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The influence of nonionic cellulosic polymers on the uptake of polyquaternium-10 by bleached hair

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Synopsis

The influence of nonionic cellulosic polymers on polyquaternium-10 cationic hydroxyethylcellulose uptake by bleached hair was examined. Colloid titration was used to measure cationic polymer concentrations before and after immersion of hair tresses in treatment solutions.

Cationic polymer uptake by mildly bleached hair decreased somewhat when high-molecular-weight hydroxyethylcellulose (HMW HEC), hydroxypropyl methylcellulose (HPMC), and hydrophobically modified HEC (HMHEC) were included in polyquaternium-10 treatment solutions. There were no differences in polyquaternium-10 uptake by mildly bleached hair when low-molecular-weight HEC (LMW HEC) was included in treatment solutions.

HPMC and HMHEC significantly increased the adsorption of polyquaternium-10 by harshly bleached hair. There were no significant differences in uptake of this cationic polymer when either HMW HEC or LMW HEC were included in treatment solutions for this hair type.

INTRODUCTION

Nonionic cellulosic ethers are widely used in hair care formulations for their viscosity modifying properties. A viscous hair care product is important for several reasons (1): (a) a thin product is difficult to transfer from its container; (b) the consumer often equates thickness with a more concentrated or effective product; (c) stability may be enhanced when the formulation is viscous; and (d) a more viscous formulation frequently facilitates the manufacturing process. Cellulose ethers are also film-forming materials and serve to stabilize foam and improve the "feel" of a formulation (2).

Several types of cellulose ethers are available. These vary in the number and nature of substituent groups attached to the cellulose backbone. These substituent groups, in turn, dictate the solubilities and compatibilities of the polymers (3). Nonionic cellulosic

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polymers commonly used in hair products include hydroxyethylcellulose (HEC) and hydroxypropyl methylcellulose (HPMC). Long-chain alkyl groups can be also incorporated onto HEC to yield a hydrophobically modified HEC (HMHEC).

Shampoo formulations often contain cationic polymers to provide hair conditioning. The efficacy of a conditioning shampoo is directly related to the amount of cationic polymer deposited on the hair surface (4). It is well known that cationic polymer deposition is decreased when surfactants are included in a formulation. This interference is most marked in the presence of anionic surfactants, but amphoteric, or cationic, surfactants, as well as nonionic surfactants (5), may also decrease the deposition of cationic polymer.

Other factors such as treatment temperature (6), cationic polymer concentration (7), and added electrolytes (8) have been examined and found to influence cationic polymer uptake. However, nothing has been reported on the effects of added cellulose ethers, which are ingredients common in hair care products, on cationic polymer deposition. This paper presents the results of work examining the influence of nonionic cellulosic polymers on the uptake of polyquaternium-10 by bleached hair.

EXPERIMENTAL

HAIR TRESS PREPARATION

Medium-dark brown, 8-inch-long virgin quality European hair (DeMeo Bros., New York, NY) was washed and bleached in a formulation of 3% hydrogen peroxide (9). Two bleach conditions were chosen, 30 minutes at 32°C and 4 hours at 40°C. This yielded hair with two degrees of damage.

CELLULOSIC POLYMERS

Polyquaternium-10 (UCARE® Polymer JR 400, Amerchol, Edison, NJ) solutions of 0.05, 0.10, and 0.20 w/v% were prepared in a 0.001 M buffer of mono- and dibasic sodium phosphate (10). In addition, polyquaternium-10 solutions of the above concentrations were prepared to contain 0.10 w/v% concentrations of nonionic cellulosic polymers. The nonionic cellulosics added were high-molecular-weight hydroxyethylcellulose (HMW HEC, NATROSOL® 250 HHR); medium viscosity (lower molecular weight) hydroxyethylcellulose (LMW HEC, NATROSOL® 250 MR); hydroxypropyl methylcellulose (HPMC, BENECEL® MP 943 PR); and hydrophobically modified hydroxyethylcellulose (HMHEC, NATROSOL® *Plus* CS, Grade 330). All nonionic cellulosic polymers were supplied by Aqualon, a Hercules Incorporated Unit (Wilmington, DE).

