

## **A preliminary investigation of the interaction of a quat with silicones and its conditioning benefits on hair**

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### **Synopsis**

Silicones, especially dimethicone and dimethiconol of higher molecular weights, have gained acceptance as conditioning agents and are used in several commercial products, frequently in conjunction with quats. In this work, the conditioning benefits of the silicones, as assessed by improvement in wet and dry combing, were investigated as a function of molecular weight as well as amount deposited on bleached hair. In addition, the combing performance of a quat was evaluated for the purpose of comparison, and its influence on the silicones, as pertaining to deposition and combing performance, was assessed.

All the silicones improved wet and dry combing performance substantially over untreated hair. Their performance was greater than that of the quat for wet combing but was comparable for dry combing. The higher molecular weight gums showed slightly improved dry combing performance over the lower molecular weight fluids, but there was no significant difference between them for wet combing.

Presence of the quat increased the amount of silicone depositing on the hair. A synergistic effect of the two was seen in that a significantly greater wet combing performance was displayed than was observed for the silicone or the quat alone. This phenomenon occurred for *all* of the silicones tested and was not observed for dry combing performance.

### **INTRODUCTION**

Hair conditioning products (along with hair cleansing products) are increasingly being used on a daily basis. Whereas a shampoo is simply used to clean hair, a conditioner is used with a variety of expectations. These expectations encompass a large number of attributes, most of which are closely related to Robbins et al.'s definition of the term "hair manageability" (1). An attribute that is closely associated with conditioning is *ease of combing*, and an instrumental technique has been established to obtain a quantitative measure of this parameter (2).

The isoelectric point of untreated hair is at pH 3.7 (3). This indicates that the hair surface attains a cationic charge at a pH under 3.7 while assuming an anionic character above that pH. Traditionally, quaternary ammonium salts (or quats) have been used as the main additive responsible for conditioning effects. Their structure can be represented as  $[N^+(R)_a(CH_3)_{4-a}]X^-$ , where R is a long chain alkyl group, X is the counter anion, and a is the number of alkyl groups attached to the quaternary nitrogen atom.

Quats have been found to be efficient at depositing on hair as well as improving its combability. The adsorption has been attributed to an electrostatic attraction between the anionic character of the hair fiber and the positively charged quat molecule (4-6). Hair has been described as being a "strong-acid ion exchanger," and one can expect some desorption of the quat upon rinsing with detergents (6). In addition to electrostatic forces, attraction owing to Van der Waals forces has also been shown to play a part in the adsorption process (7). Increasing the number of alkyl groups, as well as increasing the length of the carbon chains on the quat, has been shown to be beneficial for the conditioning of hair (8,9). If the cationic charge character is responsible for bringing the quat to the hair surface, it is the long-chain alkyl groups that are believed to be responsible for lubricity and combing performance (9).

Though quats occupy a prominent position in the list of conditioning additives, other materials have been investigated for a variety of reasons. Out of these, polydimethylsiloxanes (PDMS, silicones, siloxanes) have been identified as effective hair conditioning aids and are currently being used, frequently in conjunction with quats, in many commercial products. Because of their ease of spreading and thin film formation, along with their lubricity and emollient properties, silicones impart unique "feel" characteristics to personal care products and have gained industry-wide acceptance (10,11). Silicones are also finding favor in conditioning shampoos (12).

Silicones are homopolymers consisting of repeating units of dimethylsilicon bonded to oxygen, and their structure can be written as  $Y-O-\{Si(CH_3)_2O\}_x-Y$ . Depending on the end group, they are known as dimethicone ( $Y = Si[CH_3]_3$ ) or dimethiconol ( $Y = H$ ).

As discussed above, both quats and silicones are known to condition hair. However, the influence of one on the other, as pertaining to conditioning, has not been well documented. In this work, the combing benefits of silicones are assessed as a function of the amount of silicone deposited (as delivered from a solvent) as well as of the molecular weight of the silicone used. In addition, the interaction of a quat with the silicones and the resulting effect on deposition and combing performance is investigated. It should be noted that the results discussed below represent performances obtained from a solution. The deposition levels and other characteristics obtained from aqueous hair conditioning products may differ from these findings.

## EXPERIMENTAL

### MATERIALS AND GENERAL PROCEDURES

*Hair samples.* All tresses were prepared with 2 grams of slightly bleached human virgin European hair, purchased from DeMeo Brothers, New York. The tresses were prewashed with a 15 wt% aqueous solution of ammonium lauryl sulfate (Henkel Corporation), rinsed, and dried. The tresses were then dipped individually into chloroform for a period of 40 seconds, and the resulting tresses were considered "untreated tresses."

*Treatment samples.* Tricetylmonium chloride (Varisoft TC-90<sup>®</sup>, named *quat* for the purpose of this paper) was kindly supplied by Sherex Corporation, whereas all the polydimethylsiloxanes {three dimethicone fluids—molecular weights of 10,000, 40,000, and 64,000, named *fluids 1, 2 and 3*, respectively; two dimethiconol gums—molecular

weights of 220,000 and 280,000, called *gums 1* and *2*, respectively; and a dimethiconol gum/dimethicone fluid blend (gum 2/fluid 1) in a ratio of about 40/60, named *blend*} were obtained from Dow Corning Corporation. All other reagents and solvents were obtained from commercial sources.

#### TRESS TREATMENTS

The tresses were dipped into solution baths containing the treatments for a period of 30 seconds. The tresses were squeezed after dipping to remove excess solvent. Rinsing of the tresses was not performed. The tresses were next allowed to air dry before evaluation. The solvent used was chloroform, and the treatments consisted of four levels of the different siloxanes (from 0.03 wt%–0.5 wt%) in the absence and presence of the quat (0.5 wt%). Five tresses were dipped per level used. Three of these tresses were evaluated for combing performance, while the other two were analyzed for amount of silicone deposited. Three tresses were also dipped into a solution of quat (0.5 wt%) in chloroform in the absence of any siloxane as “control tresses.”

