# New high-charge density hydrophobically modified cationic HEC polymers for improved co-deposition of benefit agents and serious conditioning for problem hair

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#### Synopsis

A series of new high charge density Polyquaternium- $67^1$  (PQ-67) polymers have been prepared and evaluated in shampoo formulations. These new compositions represent an addition to the family of high-viscosity quaternized hydroxyethylcellulose (HEC) polymers with cationic substitution of trimethyl ammonium and dimethyldodecyl ammonium<sup>2</sup> (Figure 1A) described in (1) and (2). The evaluation protocol included objective lab methods and subjective panel studies on different hair types. Commercial conditioning polymers: PQ-67 (Polymers SoftCAT<sup>TM<sup>3</sup></sup>) and cationic guar<sup>4</sup> (Jaguar C- $13S^{@5}$ ) were used as performance benchmarks.

It was found that increasing the cationic charge density of the PQ-67 polymers above 1.45 meq/g (equivalent of 2 weight-percent (wt.%) nitrogen) resulted in a several-fold boost of their co-deposition ability. These experimental, high charge density PQ-67 polymers were shown to deliver silicones and other performance ingredients from shampoo formulations more efficiently than any other polymer currently available on the market for rinse-off hair cleansing/conditioning applications. The polymers also provided improved wet and/or dry conditioning, volume control, and could be instrumental in achieving sleek looking hair and improved control/manageability of unruly or frizzy hair. The high charge density PQ-67 polymers are also ideally suited for highly-fragranced surfactant-based formulas that are used in aromatherapy and spa products due to their superior ability to deliver fragrance.

# BACKGROUND

Hair is a diverse substrate that comes in different shapes, colors and textures. Its properties and appearance vary for different races and age groups, as do the benefits that consumers are seeking in new hair care products. As more and more consumers are shampooing, grooming, coloring, bleaching or waving/straightening their hair, they are

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<sup>&</sup>lt;sup>1</sup> Hydrophobically modified cationic conditioning HEC polymers.

<sup>&</sup>lt;sup>2</sup> Supplied by Amerchol Corporation/Dow Chemical Company under the trade name SoftCAT<sup>TM</sup> SL and SK.

<sup>&</sup>lt;sup>3</sup> Supplied by Amerchol Corporation/Dow Chemical Company.

<sup>&</sup>lt;sup>4</sup> Guar hydroxypropyltrimonium chloride.

<sup>&</sup>lt;sup>5</sup> Supplied by Rhodia.

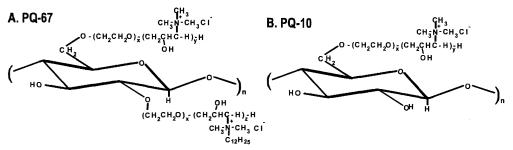


Figure 1. Cationic conditioning HEC polymers.

also damaging it, and thus the need for products that can mitigate and repair this damage is increasing dramatically. The current offering of cationic conditioning polymers is quite broad and is expanding, with HEC-based polymers representing a significant portion of this market. Varying structural parameters of these polymers, such as molecular weight, cationic and hydrophobic substitution and/or the degree of ethoxvlation significantly impacts their performance on hair and creates the much needed diversity of properties and benefits. This paper describes the impact of the charge substitution (CS) in combination with the hydrophobic substitution (HS) on the deposition properties and overall conditioning of PQ-67 polymers. New compositional features enhanced the performance of the experimental high charge density PQ-67 polymers, which were found superior when compared to any of the competitive benchmarks used in this study in deposition of performance ingredients and for overall conditioning. This performance makes the new structures a valuable addition to the family of cationic conditioning polymers. These polymers were found to be especially useful to manage hair types that benefit from volume control and extra-conditioning, such as unruly, difficult-to-manage hair or for Asian hair types.<sup>6</sup>

# **RESULTS AND DISCUSSION**

## POLYMER COMPOSITION

New experimental high charge density PQ-67 polymers belong to the family of high viscosity quaternized hydroxyethyl cellulose (HEC) derivatives with cationic substitution of trimethyl ammonium and dimethyldodecyl ammonium (Figure 1A) described in (1) and (2) and recently commercialized for personal care applications by Amerchol Corporation and the Dow Chemical Company under the trade name of Polymers Soft-CAT<sup>TM</sup> SL and SK. Similar to the commercially available grades, experimental PQ-67 samples described in this paper were produced by reacting HEC polymers with 3-chloro-2-hydroxypropyldodecyldimethyl ammonium chloride and 2,3-epoxypropyltrimethyl ammonium chloride in aqueous isopropanol (2). In this work we used polymers made of a high viscosity HEC with the degree of ethoxylation similar to one of commercially

 $<sup>^{6}</sup>$  We are currently in progress evaluating performance of experimental high charge density PQ-67 polymers on Asian hair.

available PQ-67 grades such as Polymers SoftCAT SL and SK. Low levels of hydrophobic dimethyldodecyl ammonium substitution (HS  $\leq 0.01$ ) were used to impart hydrophobic character to these polymers.

