is analyzed in a recent trade article.<sup>3</sup> The author reports that consumer-driven environmental interests started with a movement toward the elimination of pesticides, moved on to the elimination of animal-derived ingredients, then to the "Green" movement, on to "natural" products, and finally to environmentally safe products. He further states that "one of the major issues confronting these environmentally concerned manufacturers is the elimination of petrochemical derivatives..." and continues, "The systematic review of formulations to eliminate petrochemical derivatives has focused on mineral oil..." One of the author's conclusions is: "Based on this information, it would seem that silicones may offer some possibilities as replacements for mineral oil."

Recent studies summarize the environmental safety profiles of dimethicone and cyclomethicone, the two most commonly used families of silicone in personal care products.<sup>4</sup> In addition, on the consumer side, it is interesting to note that some major consumer publications position "silicones" toward the natural category. Descriptions of this type are significant, because until there are acceptable industry standards for the terms "natural" or "naturally derived," consumer beliefs are a determinant factor. For example, in one instance, silicones are described as a "derivation of natural minerals."<sup>5</sup> In another example, silicone is described in the following manner: "...it's natural—most of it comes from the sand you lie on when you're on the beach ..."<sup>6</sup>

It is also important to note that the CTFA dictionary does not classify silicones as oils. Instead, silicones are typically classified as specialty chemicals.<sup>1</sup> Similarly, chemical references define mineral oils as a mixture of liquid hydrocarbons derived from petroleum,<sup>7</sup> a definition that excludes polydimethylsiloxane (PDMS).

## Functional and Sensory Characteristics

In comparing mineral oil and silicone for cosmetics and toiletries, the subjects of emolliency, occlusivity, comedogenicity, and sensory characteristics must be considered.

### Emolliency

It is generally agreed that the primary function of min-

eral oil in a formulation is emolliency, which can be viewed as having two components, spreadability and lubricity. These parameters have been quantified and reported for dimethicone and various hydrocarbons.<sup>8</sup> Based on panel evaluations, the authors report that dimethicone, 350 cSt, has the highest spreadability and is rated as more spreadable by a factor of ten compared to mineral oil, 150 cSt.

Based on lubricity measurements obtained with a skin friction device, dimethicone has a friction factor three times lower than that of mineral oil. From formulas derived in the paper for calculating emolliency,<sup>8</sup> dimethicone shows significantly greater emolliency than mineral oil: by a factor of eight when measured during the application period, and by a factor of five when measured as residual emolliency.

Further, low molecular weight polymers of dimethicone and cyclomethicone are uniquely classified as the most astringent emollients of all thirty hydrocarbons tested. As molecular weight is increased, they become substantial protective emollients. They are the only materials to exhibit this bifunctional capability.

**Occlusivity**

Mineral oil has sometimes been characterized as providing some occlusivity, which is related to skin moisturization. But this assertion is not supported by data from transepidermal water loss measurements, which provide a fairly direct indication of occlusivity. A recent study shows that “the major ingredient affecting occlusivity of the O/W emulsion systems is petrolatum, not mineral oil.”<sup>9</sup> Most silicone fluids are recognized as non-occlusive. Some organically modified

silicone products such as stearoxytrimethylsilane and stearyl alcohol do provide considerably greater occlusivity than mineral oil although significantly less than petrolatum.

**Comedogenicity**

An initial study showed silicones of all classes tested to be non-comedogenic.<sup>10</sup> A more extensive study confirmed the earlier work, reporting that silicones showed “no significant increase in follicular keratosis,” the most innocuous rating.<sup>11</sup> The same study also indicated that mineral oil was more erratic with respect to comedogenicity, with scores ranging from no effect to mild comedogenicity. Significantly, the study listed many other oils, such as hydrogenated vegetable oil, soybean oil, sesame oil, cotton seed oil, fish oils, and some esters such as PPG-2 myristyl ether propionate, to have moderate to severe comedogenic potential.

**Sensory characteristics**

Products such as baby oil that have a light, oily feel on the skin have been generally accepted by consumers; those that feel greasy, such as petroleum jelly, have not. However, oiliness and greasiness are only two of twelve parameters that can be used to compare the sensory characteristics of products. Using guidelines recommended by ASTM Committee E18.03.01 on Sensory Evaluation, one can construct a sensory profile to scientifically evaluate feel. Sensory profiles of various grades of mineral oil and silicone provide useful comparisons of the materials.