#### COMBABILITY MEASUREMENTS

The method of Garcia and Diaz (2) was used to measure the effect of the different treatments on the ease of combing of the hair tresses. An Instron Tensile Tester (model 1122) was modified for this purpose, and the data obtained were reported in terms of average combing load (ACL) values. The effect of the treatments was calculated as the % reduction in ACL, which is given by

$$\%ACL_{\text{Red}} = 100 \times (\text{ACL}_{\text{untreated}} - \text{ACL}_{\text{treated}}) \div \text{ACL}_{\text{untreated}}$$

#### MEASUREMENT OF THE AMOUNT OF SILICONE DEPOSITED

The method of Gooch and Kohl (13) was modified and used to determine the amount of silicone deposited on the hair. The modification included replacing the enzyme digestion step with a solvent extraction protocol. An atomic absorption spectrometer (Perkin Elmer Model 1100 B) was utilized to analyze the extracted solution for silicone content. The amount of silicone deposited was reported in terms of  $\mu\text{g}$  silicone/g of hair, from which the amount of polydimethylsiloxane deposited on hair can be calculated (if desired) when one knows the percent of silicone present in the siloxane.

## RESULTS AND DISCUSSION

#### AMOUNT OF SILICONE DEPOSITED ON HAIR AS A FUNCTION OF DIP BATH CONCENTRATION

Silicone deposition on the hair was found to depend on the concentration of the siloxane in the dip bath. Figure 1 shows the linear relationship of the deposition of gum 1 to its increasing dip bath concentration, in the absence of the quat.

Presence of the quat in the dip baths did not change this linear correlation. However, surprisingly, it did affect the total *amount* of deposition. As shown in Figure 1, the amount of silicone deposited on hair, from the same concentration of gum 1 in the dip

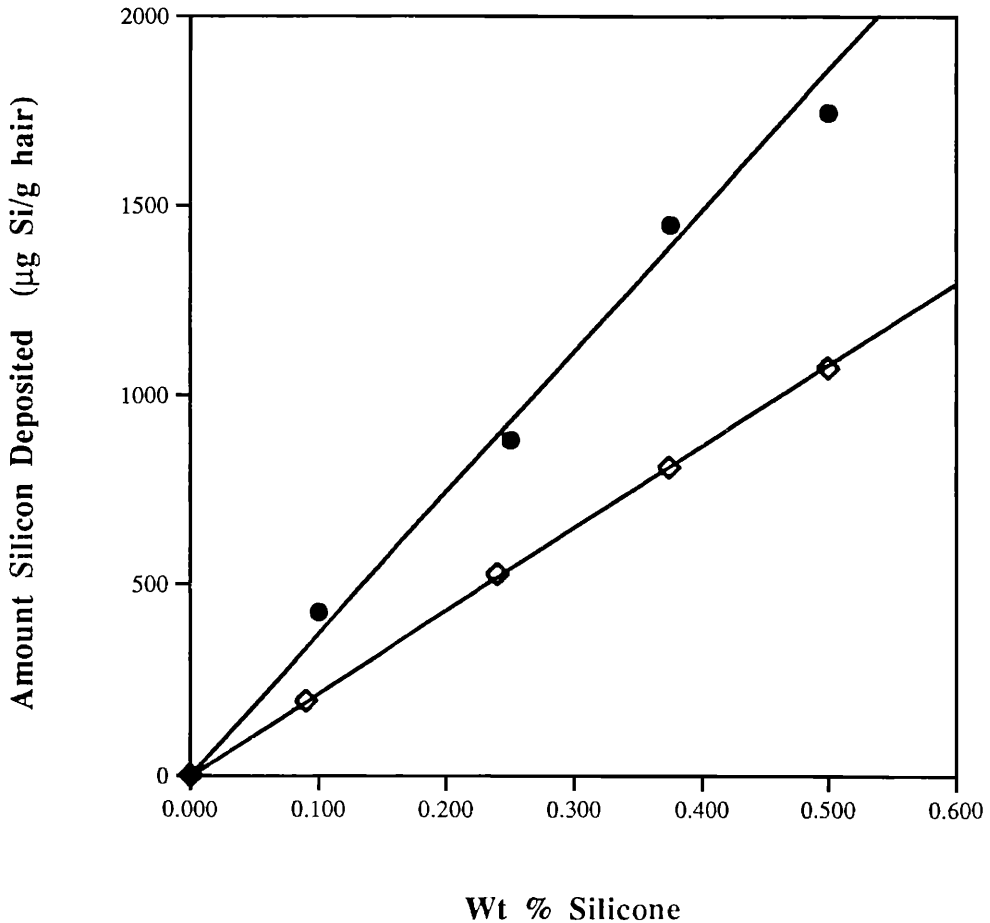


Figure 1. Deposition of gum 1 in the absence (◇) and presence (●) of the quat.

bath, almost doubled in the presence of the quat. This dependence of deposition on initial siloxane concentration, as well as the increase in the amount depositing on hair in the presence of the quat, were found to be common phenomena for *all* of the silicone materials tested.