Several structural parameters of cationic cellulosic ether derivatives, such as PQ-67 (Figure 1A) and their non-hydrophobic structural analogs, PQ-10 (Fig. 1B) polymers have a profound impact on their performance on hair and skin. These parameters include molecular weight (Mw), cationic charge (CS), as well as the degree of the side chain substitution with ethylene oxide (EO MS). Examples of such structure-performance relationships for PQ-10 polymers in surfactant systems were previously described in industry sources (3-6). On the other hand, the structural potential of PQ-67 compositions is much less explored and understood. In addition to the structural features already present in PQ-10, the structure of PQ-67 polymers offers one more variable-the degree of hydrophobic substitution (HS), which is another useful tool for modifying, controlling, and improving certain performance aspects of these polymers on hair (1) and skin (7). The new results presented below demonstrate that increasing the cationic charge to above 2 wt.% N in the hydrophobically modified quaternized HEC polymers, such as PO-67, resulted in a several fold boost of their deposition and delivery properties, and significantly improved the overall performance of these polymers on hair, especially non-chemically treated, coarse, difficult to manage and unruly hair types.

The high charge density PQ-67 polymers were evaluated in shampoo formulations using objective quantitative lab methods and subjective panel evaluation on hair tresses. Commercial conditioning polymers: PQ-67 with charge density less then 1.45 meq/g (SoftCAT<sup>TM</sup> SL and SK) and cationic guar (Jaguar<sup>®</sup> C-13S) were used as performance benchmarks.

# PERFORMANCE IN SHAMPOOS WITH SILICONES

The principal intent of shampooing is to clean the hair. However, products that are designed solely for cleansing can leave hair tangled and unmanageable when wet, and raspy dry and dull-looking upon drying ((1) and references therein).

As previously described in (1), many conditioning polymers and various other performance ingredients, e.g. insoluble silicones, can improve the hair condition by reducing the combing friction of hair and providing a soft, smooth feel and healthy, shiny appearance. Cationic polymers, such as PQ-10, PQ-67, and cationic guar, are known to work in these ways, in these systems, alone or in combination with other actives. They are assumed to form a polymersurfactant complex (coacervate phase) that separates and precipitates onto the hair during the rinse-off cycle (1,8–10). Coacervates can optionally incorporate performance ingredients such as silicones, fragrance, sunscreens, and other benefit agents thus assisting in their deposition on hair (1,3,4). Experimental polymers described in this paper are conjectured to perform along this line.

Deposition of silicones on hair has been evaluated in two shampoo systems that included different surfactant bases and different types of silicones: *Shampoo Formulation A* containing sodium laureth sulfate (SLES)/ disodium cocamphodiacetate (DSCADA), 1 wt.%

dimethicone with an average particle size  $\sim 0.3$  microns,<sup>7</sup> and conditioning polymers incorporated at 0.25% level and Shampoo Formulation B containing sodium laureth sulfate (SLES)/ disodium laureth sulfosuccinate (DSLSS)/ cocamidopropyl betaine (CAPB), 1 wt. % dimethiconol with average particle size  $\sim 0.5$  micron<sup>8</sup> and conditioning polymers incorporated at 0.2% level. Deposition of silicones from shampoo formulations depends upon many factors; type of silicone, its average particle size, the surfactant base, the presence and type of cationic polymers are amongst the most important (6,11). Hair type can also play a significant role in the deposition of silicones and, therefore, impact the choice of cationic polymers to assist in and/or control this deposition. For example, as we previously described in (1) and the SoftCAT product literature, the low to medium charge density (~1.0 to 1.45 wt.% N) PQ-67 polymers ideally suit the needs of bleached damaged hair. They do not overload this susceptible-to-cationic-deposition hair type while maximizing the deposition of much needed silicone as compared to cationic guar and PQ-10 polymers. Deposition of silicone on virgin hair as well as on any "intermediate" hair type varies significantly depending on a specific shampoo formulation. Examples of systems where high-viscosity high-charge PQ-10 grades outperformed their cationic guar counterparts have been previously described in (11). As we show later, Shampoo Formulation B also falls into this category. At the same time, the Shampoo Formulation A yielded significantly better silicone deposition on European virgin brown hair when formulated with cationic guar.<sup>9</sup> One of the goals of the present study was to further explore and tune structural parameters of PQ-67 polymers in order to close this gap. We, therefore, began our investigation with the Formulation A, where the shortcoming was first identified, and then expended our evaluation scope to include other systems.