Based on the ASTM guidelines, the sensory evaluation program employed for these studies used a 20-mem-

**Table II. System used to quantify sensory evaluation of personal care materials.**

Observations		0	1	2	3	4	5	6	7	8	9	10	
<b>Stickiness</b>	Not sticky	Baby oil										Lanolin	Sticky
<b>Wetness</b>	Dry	Baby powder										Water	Wet
<b>Spreadability</b>	Hard	Lanolin										Baby oil	Easy
<b>Absorbency</b>	Low	Lanolin										Protein	High
<b>Gloss</b>	Dull	Denture adhesive										Baby oil	Shiny
<b>Slipperiness</b>	Draggy	Lanolin										Baby oil	Slippery
<b>Residue</b>	No residue	Untreated skin										Zinc oxide ointment	Lot of residue
<b>Smoothness</b>	Rough	Denture adhesive										Glass	Smooth
<b>Tackiness</b>	Not tacky	Untreated skin										Lanolin	Very tacky
<b>Oiliness</b>	Not oily	Untreated skin										Baby oil	Very oily
<b>Greasiness</b>	Not greasy	Untreated skin										Petroleum jelly	Very greasy
<b>Waxiness</b>	Not waxy	Untreated skin										Lanolin	Very waxy

ber trained panel to evaluate skin feel properties. The descriptive analysis method summarized in Table II is used to quantify each of the twelve sensory attributes on a scale from 1 to 10. For example, lotion stickiness is evaluated based on baby oil, which is given a reference rating of zero (representing “not sticky”) and lanolin, which is given a reference rating of ten (representing “sticky”).

Figure 1 shows the sensory profile of mineral oil (8 cSt) compared to linear PDMS (5 cSt). The profiles are essentially identical. However, this is not the case with all viscosities: in Figure 2, a comparison of mineral oil (350 cSt) to linear PDMS (350 cSt) shows significant

differences between the mineral oil and silicone. The difference is most pronounced in the comparison of tackiness, absorbency, and spreadability parameters. There are lesser but significant differences in the perceptions of the perceptions of greasiness, slipperiness, stickiness, and wetness. In comparison, linear PDMS (50 cSt) has a remarkably similar sensory profile to mineral oil (350 cSt) as shown in Figure 3. The sensory profile of mineral oil (130 cSt) can be matched quite well with phenyltrimethicone, a silicone fluid with a viscosity of 50 cSt. Figure 4 shows this comparison.

Duplicating the sensory profile of petrolatum with a simple silicone compound is more difficult. Linear PDMS

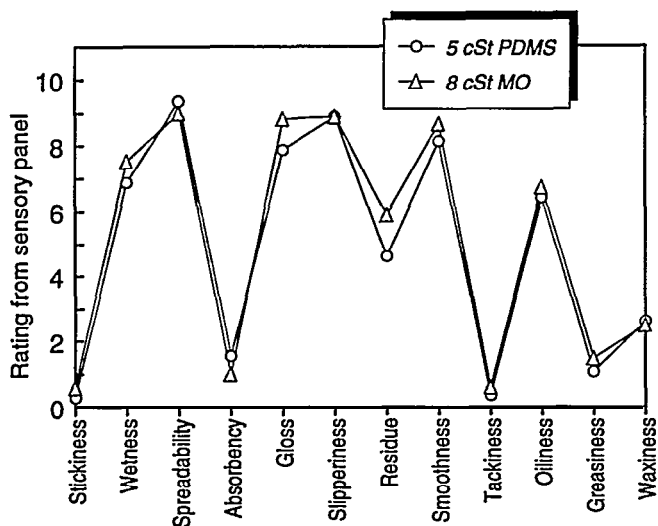


Figure 1. Sensory profiles of low viscosity mineral oil and silicone are similar.

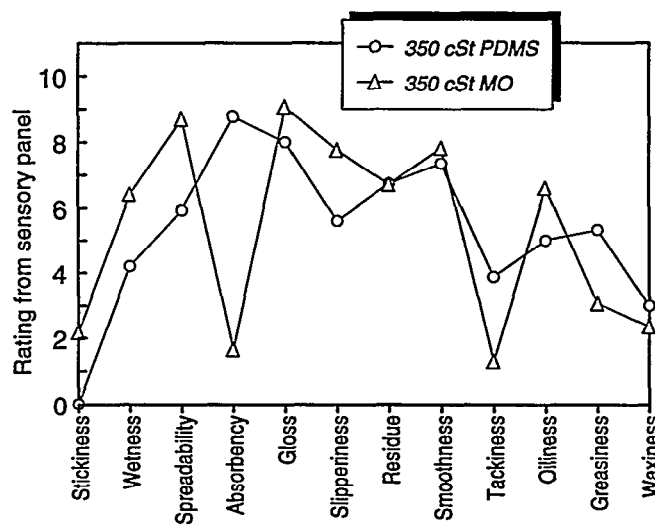


Figure 2. Profiles of intermediate viscosity materials show significant differences.