The exact mechanism of the enhanced deposition of the siloxanes in the presence of the quat is not known. The quat could potentially help drive the siloxane to the fiber surface (simultaneous deposition; i.e. a quat-silicone interaction, of some sort, in solution prior to deposition) or it could first coat the hair fiber and then facilitate deposition of the silicone (sequential deposition). Berthiaume and Jachowicz (14) carried out a study involving the deposition on hair of six polydimethylsiloxanes (viscosities ranging from 50 to 12,500 centistokes) in the form of aqueous emulsions. They found that the rates, as well as the amounts of deposition of all of the silicone oils, were higher on hair pretreated with a polymeric quaternary compound {poly(methacrylamidopropyltrimethyl ammonium chloride)} than on untreated hair, indicating that sequential deposition may play a role in the mechanism.

AMOUNT OF SILICONE DEPOSITED ON HAIR AS A FUNCTION OF TYPE OF POLYDIMETHYLSILOXANE

Viscosity of the materials tested was not expected to play a role in the deposition parameters because dilute solutions of the silicones were used in the dip baths. It was thought, however, that the different polymer chain lengths in the different materials tested may affect the deposition in some fashion. This was found not to be the case. For any given concentration of the dip bath, almost the same amount of silicone deposited, irrespective of which of the polydimethylsiloxanes was used. The trend of increased deposition in the presence of the quat, as compared in the absence of quat, for all of the materials, is shown in Figure 2.

EFFECT OF SILICONE ON COMBING PERFORMANCE IN ABSENCE OF THE QUAT

Both wet and dry combing performances were assessed for the different levels of the treatments used. In general, it was found that ease of wet and dry combing improved

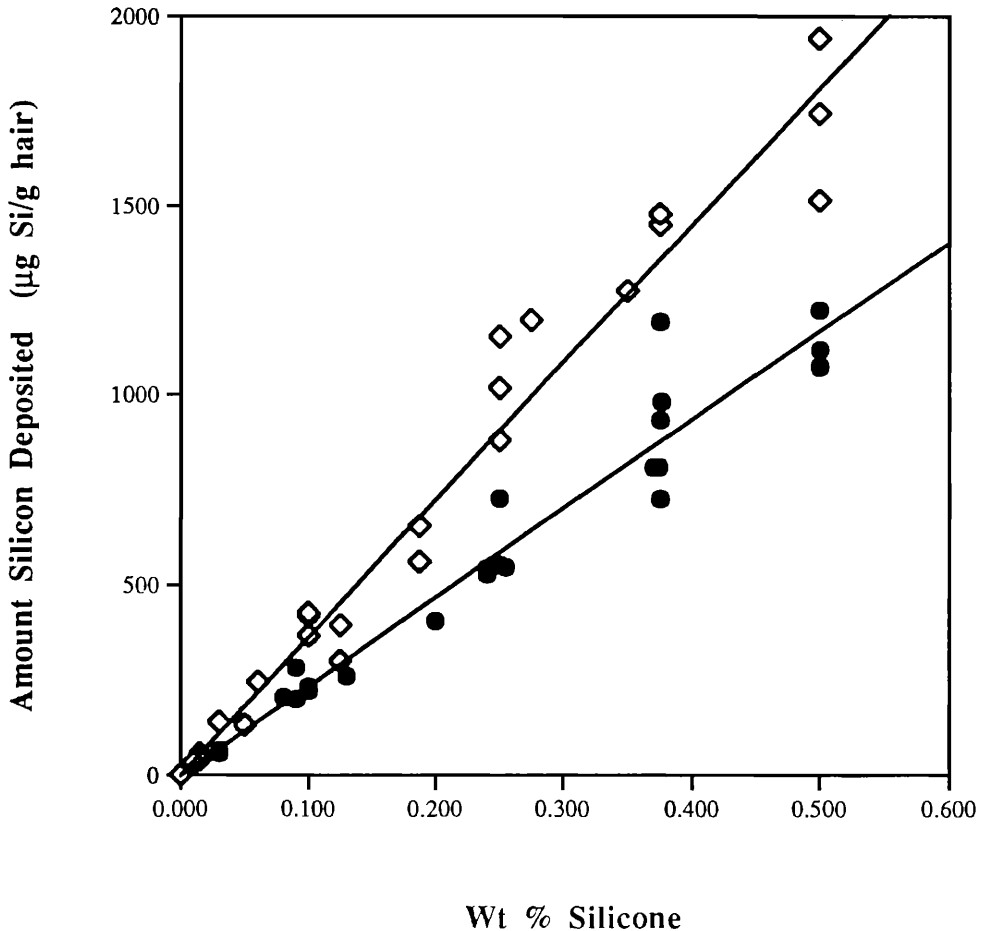


Figure 2. Deposition of all silicones in the absence (●) and presence (◇) of the quat.

substantially with the deposition of a little amount of silicone. However, this improvement seemed to level off with increasing deposition.

*High-molecular-weight silicones (gums and the gum blend).* The % ACL reductions of the three treatments (gums 1 & 2 and blend) were in the 25%–50% range for wet combing and in the 65%–85% range for dry combing. As seen in Figure 3 (A for gum 1, B for gum 2, and C for blend), there is an initial rapid increase in combing performance improvement (for both wet and dry combing) followed by a gradual leveling off with increasing silicone deposition on hair. The leveling off of the performance occurs with our lowest data point, which is around 200  $\mu\text{g}$  silicone/g hair. Thus the minimum amount of silicone required for the improved performance, as well as the threshold level at which the improvement levels off, is between 0–200  $\mu\text{g}$  silicone/g hair. Yahagi (15) has shown that the kinetic frictional coefficient ( $\mu_k$ ) of dry hair fibers was reduced when amounts greater than 100  $\mu\text{g}$  silicone/g hair were deposited on the fibers (using a polydimethylsiloxane of molecular weight of 220,000). This amount was explained as perhaps being the critical level that is needed to form a lubricating, thin film on the surface of the hair.