Conditioning performance of two prototype shampoo systems described below is largely due to the presence of silicones and their ability to reach hair and stay behind (in small amounts) after the rinse-off cycle is complete. Ability to deposit silicone is therefore crucial in these systems and greatly contributes to the overall conditioning effect. On the other hand, the contribution of the cationic conditioning polymers and other ingredients found in shampoos can also play an important role in the overall performance. In order to account for these effects and make sure that the performance differences are likely to be noticed and appreciated by the end consumer, we included subjective panel studies on hair tresses in our evaluation.

# Performance in Shampoo Formulation A

Silicone deposition. The total amount of silicone deposited on hair treated with the Shampoo Formulation A was measured using atomic absorption spectrophotometry. Commercial European virgin hair<sup>10</sup> was washed two times<sup>11</sup> with each formulation. The

 $<sup>^7</sup>$  Dow Corning<sup>®</sup> Emulsion 1664 (supplied by Dow Corning) is a non-ionic emulsion of high molecular weight polydimethylsiloxane with 50% silicone content.

<sup>&</sup>lt;sup>8</sup> Dow Corning<sup>®</sup> Emulsion 1785 (supplied by Dow Corning) is an anionic emulsion of high molecular weight polydimethylsiloxane with 60% silicone content.

<sup>&</sup>lt;sup>9</sup> Note that the exact same shampoo formulation with lower charge density PQ-67 polymers (SoftCAT SL grade) yielded superior deposition of silicones on <u>single-bleached hair</u> compared to cationic guar (1).

<sup>&</sup>lt;sup>10</sup> All hair used in this work and described in this paper was supplied by International Hair Importers Co.

<sup>&</sup>lt;sup>11</sup> Consecutive washings, no drying in-between.

silicone was extracted from the hair by a 50/50 (v/v) methyl isobutyl ketone/toluene solution. The silicone content was measured, and then the micrograms of silicone per gram of hair was calculated.

Deposition of silicone on European virgin brown hair from the prototype Shampoo A formulated with PQ-10 polymers, PQ-67 polymers, and cationic guar is shown on Figure 2A. According to this data, increasing the charge substitution in PQ-10 polymers (HS = 0) resulted in more silicone deposited on hair. A moderate increase from ~45 to 95 micrograms of silicone per gram of hair was observed. This trend became more pronounced in the PQ-67 group compared to PQ-10. The same increase of cationic charge from ~1.0 to 1.8 wt.% N resulted in a several fold boost of silicone deposition from PQ-67 formulas: from ~45 to 215 micrograms of silicone.

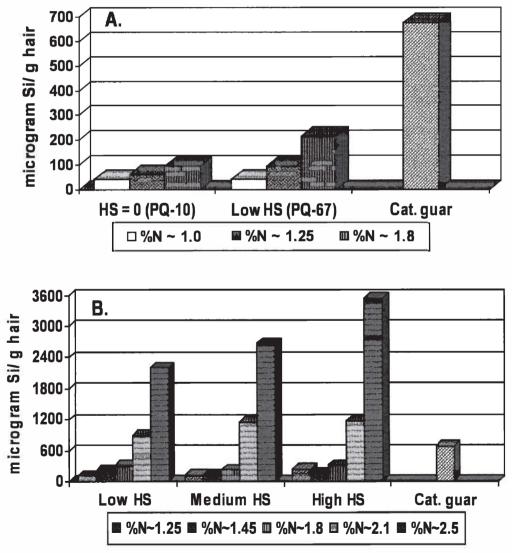


Figure 2. Silicone deposition from Shampoo Formulation A on European virgin brown hair. A. Polymers PQ-10 and PQ-67 with CS of 1.0–1.8 wt.% N. B. PQ-67 with CS 1.25–2.5 wt.% N and cationic guar.

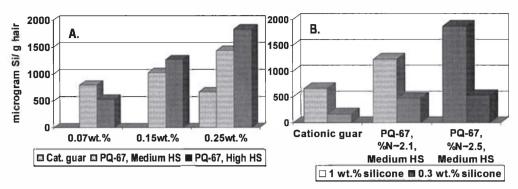


Figure 3. Silicone deposition on European virgin brown hair: formulations with fractional amounts of PQ-67 polymer or silicone. A. Formulations with 0.007 to 0.25 wt.% Polymer and 1 wt. % Silicone. B. Formulations with 0.25 wt.% Polymer and 0.3 to 1 wt.% Silicone.