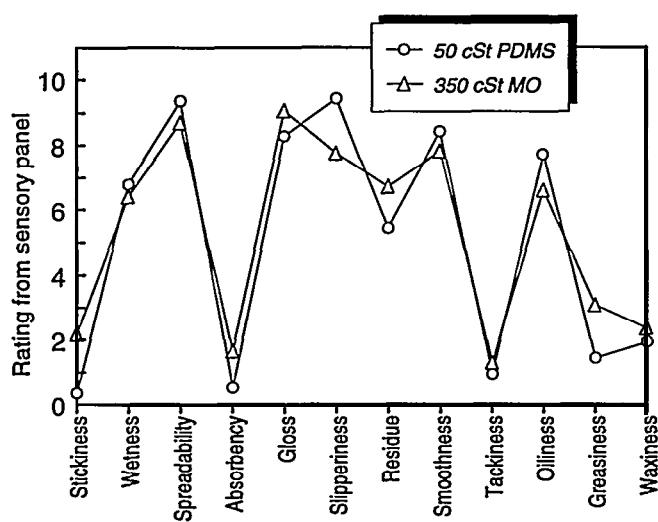


Figure 3. Profile of 50 cSt linear PDMS is similar to 350 cSt mineral oil.

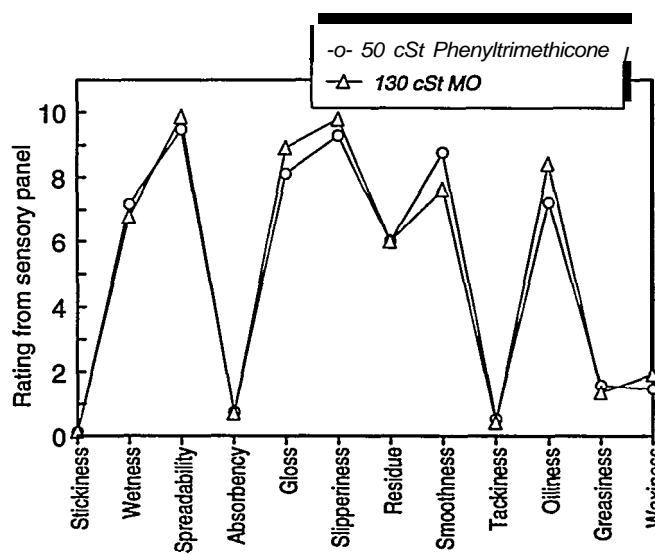


Figure 4. Profile of 50 cSt phenyltrimethicone is similar to 130 cSt mineral oil.

(5,000 cSt) is a relatively close match. Examination of these profiles in Figure 5 shows a similarly shaped profile with quantitative differences, especially in the parameters of tackiness, smoothness, slipperiness, and gloss.

One general difference between silicones and mineral oil in these sensory evaluations appears to be their wide differences in sensitivity to changes in viscosity. The perceived feel of mineral oil is remarkably insensitive to changes in viscosity. This relationship is illustrated in Figure 6, which shows the sensory profiles of four mineral oils with viscosities from 8 to 350 cSt. The profiles are essentially similar.

For some sensory parameters, in contrast to mineral

oil, silicones do show significant differences with viscosity changes. For example, Figure 7 shows how the sensory parameter of residue changes with viscosity for both linear and cyclic methyl silicones, while mineral oil displays little if any difference to perceptions of residue with variations in viscosity. In other words, all viscosities of mineral oil measure relatively high on the residue scale.

Another facet of sensory perception is the ability of some silicones to lessen the oiliness and greasiness of mineral oil when incorporated as additives. For example, some baby oil products on the market contain significant quantities of cyclomethicone to enable improved feel claims.