These high-molecular-weight siloxanes (HMWS) thus improve wet and dry combing

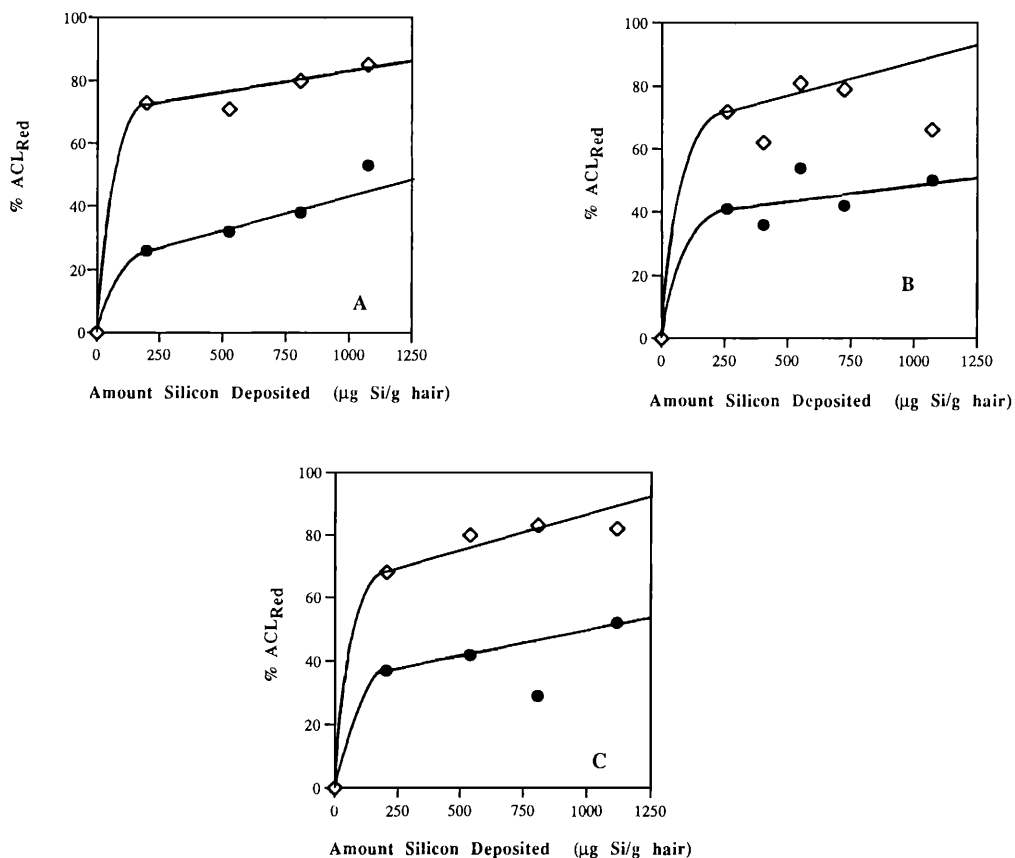


Figure 3. Dry (◇) and wet (●) combing performance of gum 1 (A), gum 2 (B), and blend (C) in absence of the quat.

performances, the dry combing improvement being noticeably superior to the wet combing effects (based on %ACL reduction).

*Low-molecular-weight silicones (fluids).* The data points are a lot more scattered for members of this class, especially for fluid 1. As shown in Figure 4 (A for fluid 1, B for fluid 2, and C for fluid 3), there does not appear to be much of a difference between dry combing and wet combing improvement. The %ACL reductions of the three treatments were in the 35%–60% range for both wet and dry combing. The same trend (of improved performance for low amounts of silicone deposited followed by leveling off) is seen with these lower molecular weight polydimethylsiloxanes (LMWS). Our lowest data point (for fluids 2 and 3) in this case is around 55  $\mu\text{g}$  silicone/g hair, so that the minimum amount of silicone required for the improved performance and the threshold level at which the improvement levels off is now between 0–55  $\mu\text{g}$  silicone/g hair.

*Comparison between HMWS and LMWS.* As Figure 5A shows, the HMWS display dry combing performance superior to that of the LMWS. This is in good correlation with a study where the  $\mu_k$  value of dry hair fibers was measured as a function of the molecular weight (Mw) of the PDMS depositing on the hair (15). It was found that the coefficient decreased (i.e., improved lubricity) as the molecular weight of the silicone increased, provided that the Mw was greater than 20,000.