Further studies revealed that even minimal amount of hydrophobe, such as, for example, the low level hydrophobic substitution present in the commercial products SoftCAT SL-5, SK-M, and SK-H, was sufficient to observe the significant boost in silicone deposition between PQ-10 and PQ-67 polymers. At the same time, varying HS in polymers with the CS corresponding to 1.0-1.8 wt.% N did not result in significant changes in silicone deposition. As discussed earlier and according to the data presented on Figure 2A, the prototype benchmark Formulation A prepared with cationic guar deposited significantly more silicone (~675 microgram silicone per gram of hair) on virgin brown hair compared to either group of cationic cellulosic polymers. In order to close this gap, we focused on the PQ-67 structures with the idea of combining the impacts of CS and HS on deposition performance. The charge substitution was further increased and high charge density polymers were prepared at three levels of hydrophobic substitution: low, medium, and high<sup>12</sup> (Fig. 2B). According to the data presented in Figure 2B, a step-change in silicone deposition on hair from PQ-67 shampoos occurred when the charge substitution in polymers exceeded 2 wt.% cationic nitrogen. Experimental high charge density PQ-67 polymers deposited up to ~3,500 microgram silicone per gram European virgin brown hair, depending on their CS and HS. They significantly outperformed other PQ-67 and cationic guar benchmarks used in the study. In a second study a series of high charge density PO- $67^{13}$  shampoos were formulated with fractional amounts of polymer (0.07-0.25 wt.%) or silicone (0.3 wt.%). These shampoos were evaluated for silicone deposition in comparison to complete formulations (Shampoo Formulation A) containing 0.25 wt.% cationic guar and 1 wt.% silicone. According to Figure 3A, the amount of deposited silicone was proportional to the amount of the high charge density PQ-67 polymer added to the formulation. Less then one third of the PQ-67 amount (0.07 wt.% versus 0.25 wt.%) was enough to match the silicone deposition from the cationic guar formula. In addition, data presented on Figure 3B shows that the formulation containing one third of the amount of silicone (0.3 wt.% versus 1.0 wt.% versuswt.% silicone in a "complete" Shampoo Formulation A) and high charge density PQ-67 polymers yielded silicone deposition on hair that was similar to the deposition from a "complete" formulation containing cationic guar.

 $<sup>^{12}</sup>$  All polymers described in this paper had HS < 0.01.

<sup>&</sup>lt;sup>13</sup> PQ-67 polymers containing 2.5 wt.% N.

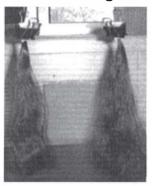
A. Baseline (untreated)





**PQ-67** Cationic guar Figure 4. Volume and frizz control.

C. After combing



PQ-67 Cationic guar

Subjective panel evaluation on tresses. To confirm that the effects described above were perceivable to human subjects, pairs of commercial frizzy hair tresses were shampooed, dried overnight and distributed to five expert panelists skilled in evaluating conditioning and other properties of hair. Each pair had one tress treated with *Shampoo A* formulated with a high charge density PQ-67 polymer<sup>14</sup> and one tress treated with a control shampoo containing cationic guar. Panelists were asked to evaluate three attributes: they were asked to choose one hair swatch in each pair that had less volume/ frizz, was easier to comb and felt smoother/softer. Each panelist performed evaluations twice on different pairs of hair tresses. Photos of the swatches were taken before treatment (Figure 4A), after treatment before combing (Figure 4B), and after repeated combing (Figure 4C).

As shown in Figure 4, the high charge density PQ-67 formulation provided excellent volume control for frizzy hair. Its superior performance compared to the cationic guar control was clearly noticeable before and after the hair was combed (Figure 4). The results of the subjective panel evaluation are presented in Figure 5A. The study confirmed that the PQ-67 formulation was perceived by panelists as providing better volume control (10/10) and also significantly improving dry feel (8/10)<sup>15</sup> and dry comb (9/10)<sup>16</sup> of frizzy hair against the cationic guar. As previously discussed, the high charge density PQ-67 polymers were significantly more efficient in depositing silicones on hair compared to the cationic guar control (Figure 3B). Therefore, a second panel evaluation study was conducted to compare a complete formulation with cationic guar to a sample formulation containing a PQ-67 polymer<sup>17</sup> and only about one third of the amount of silicone (0.3 wt.% versus 1.0 wt.%). Hair tresses treated with the formulations were evaluated wet and dry in pairs in the same way as described above. The results of wet/dry comb and feel property evaluations are presented in Figure 5B. It was found that the high charge density experimental PQ-67 polymer used in this study significantly im-

<sup>&</sup>lt;sup>14</sup> PQ-67 polymer with %N ~2.5 and medium HS was used in this study.

