

**New Approaches for Assessing Conditioning and  
Quantifying Silicone Deposition on Hair**

Beth Johnson  
Lylene Canfield  
Dow Corning Corporation  
Midland, MI USA

Stephane Van Oycke  
Christophe Dubois  
Anne Dupont  
Claude Letouche  
Tina Scavuzzo  
Dow Corning S.A.  
Seneffe, Belgium

**S**avvy consumers want it all. Less frizz and flyaway. More body and control. Less breakage and dryness. More shine. Easy combing. Silicones have represented solutions in hair conditioners for a number of years. In some cases, their penetration grew faster than the market itself (1). Despite the broad use of silicones, maximizing their conditioning benefits continues to be an area of investigation. In addition, exact knowledge of the amount of silicone deposited on hair after treatment with a conditioning formulation is an important tool for the formulator, allowing practical correlation between product composition and sensory evaluation results. This information can also help screen ingredients to speed product development.

The first step in optimizing silicone deposition is to determine how broadly the deposition mechanism can be applied to several different types of polyquaternium materials and silicones, as well as any synergies that exist in terms of conditioning performance. The variables investigated included composition, viscosity and charge density of the polyquaternium materials and internal phase viscosity and surfactant type for the silicone emulsions. Secondly, a new analytical method was developed to quantify the amount of silicone deposited on hair.

### **The Mechanism for Silicone Deposition**

The deposition of some silicones onto hair from a shampoo can be significantly increased by the use of specific cationic polymers that form complexes with the anionic surfactant of the shampoo. The cationic polymers are soluble in the undiluted shampoo but become insoluble at low surfactant concentrations (i.e., after lath-

ering and during rinsing). When the shampoo is diluted by the wet hair and rinse water, the polymer surfactant complex precipitates out of solution and onto the hair through a process called coacervation (2). The hydrophobic colloidal coacervate then helps deposit other particulate material such as silicone fluids and emulsions onto the hair. For fine particle size polydimethylsiloxane emulsions (< 2 microns), this mechanism ensures the most efficient deposition onto the hair from a shampoo. Previous studies also have demonstrated synergistic effects between polyquaternium materials and dimethicone copolyols (3).

### **Materials and Methods**

The shampoo formulation used for this study was a basic sodium lauryl ether sulfate system. The active concentration of silicone and polyquaternium in the shampoo formulation was 2% and 0.5% by weight, respectively. Lower levels of the polyquaternium material, 0.2 and 0.3% by weight, were also investigated.

The following silicone materials were evaluated:

- Dimethiconol (and) TEA-dodecylbenzenesulfonate (an anionic emulsion)
- Divinyldimethicone/dimethicone copolymer (and) C12-C13 pareth-23 (and) C13-C15 pareth-3 (a nonionic emulsion)

Polyquaternium test materials included:

- Polyquaternium-4
- Polyquaternium-7
- Polyquaternium-10
- Polyquaternium-11
- Guar hydroxypropyltrimonium chloride

The conditioning properties of the

polyquaternium and silicone materials in the shampoo formulation were evaluated using a standard combing method and an Instron<sup>a</sup> device. Slightly bleached hair tresses<sup>b</sup> were used for the studies. An average of three tresses per formulation and an average of five combings per tress were evaluated. Baseline measurements were taken with each untreated hair tress before 0.8 g of shampoo was applied. The tresses were rinsed after application and the dry and wet combing forces were measured. The percent reduction in combing forces was calculated, and statistical analyses were performed to determine differences between treatments.

Deposition of silicone was measured using a new analytical technique described in a separate section of this article. The method is based on acidic digestion and derivatization of the silicone deposited on the hair surface followed by analysis by capillary gas chromatography with flame ionization detector.