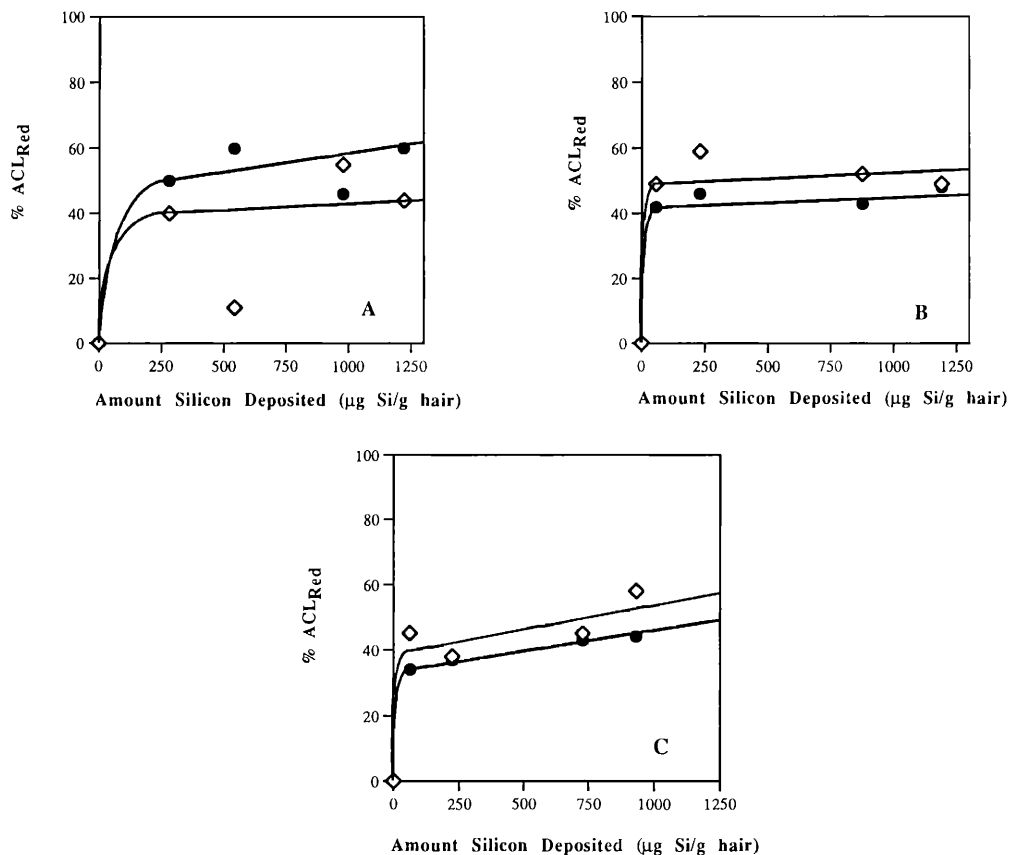


Figure 4. Dry ( $\diamond$ ) and wet ( $\bullet$ ) combing performance of fluid 1 (A), fluid 2 (B), and fluid 3 (C) in absence of the quat.

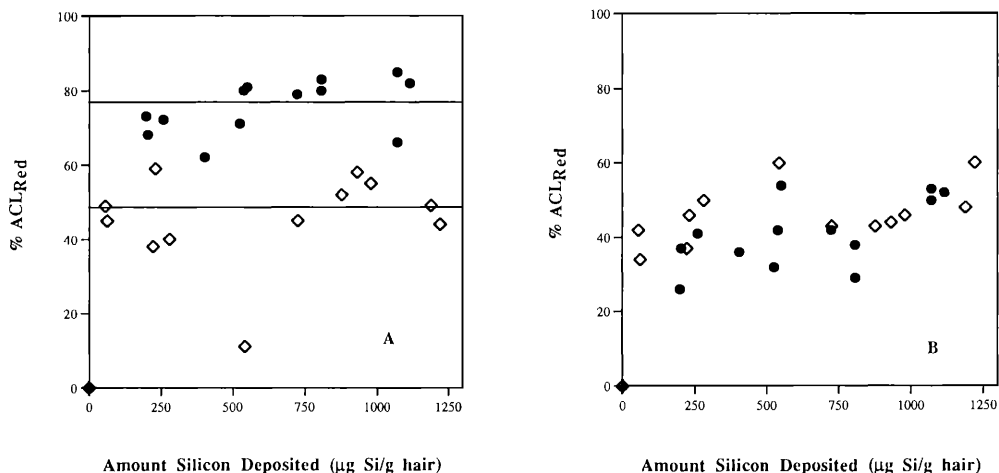


Figure 5. Dry (A) and wet (B) combing performance of all the fluids ( $\diamond$ ) and gums/blend ( $\bullet$ ) in absence of the quat.

There is no significant difference between the HMWS and LMWS as pertaining to wet combing improvement. They both reduce the average combing load by about 35%–50%, as shown in Figure 5B.

#### EFFECT OF SILICONE ON COMBING PERFORMANCE IN PRESENCE OF THE QUAT

Again, both wet and dry combing performances were assessed for the different levels of the treatments used. In addition, tresses treated only with the quat were combed for comparison purposes.

*High-molecular-weight silicones (gums and the gum blend).* The %ACL reductions of the three treatments (gums 1 & 2 and blend) were in the 87%–94% range for wet combing and in the 56%–87% range for dry combing. The same trends of initial rapid increase followed by a gradual leveling off in combing performance improvement is valid for the experiments in the presence of the quat, as shown in Figure 6 (A for gum 1, B for gum 2, and C for blend).

*Low-molecular-weight silicones (fluids).* The %ACL reductions of the three treatments were in the 73%–91% range for wet combing and in the 47%–79% range for dry combing. The same trend (of improved performance for low amounts of silicone deposited, followed by leveling off) is seen with these lower molecular weight polydimethylsiloxanes (LMWS), as shown in Figure 7 (A for fluid 1, B for fluid 2, and C for fluid 3).

*Comparison between HMWS and LMWS.* As in the case of the experiments involving the absence of the quat, HMWS show better dry combing benefits when compared to the LMWS (see Figure 8A). They may also have a slight edge when considering wet combing benefits (see Figure 8B).