<sup>&</sup>lt;sup>15</sup> Exact significance level = 89% (binomial distribution).

<sup>&</sup>lt;sup>16</sup> Exact significance level = 98% (binomial distribution).

<sup>&</sup>lt;sup>17</sup> PQ-67 polymer with 2.5 wt.%, medium HS.

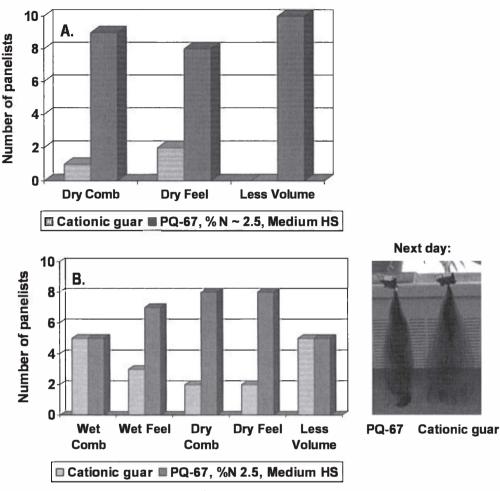


Figure 5. Subjective panel evaluation on frizzy hair. A. Shampoo Formulation A: 0.25 wt.% polymer, 1 wt.% silicone. B. Shampoo Formulation A: 0.25 wt.% PQ-67, 0.07 wt.% silicone versus 0.25 wt.% cationic guar, 1.0 wt.% silicone.

proved both dry comb and feel (8/10)<sup>18</sup> and, possibly, wet feel of frizzy hair despite the fact that it was used in a system with three times less silicone compared to the cationic guar formulation. On the day of the evaluation, after all the manipulations on hair were completed the panelists were not able to see differences in volume. Nevertheless, one day later hair tresses treated with the cationic guar formula showed significantly more frizz and unwanted volume<sup>19</sup> Figure 5B, while the PQ-67 formulation continued to provide much needed volume and frizz control.

Performance in Shampoo Formulation B

Silicone deposition. The total amount of silicone deposited on European virgin hair

<sup>&</sup>lt;sup>18</sup> Exact significance level = 89% (binomial distribution).

<sup>&</sup>lt;sup>19</sup> Frizz and volume increase are typical to this hair type and can be caused by atmospheric moisture.

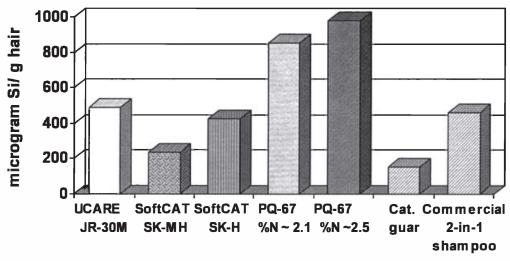


Figure 6. Silicone deposition from Shampoo Formulation B on European virgin brown hair.

treated with Shampoo Formulation B was measured following the procedure described above. Polymers PQ-10 (UCARE™ JR-30M), PQ-67 (SoftCAT™ SK-MH and H), and cationic guar (Jaguar C-13S®) were used as benchmarks. A market leading commercial shampoo product that had an SLES/DSLSS/CAPB surfactant base, dimethiconol, and guar hydroxypropyl trimethylammonium chloride listed on the ingredient label was also included in the study as an additional benchmark. The results obtained for the silicone deposition from each formulation are presented in Figure 6. It has been found that the PQ-10 polymer with medium-high cationic charge (UCARETM JR-30M, %N ~1.8) and PQ-67 polymer with medium cationic charge (SoftCAT<sup>TM</sup> SK-H, 1.45 wt.% N) outperformed cationic guar n the prototype formulation B. They yielded silicone deposition in the range of ~430 and 490 micrograms of silicone per gram of hair, respectively, which was close to the amount delivered by the commercial shampoo product that listed an SLES/DSLSS/CAPB surfactant system and cationic guar: ~460 micrograms of silicone. Experimental high charge density PQ-67 polymers described in this paper delivered significantly more silicone (~850 and 1,100 micrograms, respectively, depending on the CS) showing again a significant increase in silicone deposition over the benchmarks.