### **Results**

Results from the Instron tests showed improved wet and dry combing performance over the polyquat materials alone for hair tresses treated with shampoos containing the high molecular weight anionic or nonionic silicone emulsions and polyquaternium-7, polyquaternium-10 and cationic guar. An additional study was performed using 0.2 and 0.3% polyquaternium-7, polyquaternium-10 and guar in the shampoo formulation with the nonionic silicone emulsion. Synergistic effects were observed for wet and dry combing with all combinations except polyquaternium-7. Figures 1 and 2 summarize the Instron combing results with the anionic and nonionic silicone emulsions.

<sup>a</sup> Manufactured by Instron Corporation, Norwood, MA USA.

<sup>b</sup> DeMeo Brothers, New York, NY.

## A New Method for Quantifying Silicone Deposition

A number of analytical methods have been developed to quantitatively assess silicone deposition (4), but they generally are lacking either in sensitivity or in selectivity. The most commonly applied are X-ray fluorescence (XRF) and atomic absorption (AA). These two methods are not specific because they are based on the total *silicon* content of the hair or the surface film rather than on the measurement of *silicone* from the deposited polymer. In addition, for the atomic absorption method, inefficient extraction of more strongly adsorbing siloxanes such as amodimethicones, in our experience, leads to high variability, making it unsuitable for quantitative measurements of these analytes.

To overcome these issues, we extended the scope of the functionality test method. This method is based on the cleavage of the siloxane polymer chain by a strong acid or base, followed by derivatization of the resulting species and analysis of the products of derivatization after neutralization. This method was originally developed to quantify low level branching in siloxane fluids and has now been successfully extended to siloxane fluids on various fibrous and nonfibrous surfaces.

The method consists of immersing 0.2 g hair samples (cut close to the tip, the root or the middle of the hair tress) in a large excess of a siloxane dimer (e.g., hexaalkyldisiloxane) and a soluble strong acid. A suitable internal standard is added. The sealed reaction vial is agitated for at least 30 min after which the solution is neutralized. This treatment breaks all Si-O bonds and pro-

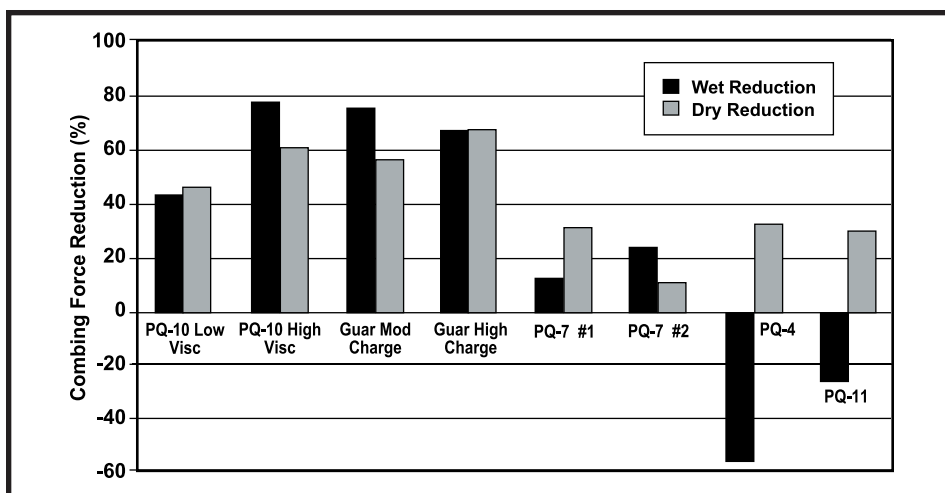


Figure 1. Instron combing results with the anionic silicone emulsion.