*Comparison between wet combing in the absence and presence of the quat.* The quat by itself was not effective in reducing the wet combing load ( $\%ACL_{red} = 3\%$ ). The silicones did a much better job, however; there was a *dramatic* improvement in the wet combing



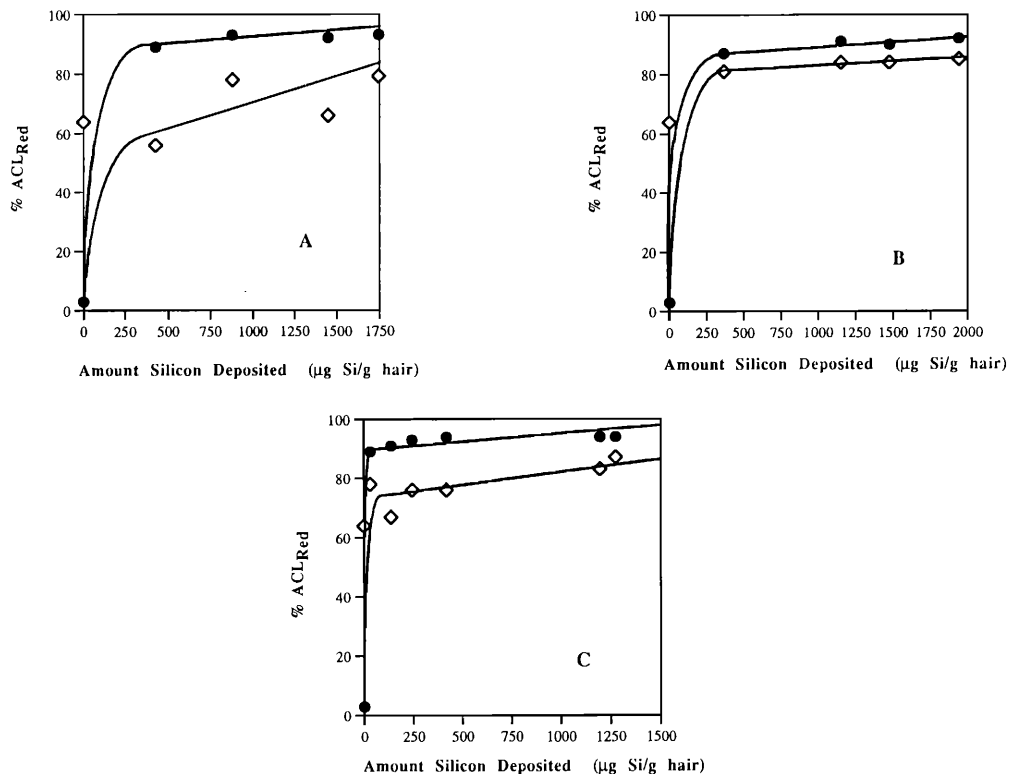


Figure 6. Dry ( $\diamond$ ) and wet ( $\bullet$ ) combing performance of gum 1 (A), gum 2 (B), and blend (C) in presence of the quat. The values shown at x-axis = 0 are the dry ( $\diamond$ ) and wet ( $\bullet$ ) combing benefits of the quat in the absence of any silicones.

performance when *both* silicone and the quat were present together as shown in the table below:

Treatment	Wet %ACL <sub>red</sub>
Quat alone	3%
Silicone alone (average of all HMWS and LMWS)	43%
Silicone and quat (average of all HMWS and LMWS)	87%

This is also illustrated in Figure 9A. The synergistic effect of the two simply cannot be explained by the improved deposition of the silicone in the presence of the quat. Similar amounts of silicone deposited on hair, in the absence and in the presence of the quat, display very different wet combing benefits. For example, in Figure 10, a level of 500  $\mu\text{g}$  silicone/g hair provides a 30% reduction of combing force in the absence of the quat but a 90% reduction in the presence of the quat.

*Comparison between dry combing in the absence and presence of the quat.* There is no advantage in dry combing performance when both silicone and the quat are present together, as compared to the effect of the quat or the silicones alone as shown in the table below:

Treatment	Dry %ACL <sub>red</sub>
Quat alone	64%
Silicone alone (average of all HMWS)	76%
Silicone and quat (average of all HMWS)	77%
Silicone alone (average of all LMWS)	50%
Silicone and quat (average of all LMWS)	57%

This is also illustrated in Figure 9B. The quat by itself substantially reduces dry combing load. Both the HMWS and LMWS also improve the dry combing performance. Interestingly, the reduction in %ACL change for the LMWS, in the presence or absence of the quat, is by and large *lower* than that of the quat used by itself. However, the reduction caused by the HMWS, either in the absence or presence of the quat, is *higher* than that of the quat by itself.