Subjective panel evaluation on tresses. In order to further validate the outstanding conditioning performance of the high charge density PQ-67 polymers in the prototype Shampoo Formulation B, a sample shampoo containing one of these polymers (~2.1 wt.% N, medium HS) was compared to the market-leading commercial shampoo used in the silicone deposition study (Figure 7A). Pairs of European virgin brown hair tresses were prepared as described above and distributed to panelists. The hair was evaluated for wet/dry comb and feel properties. According to the results presented in Figure 7A, the panelists preferred the prototype Formulation B containing a high charge density PQ-67 polymer over the commercial shampoo for both wet comb  $(9/10)^{20}$  and feel (8/10).<sup>21</sup>

<sup>&</sup>lt;sup>20</sup> Exact significance level = 98% (binomial distribution).

<sup>&</sup>lt;sup>21</sup> Exact significance level = 89% (binomial distribution).

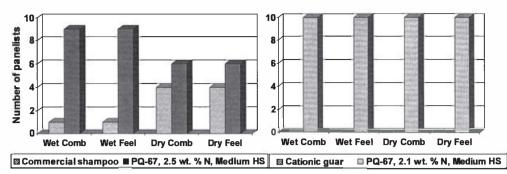


Figure 7. Subjective panel evaluation on European virgin hair. A. Shampoo Formulation B: PQ-67 versus commercial shampoo. B. Shampoo Formulation B: PQ-67 versus cationic guar.

After the hair dried, panelists' choices indicated no statistical difference in dry comb and feel between swatches (Figure 7A). A second panel study was conducted to compare the Shampoo Formulation B made with a high charge density PQ-67 polymer<sup>22</sup> to an identical formulation containing cationic guar.<sup>23</sup> As expected from the silicone deposition data, the PQ-67 formulation outperformed the guar control in both comb and feel in the wet and dry state, Figure 7B.

#### DEPOSITION OF FRAGRANCE

Fragrance is another important performance ingredient besides silicones that greatly contributes to the overall aesthetics of shampoo products and their acceptance by consumers. Delivery of long-lasting fragrance to the hair from rinse-off formulations such as shampoos and conditioners represents a serious challenge. The high charge density PQ-67 polymers that demonstrated remarkable performance in assisting the deposition of silicones on hair were also tested for deposition of fragrance from a shampoo formulation. White Tea Fragrance<sup>24</sup> was formulated at 1 wt.% in an SLES/DSCADA<sup>25</sup> prototype shampoo formulation along with 0.4 wt.% cationic conditioning polymer. The fragrance deposition from a shampoo containing a high charge density PQ-67 polymer<sup>26</sup> was evaluated against similar shampoos containing no polymer, SoftCAT SK-MH,<sup>27</sup> and cationic guar in a series of subjective panel evaluation studies on European virgin hair tresses conducted in the same manner as described above. The results of these studies are summarized in Figure 8. It was shown that the high charge density PQ-67 polymer used in this study improved deposition of the white tea fragrance on virgin brown hair and that the difference was perceivable to the panelists in all three cases (9/10<sup>28</sup> or 8/10<sup>29</sup>).

<sup>&</sup>lt;sup>22</sup> PQ-67 polymer with 2.1 wt. %N and medium HS was used in this study.

<sup>&</sup>lt;sup>23</sup> Jaguar C-13S.

<sup>&</sup>lt;sup>24</sup> Provided by Fragrance Resources, Inc.

<sup>&</sup>lt;sup>25</sup> The same surfactant system as used in the Shampoo Formulation A.

<sup>&</sup>lt;sup>26</sup> PQ-67 polymer with 2.5 wt.% N and medium HS.

<sup>&</sup>lt;sup>27</sup> SoftCAT SK-MH was found to deliver more fragrance on skin from rinse-off formulations compared to other PQ-67 and PQ-10 polymers and cationic guar (*SoftCAT SK Conditioning Polymers*, product brochure issued by Amerchol Corporation/Dow Chemical Company (2005)).

<sup>&</sup>lt;sup>28</sup> Exact Significance level = 98% (binomial distribution).

<sup>&</sup>lt;sup>29</sup> Exact Significance level = 89% (binomial distribution).

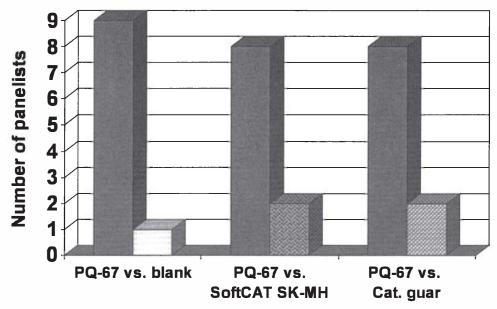


Figure 8. Fragrance deposition on European virgin brown hair, wet subjectives.