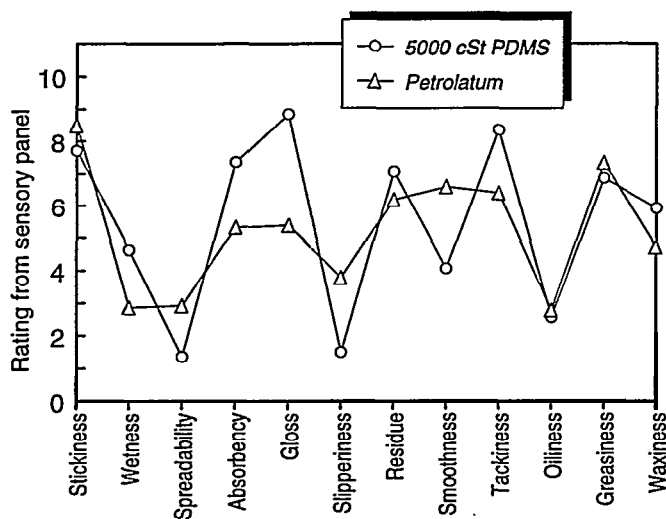


Figure 5. Sensory profile of high viscosity linear PDMS compared to petrolatum.

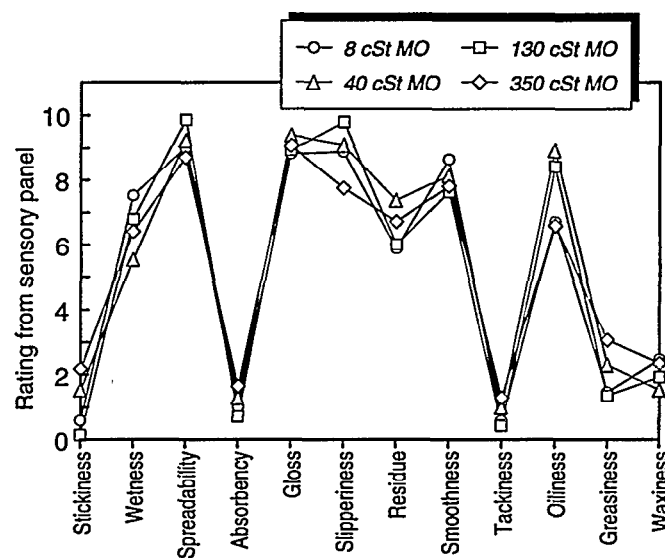


Figure 6. Profiles of mineral oils show relative insensitivity to viscosity.

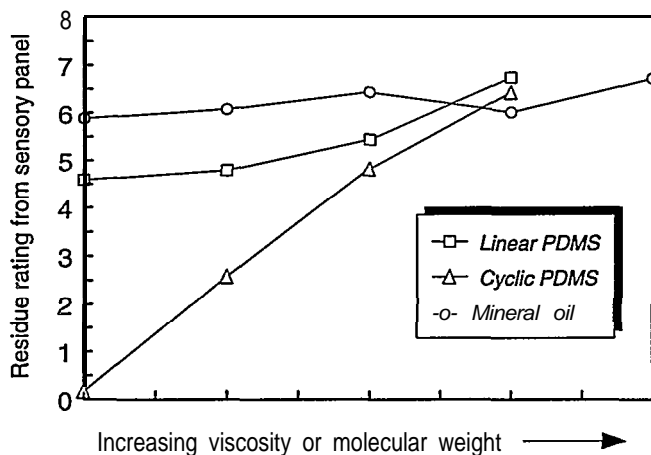


Figure 7. For silicones, residue changes with viscosity, but not for mineral oil.

### Silicone Alternatives

Several silicones are candidates to replace mineral oil in cosmetics and toiletries. The following summary highlights their significant characteristics.

- **Cyclomethicone:** a classification for low viscosity polydimethylsiloxane fluids that volatilize at skin temperatures. Their sensory profile is similar to very low viscosity mineral oil.
- **Cyclomethicone and dimethicone copolyol:** a silicone formulation aid used to emulsify water into cyclomethicone. Emulsions of this type have many of the sensory characteristics of cyclomethicone.
- **Dimethicone:** a classification for polydimethylsiloxane fluids available in a wide range of viscosities. These fluids are generally non-volatile and widely used as skin protection ingredients. Their profiles may be similar to those of mineral oil, but may not be alike for equal viscosities.

- **Phenyltrimethicone:** a phenyl-substituted silicone with broad organic compatibility. This 50-cSt fluid has a sensory profile similar to that of 350-cSt mineral oil; uses are similar to those of dimethicone.
- **Stearoxytrimethylsilane and stearyl alcohol:** a wax-like solid with higher occlusivity than most silicones and mineral oil. The sensory profile indicates a waxiness component approaching that of petrolatum, but with significantly less tackiness, stickiness, and greasiness. Figure 8 compares this silicone with petrolatum.