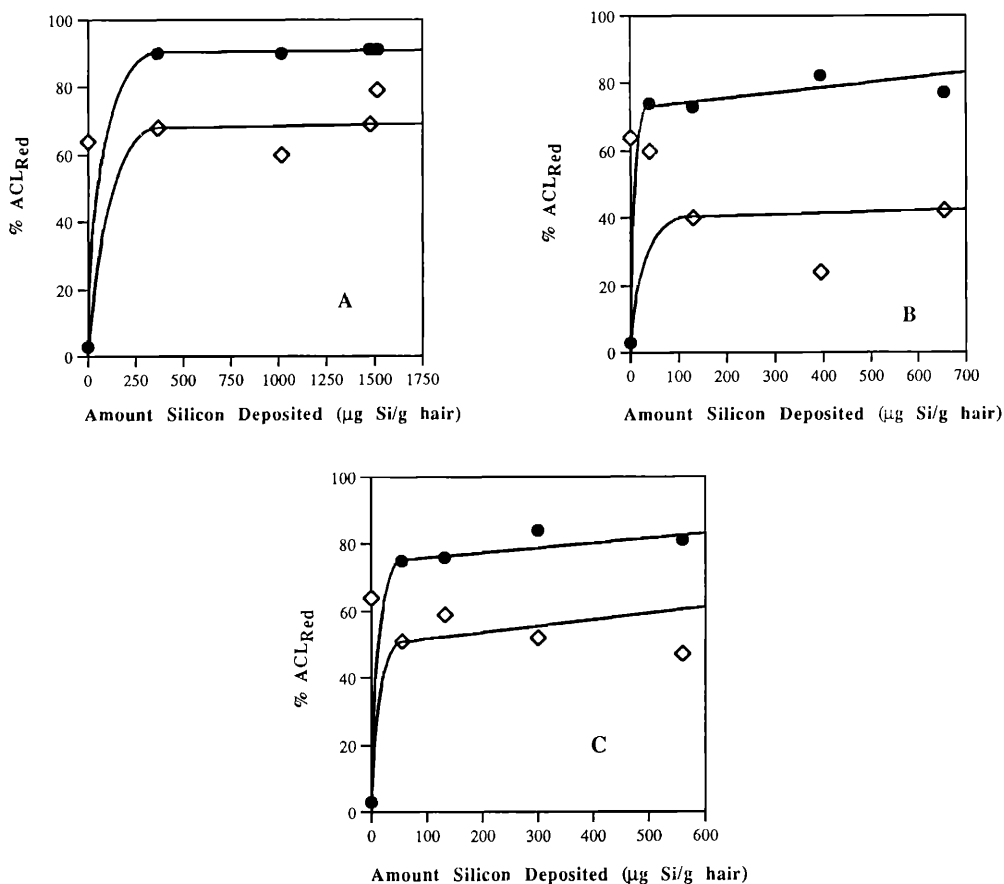
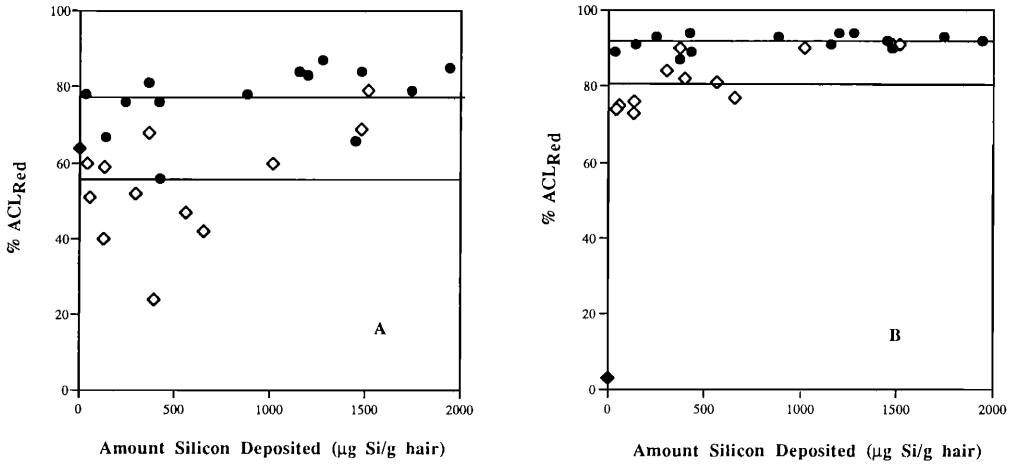


Figure 7. Dry (◇) and wet (●) combing performance of fluid 1 (A), fluid 2 (B), and fluid 3 (C) in presence of the quat. The values shown at x-axis = 0 are the dry (◇) and wet (●) combing benefits of the quat in the absence of any silicones.

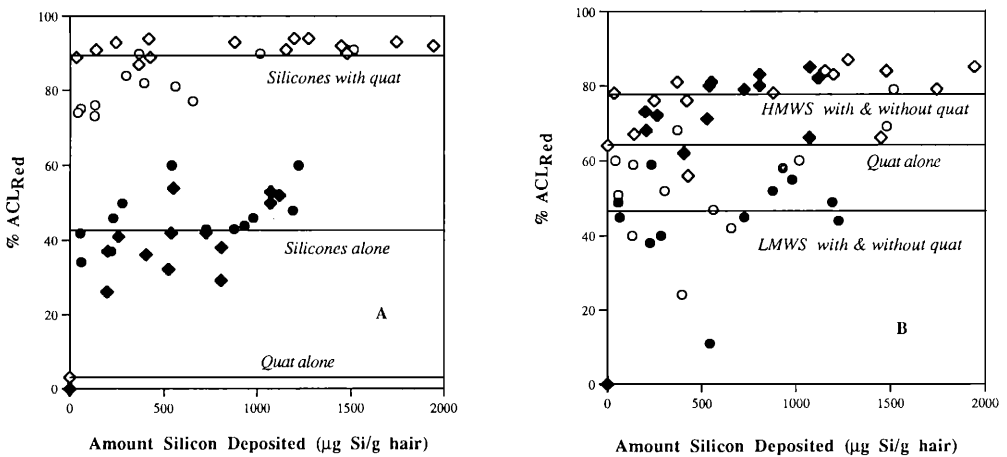


**Figure 8.** Dry (A) and wet (B) combing performance of all the fluids ( $\diamond$ ) and gums/blend ( $\bullet$ ) in presence of the quat. The values shown at x-axis = 0 are the combing benefits of the quat in the absence of any silicones.

**CONCLUSIONS**

**DEPOSITION**

The amount of deposition of silicone on bleached hair was found to be a linear function of the initial silicone concentration in the solution dip bath. The amount of silicone depositing did not depend on the molecular weight or the type (dimethicone fluids vs dimethiconol gums) of polydimethylsiloxane used; however, it was affected by the presence or absence of the quat. Presence of the quat in the dip bath led to increased deposition, up to double the amount, of the siloxane on the hair.



**Figure 9.** Wet (A) and dry (B) combing performance of all the fluids in the presence of ( $\circ$ ) and absence ( $\bullet$ ) of the quat, and of all the gums/blend in the presence ( $\diamond$ ) and absence ( $\blacklozenge$ ) of the quat. The values shown at x-axis = 0 are the combing benefits of the quat in the absence of any silicones.