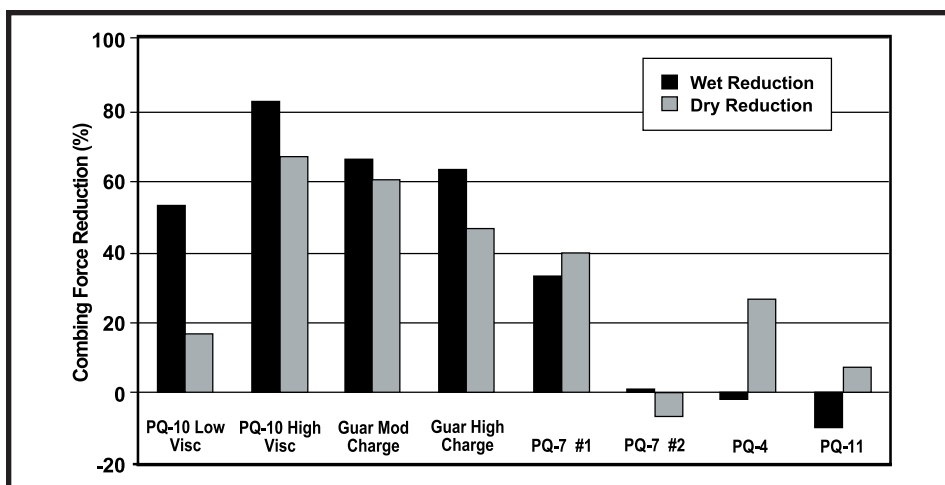


Figure 2. Instron combing results with the nonionic silicone emulsion.

Table 1. Polyquat and Silicone Synergies

Polyquat Material	Nonionic PDMS Emulsion; Dry Treatment	Nonionic PDMS Emulsion; Wet Treatment	Anionic PDMS Emulsion; Dry Treatment	Anionic PDMS Emulsion; Wet Treatment
PQ-10 Low Visc				
PQ-10 High Visc				
Guar Mod Charge				
Guar High Charge				
PQ-7 #1				
PQ-7 #2				
PQ-4				
PQ-11				

Statistical Difference:   
 p < 0.1   
 p < 0.05

Comparisons were made between the polyquaternium alone and combined with the silicone emulsions. As Table 1 indicates, several synergies between the polydimethylsiloxane emulsions and polyquaternium materials were observed in this study.

From a patent perspective, the studied art suggests much greater freedom to use polyquats

such as polyquaternium-10 and polyquaternium-7 with pre-formed dimethicone emulsions in shampoos (although restrictions appear to still exist with dimethiconol preformed emulsions as well as microemulsions). Formulators should be prepared to fully research how current patents may impact their proposed developments.

duces a volatile trisiloxane. The amount of dimethylsiloxo units contained in the deposited polymer is quantitatively analyzed by injecting a fraction of the organic phase in a gas chromatograph with a flame ionization detector (GLC-FID) and comparing the relative peak areas corresponding to the derivatized dimethylsiloxo units versus the internal standard. For each series of sample, at least one blank (untreated) hair sample is measured.

For the analysis of silicone deposition from hair<sup>c</sup> treatment formulations, 2 g tresses of natural brown or slightly bleached oriental hair were first washed with a 30% sodium lauryl sulfate solution then treated with 0.4 g of shampoo or rinse-off conditioner per tress. The tresses were lathered for one min-

ute, allowed to stand for another minute, and rinsed under running water (37° C) for one minute. For multiple washes, the second part of the treatment was repeated as required. The tresses were allowed to dry at room temperature overnight before analysis.

*Recovery.* Tests performed using a standard addition of known siloxane fluids to normal and bleached hair tresses (3) have shown recoveries ranging from 80 to 140%, including for amodimethicone and cationic materials such as silicone quaternium-16. Table 2 summarizes the theoretical and actual amounts of silicone recovered from the treated tresses.

*Limit of detection and repeatability.* The limit of detection is 10 ppm and limit of quantification is 50 ppm. All analyses were run

at least as duplicates. Relative standard deviation for silicone levels on hair in the range 100-500 ppm was about 20%; for the range 500-1000 ppm, it was 15% and for silicone levels greater than 1000 ppm it was less than 10%.

*Measurement of deposition from conditioning shampoos.* The natural brown hair tresses were repeatedly treated under standard conditions with a selection of leading-brand conditioning shampoos for up to ten consecutive washes. Table 3 compares results of silicone analyses on the tresses after 1, 3, 5 and 10 washes showed differing levels of deposition.