*Coacervate studies.* In order to understand the origin of the step-change boost in assisted deposition of performance ingredients observed for the high charge density PQ-67 polymers, their coacervate formation was studied in clear shampoo systems formulated with no silicone and 0.3 wt.% polymer in a SLES/DSCADA surfactant<sup>30</sup> base and 0.3 wt.% polymer. Haze measurements were performed using the Nippon Denshoku 300A hazemeter in a 50 mm path length cell. As discussed above, cationic polymers are known to form coacervates with anionic surfactants. Clear in a concentrated form, surfactant solutions with PQ-10 and PQ-67 cationic polymers become hazy upon dilution. This haziness, which is an indicator of coacervate formation, was measured over a dilution range of 0–10 and haze (coacervate) curves were studies. As shown in Figure 9, the coacervate curves of PQ-67 polymers with wt.% N ranging from 1.25 to 2.5% changed their shape and position depending on charge. In the range of 1.25 up to 1.8 wt.% N, their shape progressively evolved from lower and broader curves (low CS) to higher and "sharper" (narrower) curves (higher CS). In addition, these curves progressively shifted toward the lower dilution ratio.

This trend was earlier noticed and described for the PQ-10 polymers, such as, for example UCARE<sup>TM</sup> LR-30M (%N ~1.0) and JR-30M (%N ~1.8).<sup>31</sup> On the contrary, the haze curves for the high charge density PQ-67 polymers with % N above 2.0 did not follow the same trend. They became higher and broader at the same time (Figure 9) extending over a broader range of dilution compared to their 1.8% N predecessor. This is a known indicator of more coacervate being formed that raises expectations of superior deposition/co-deposition and conditioning performance. Therefore, these observations are in agreement with earlier findings from the silicone and fragrance deposition studies

<sup>&</sup>lt;sup>30</sup> The same surfactant system as used in the Shampoo Formulation A.

<sup>&</sup>lt;sup>31</sup> UCARE<sup>TM</sup> product literature, Amerchol Corporation.

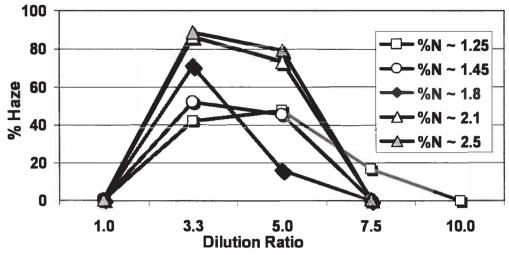


Figure 9. Coacervate formation in shampoos containing PQ-67 polymers.

described in this paper. This provides some insights on the mechanistic aspects of the high charge density PQ-67 polymers' outstanding performance.

### OTHER PROPERTIES IN SHAMPOOS

As shown above, novel high charge density PQ-67 polymers demonstrated improved overall performance and, in particular, showed outstanding ability to deposit benefit agents on hair from shampoo formulations. At the same time, these polymers were found to retain the good qualities of the PQ-10 and their lower charge density PQ-67 counterparts, such as enabling crystal clear formulations, <sup>32</sup> showing no excessive build-up on hair<sup>33</sup> (as shown on Figure 10), and having no negative impact on foam<sup>34</sup> (as shown on Figure 11).

## CONCLUSIONS

A series of new experimental high charge density PQ-67 polymers were prepared and evaluated in shampoo formulations. These new compositions demonstrated outstanding performance in assisting deposition of performance ingredients such as silicone and fragrance on human hair. They were found superior compared to PQ-10, lower charge density PQ-67 polymers, and cationic guar benchmarks. In several studies experimental polymers outperformed the cationic guar benchmark even when less polymer or silicone

<sup>&</sup>lt;sup>32</sup> Measuring less than 4% haze on Nippon Denshoku 300A hazemeter, 50 mm pathlength, 0.3% polymer. <sup>33</sup> The amount of deposited polymer was assessed by detecting the amount of anionic Red 80 dye bound to the cationic polymer deposited to the hair as described in (1). The deposition values were normalized per amount of polymer deposited after one wash. The prototype formulation included 0.3 wt.% polymer (experimental high charge density PQ-67 polymer with 2.1 wt.% N and medium hydrophobic substitution, UCARE<sup>TM</sup> JR-30M (PQ-10), or Jaguar<sup>®</sup> C-13S) in a SLES/DSCADA surfactant base.

<sup>&</sup>lt;sup>34</sup> Quantitative foam measurements were performed as described in (12): all foam generated while shampooing a hair tress was collected and weighed and then its volume and density were calculated.). The prototype formulation included 0.3 wt.% polymer (experimental high charge density PQ-67 polymer with 2.1 wt.% N and medium hydrophobic substitution, UCARE™ JR-30M (PQ-10), or Jaguar® C-13S) in a SLES/DSCADA surfactant base.