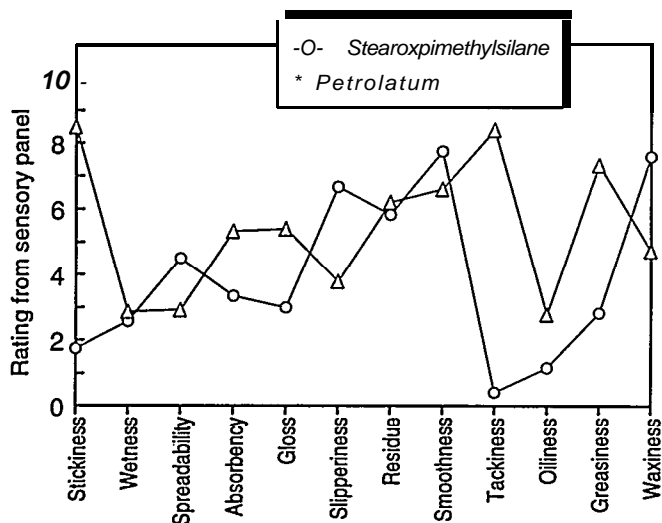


Figure 8. Wax-like silicones can approach waxiness of petrolatum with less tack, stick, and greasiness.

## Formulations

A growing number of formulations in the industry literature illustrate how silicones can be used to reformulate traditionally mineral oil-based products with little or no mineral oil. Clearly, some ingredients and quantities must be adjusted due to differences in solubilities and viscosities. Table III illustrates the ingredient category for several product forms (cream foundation, lipstick, sunscreen lotion, and sunscreen oil) and compares two typical formulations for each category: one that incorporates mineral oil and the other silicone.

## Conclusions

In summary, many of the important characteristics of mineral oil in cosmetic and toiletry formulations can be duplicated or improved with silicones, and silicones can be used to formulate a variety of products in the oil-free category. Several silicones are available to impart characteristics such as emolliency, tactile properties, and non-comedogenicity to formulations. In addition to simulating components of the sensory characteristics of many mineral oils, silicones offer considerable flexibility in designing sensory profiles with improved consumer-perceptible components.

Table III. Typical formulations for several personal care product categories.

<i>Cream foundation</i> <i>with:</i>	Mineral oil <sup>a</sup> (%)	Silicone <sup>b</sup> (%)
Emulsifier	9.0	2.4
Emollients	7.0	2.2
Moisturizers	5.7	10.0
Thickeners	1.0	0.5
Pigments	11.0	16.5
Water	40.0	53.0
Mineral oil	20.0	-
Cyclomethicone	-	15.0
Preservative and fragrance	q.s.	q.s.

<sup>a</sup> *Cosmetics and Toiletries*, April 1992, formulary, page 93.

<sup>b</sup> Dow Corning Formulary, E9362-22D.

<i>Lipstick</i> <i>with:</i>	Mineral oil <sup>c</sup> (%)	Silicone <sup>d</sup> (%)
Pigment grind	20.0	32.4
Waxes	15.0	16.0
Stearoxytrimethylsilane (and) stearyl alcohol	-	4.5
Lanolin oil	5.0	10.0
Avocado oil	-	29.6
Esters	14.0	7.0
Mineral oil	40.0	-
Preservative and fragrance	q.s.	q.s.

<sup>c</sup> *Cosmetics and Toiletries*, April 1992, page 96.

<sup>d</sup> Dow Corning Formulary, E2-1452.

<i>Moisturizing sunscreen lotion</i> <i>with water in:</i>	Mineral oil <sup>e</sup> (%)	Silicone <sup>f</sup> (%)
Emulsifier	4.00	10.00
Mineral oil	15.00	-
UV absorber	7.50	7.00
Water	61.35	64.97
Humectant	6.00	3.00
Emollient	5.00	5.00
Silicone	-	10.00
Preservative and fragrance	q.s.	q.s.

<sup>e</sup> Grillo-Werke AG.

<sup>f</sup> Dow Corning Formulary, 90-CMD012.

<i>Clear sunscreen "oil"</i> <i>with:</i>	Mineral oil <sup>g</sup> (%)	Silicone <sup>h</sup> (%)
Mineral oil	68.0	-
Cyclomethicone (tetramer)	16.0	57.0
Cyclomethicone (pentamer)	-	16.0
Dimethiconol	-	3.0
Ester	13.0	20.0
UV Absorber	3.0	4.0

<sup>g</sup> *Cosmetics and Toiletries*, Vol. 102, March 1987, page 102.

<sup>h</sup> *Drug and Cosmetic Industry*, February 1986.

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