*Removal of deposited silicones.* The tresses were treated by repeated dipping into diluted silicone fluid emulsion, resulting in deposition of a large excess of silicone fluid on the surface. Further washing of these tresses with a commercially available leading brand clarifying shampoo easily removed the excess deposit.

*Quantifying deposition and synergy in conditioning.* This new analytical method was also used successfully to quantify the impact of the various polycationic polymers on the deposition of dimethicone from the anionic and nonionic silicone emulsions described in the first part of this study. Table 4 summarizes these results. Polyquaternium-10, or cationic guar, in combination with the anionic emulsion, resulted in the highest level of deposition onto the hair, followed by cationic guar and polyquaternium-7. The high molecular weight nonionic emulsion, in combination with polyquaternium-10, also resulted in good deposition.

**Table 2. Recovery of Various Silicones from Treated Hair**

Silicone	Bleached Hair		Normal Hair	
	Theoretical Amt (ppm)	Measured Amt (ppm)	Theoretical Amt (ppm)	Measured Amt (ppm)
Dimethicone	--	--	100	97
	--	--	200	243
	--	--	1000	1378
Dimethiconol	--	--	100	91
Trimethylsilylamodimethicone	100	123	100	--
	1000	1097	1000	1248
Amodimethicone	200	169	200	174
	2000	1654	2000	1609
Silicone Quaternium-16	100	82	100	94
	1000	822	1000	932

**Table 3. Deposition of Silicone on Sample Tresses After Repeated Washes**

Shampoo	No. of Washes	Deposition (ppm)
Repairing shampoo for damaged hair	1	222
	3	192
	5	382
	10	279
Fortifying shampoo for frequent use	1	187
	3	284
	5	324
	10	425
Repairing shampoo for dry hair	1	597
	3	989
	5	937
	10	1190

<sup>c</sup>International Hair Importers, White Plains, N.Y.

**Table 4. Deposition of Silicone (ppm) from Various Anionic and Nonionic Emulsions**

Treatment	Average Deposition (ppm)
Anionic PDMS Emulsion	ND
Anionic PDMS Emulsion + PQ-7	17
Anionic PDMS Emulsion + Guar	1050
Anionic PDMS Emulsion + PQ-10	1287
Nonionic PDMS Emulsion	20
Nonionic PDMS Emulsion + PQ-7	38
Nonionic PDMS Emulsion + Guar	172
Nonionic PDMS Emulsion + PQ-10	572

### Conclusions

Instron combing results showed improved wet and dry combing performance for hair tresses treated with shampoos containing dimethiconol (and) TEA-dodecylbenzenesulfonate (the anionic silicone emulsion) or divinyl-dimethicone/dimethicone copolymer (and) C12-C13 pareth-23 (and) C13-C15 pareth-3 (the nonionic silicone emulsion) and polyquaternium-7, polyquaternium-10 and cationic guar. The deposition results correlated well with the conditioning results. Polyquaternium-10, in combination with either silicone emul-

sion resulted in the highest level of deposition onto the hair, followed by cationic guar and polyquaternium-7. By maximizing the synergy of silicones with polyquaternium materials, formulators gain increased flexibility to optimize the desired level of conditioning benefits.

The new analytical method was successfully used to quantify the impact of various polycationic polymers on the deposition of dimethicone from emulsion. It has the benefit of being widely applicable, including polar siloxanes, and is specific to the determination of siloxanes instead of

total silicon. It is also based on affordable analytical equipment (GLC-FID) routinely available in most analytical or QA laboratories. This method is now used on a routine basis in our laboratory to help formulators assess the efficacy of conditioning formulations by a method other than qualitative sensory testing. Results from the deposition evaluations and analytical studies show promise for the creation of hair care products that meet specific demographic needs or those of regional markets. This approach can serve as a useful screening tool to help formulators more quickly select the most appropriate materials for product development.

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