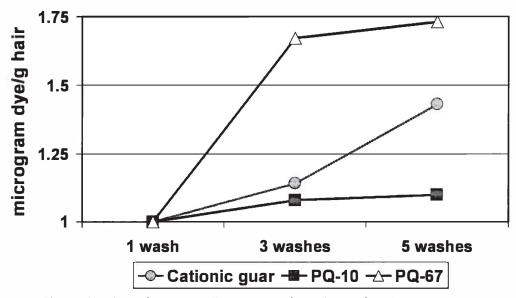


Figure 10. Polymer deposition on European virgin brown hair. Red 80 Anionic Dye Test.

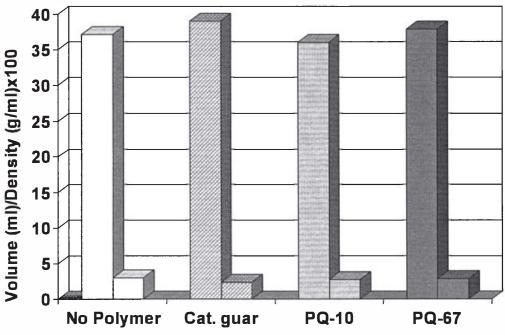


Figure 11. Foam volume and density measurement.

was used in the formulation containing PQ-67. Along with excellent overall conditioning, shampoos formulated with new PQ-67 polymers provided improved volume control and manageability to problem hair—a much needed benefit for anti-frizz/smoothing formulas and products that target sleek hair look. Perceivable improvement in delivery of fragrance to the hair was also substantiated. This could also make the polymers described here well suited for aromatherapy and spa formulas. According to the performance data presented in this paper, the new high charge density PQ-67 polymers should be recommended for a range of hair types that would benefit from enhanced deposition, premium conditioning and volume control: from normal, not chemically treated to problem hair (frizzy, unruly, coarse etc.) as well as Asian hair types.

#### REFERENCES

- T. V. Drovetskaya, R. L. Kreeger, J. L. Amos, and C. B. Davis, Effects of low-level hydrophobic substitution on conditioning properties of cationic cellulosic polymers in shampoo systems, *J. Cosmet. Sci.*, 55(Suppl.), S195–S205 (2004).
- (2) R. L. Kreeger and S. Zhou, Cellulose ethers, International Patent Application WO 2005/000903 (2006).
- (3) M. Gamez-Garcia, Polycation substantivity to hair, IFSCC, 4, 99-107 (2001).
- (4) W. Li and S. L. P. Jordan, Cationic cellulosic polymers with multifunctional and outstanding performance for personal care, *Cosmet. Toiletr. Manufact. Worldwide*, 1–4 (2003).
- (5) S. Zhou, C. Xu, J. Wang, P. Golas, J. Batteas, and L. Kreeger, Phase behavior of cationic hydroxyethyl cellulose-sodium dodecyl sulfate mixtures: Effects of molecular weight and ethylene oxide side chain length of polymers, *Langmuir*, 20, 8482–8489 (2004).
- (6) W. Li, J. Amos, S. Jordan, A. Theis, and C. Davis, Selecting the optimum silicone particle size/cationic polymer structure to maximize shampoo conditioning performance, *J. Cosmet. Sci.*, 57(2), 178–180 (2006).
- (7) X. Zhang, L. Kreeger, L. Kosensky, C. Barbeito, and J. Amos, Effect of cationic hydroxyethylcellulose polymer architecture on triglyceride deposition from body washes, *IFSCC Congress* (2004).
- (8) R. Y. Lochhead, "Shampoos," in *The Chemistry and Manufacture of Cosmetics*, 3<sup>d</sup> ed., M. L. Schlossman, Ed. (Allured Publishing Corporation, Carol Stream, IL, 2002), Vol. 2, pp. 277–326.
- (9) R. Y. Lochhead, Conditioning shampoo, Soap Cosmet. Chem. Spec., 42-49 (October 1992).
- (10) E. D. Goddard, "Polymer/Surfactant Interaction in Applied Systems," in *Principles of Polymer Science and Technology in Cosmetics and Personal Care*, E. D. Goddard and J. V. Grubber, Eds. (Marcel Dekker, New York, 1999), pp. 181.
- (11) B. G. Johnson and S. Van Oycke, Towards optimum hair conditioning, Personal Care, 17-19 (2006).
- (12) W. Li, S. L. P. Jordan, X. Zhang, J. Amos, and C. Davis, Synergistic effects of high molecular weight polyethylene oxide (PEO) and cationic cellulosic polymers on conditioning properties of hair and skin care products, *Cosmet. Toiletr. Manufact.* Worldwide, 31–34 (2004).