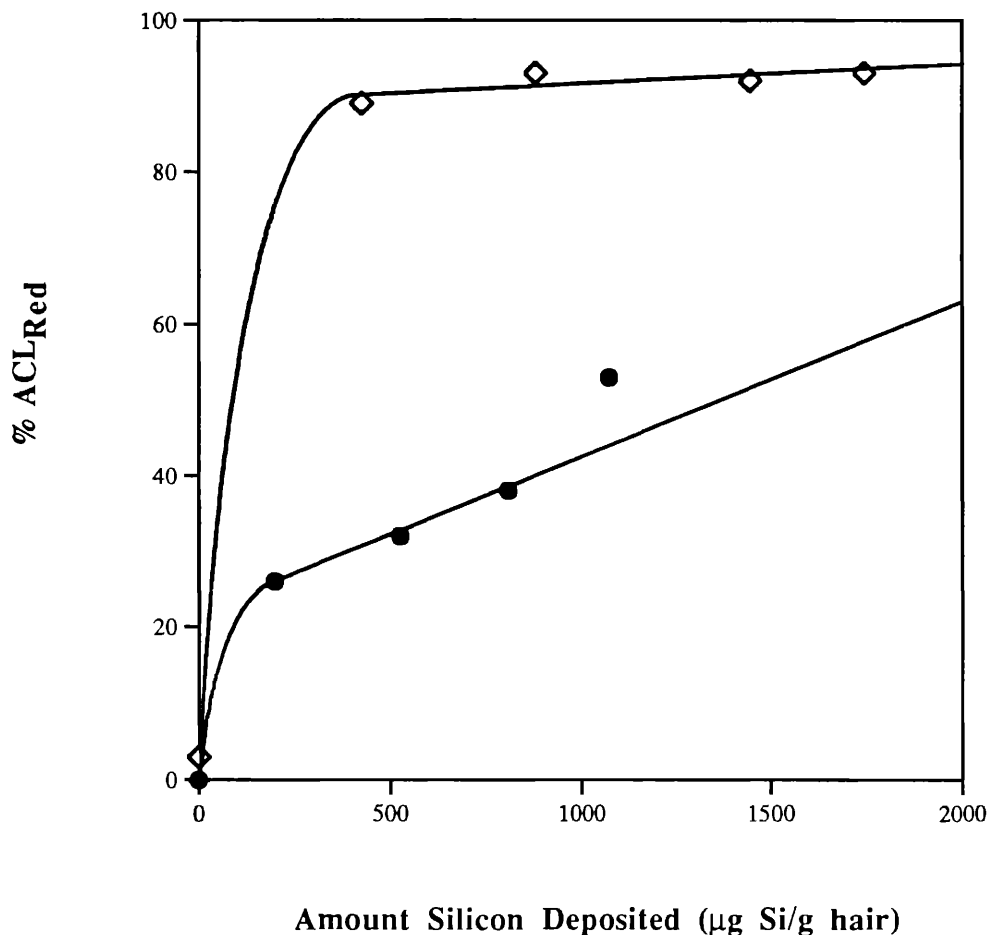


Figure 10. Wet combing performance of gum 1 in the absence (●) and presence (◇) of the quat.

#### COMBING PERFORMANCE

All the silicones were effective in lowering the wet and dry combing load of hair. Very low levels were required to effect substantial improvement in combing. A threshold amount of deposition was reached after which saturation of the performance improvement occurred. After this point, deposition of more silicone did not result in any further improvement.

The quat by itself did not improve wet combing characteristics of the bleached hair. The silicones proved superior to the quat in this respect. However, presence of the quat along with the siloxane *dramatically improved* the wet combing benefits offered by the silicones, a fact not explainable solely by increased silicone deposition. The maximum wet combing benefit level obtained was roughly the same for each of the siloxanes used, irrespective of its molecular weight. Thus, the high-molecular-weight and low-molecular-weight silicones behave similarly as far as wet combing performance, in the presence or absence of the quat, is concerned.

On the other hand, the quat did improve dry combing characteristics of the bleached

hair. The silicones were also effective in this respect. However, presence of the quat had *no effect* on the dry combing characteristics of the silicones. The low-molecular-weight silicones, in the presence or absence of the quat, were as good or slightly inferior to the quat by itself, whereas the high-molecular-weight silicones, in the presence or absence of the quat, were found to be superior to the quat in terms of dry combing load reduction.

Thus the polydimethylsiloxanes tested (molecular weights ranging from 10,000–280,000) were found to be very effective in substantially improving the wet and dry combing performance of bleached hair. They were shown to have superior wet combing performance and comparable dry combing performance to that of the quat used. However, a synergistic effect was seen, as measured by wet combing improvement, when both the silicone and quat were used together. This combing improvement far outperformed the effects of the quat or the siloxane alone, and this effect was not confined to a siloxane of a specific molecular weight. This synergistic effect was not observable for dry combing performance. The quat, the silicones, and the two together all performed equally well in lowering the dry combing load.

#### TYPE OF SILICONE

The dimethicone fluids and dimethiconol gums were essentially equivalent in their performance with regard to amount of deposition and to wet combing in the absence/presence of the quat. The only difference seen was in dry combing performance, both in the presence and absence of the quat, where the dimethiconol gums (and the dimethiconol gum/dimethicone fluid blend) outperformed the dimethicone fluids. The difference in performance can be attributable to either the increased molecular weight or to the different endgroups present on the polymer chain going from dimethicone to dimethiconol. These results suggest that dimethiconol gums should be either equivalent to dimethicone gums in combing performance if the former hypothesis is true or outperform them if the latter holds true.

#### ACKNOWLEDGMENTS

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