COLLOID TITRATION

The uptake of cationic polymer from treatment solutions by hair was determined by a colloid titration method discussed elsewhere (10). System parameters described previously were identical in this study.

SUBSTRATE TREATMENT

Approximately one gram of bleached hair was accurately weighed and placed in a 125-ml Erlenmeyer flask. About 20 g of the polyquaternium-10 or polyquaternium-10/nonionic cellulosic polymer solution was accurately weighed and dispensed onto the hair using a syringe. The flask was tightly covered and placed in a 40°C shaker bath for 45 minutes. The solution was then decanted for concentration analysis by colloid titration (10).

Cationic uptake for the two bleached hair types was determined by measuring solutions containing polyquaternium-10 before and after immersion of a hair tress. Differences in solution concentration were attributed to sorption of the polymer by the hair. Identical measurements were made for solutions containing polyquaternium-10 at the same concentration but which also contained one of the nonionic cellulosic polymers.

DATA ANALYSIS

Statistical analyses were performed on an IBM-compatible, personal computer using the MINITAB® (State College, PA) statistical analysis software program.

All data are reported as average values of $n = 3$ determinations, unless otherwise noted. Standard deviations are reported for all data and illustrated in the accompanying figures.

Tests of differences in cationic polymer uptake between solutions containing nonionic cellulosic polymers with cationic polymer and control solutions of cationic alone were examined using a pooled t-test for the difference between two sample means. p-Values of 0.05 or less were noted and indicate significant differences in the data.

RESULTS AND DISCUSSION

COLLOID TITRATION

Because the colloid titration method is susceptible to contaminants (11), the nonionic cellulosic polymers were first analyzed to assess their possible influence on titration endpoints. Titrations of 300-μL aliquots of 0.10% nonionic cellulosic polymer solutions showed no difference in their equivalence points when compared to the normal indicator blank. This is not unexpected, since cellulose ethers are uncharged and should not participate in the titration. The titration endpoints determined in this method are therefore due solely to the presence of polyquaternium-10 in the various treatment solutions.

Polyquaternium-10 uptake onto "mildly" and "harshly" bleached hair was measured from control solutions containing the cationic alone. These adsorptions measured 2.6 ± 0.1 mg/g hair and 8.6 ± 0.2 mg/g hair, respectively. Uptake was then determined from polyquaternium-10 solutions containing 0.10 w/v% of one of the four nonionic cellulosics: LMW HEC, HMW HEC, HPMC, and HMHEC. Sorption data are found in Table I.

Uptake by mildly bleached hair (Figure 1) from polyquaternium-10 solutions containing HMW HEC was significantly less ($p = 0.002$) than the cationic control. There were also strongly directional and significant decreases in cationic adsorption from poly-

Table I
Effect of Added Nonionic Cellulosic Polymers on Polyquaternium-10 Uptake by Bleached Hair (Average N = 3)

	Mildly bleached hair (mg/g)	Harshly bleached hair (mg/g)
0.10% Polyquaternium-10	2.6 (0.1)[a]	8.6 (0.2)
0.10% HMW HEC/0.10% Polyquaternium-10	1.8 (0.2)	7.3 (0.2)[b]
0.10% LMW HEC/0.10% Polyquaternium-10	2.8 (0.2)	8.5 (0.2)
0.10% HMHEC/0.10% Polyquaternium-10	2.2 (0.2)	9.7 (0.3)
0.10% HPMC/0.10% Polyquaternium-10	2.4 (0.1)	11.4 (0.8)

[a] Numbers in parentheses indicate standard deviation.
[b] Polyquaternium-10 uptake control = 7.3 (0.7).

quaternium-10 solutions containing either HPMC or HMHEC ($p = 0.06$ and $p = 0.025$, respectively), but not from those containing LMW HEC.

HEC adsorbs slightly onto the surface of a hair fiber, even though the polymer is uncharged (7). This behavior is apparently extended to solutions containing cationic polymer, where the nonionics can compete with the latter for adsorption sites on hair. In keeping with general trends noted for the effect of molecular weight on polymer adsorption, HMW HEC, once adsorbed, would be less easily displaced than LMW HEC. This phenomenon would explain the relative effectiveness in modifying the adsorption of polyquaternium-10.

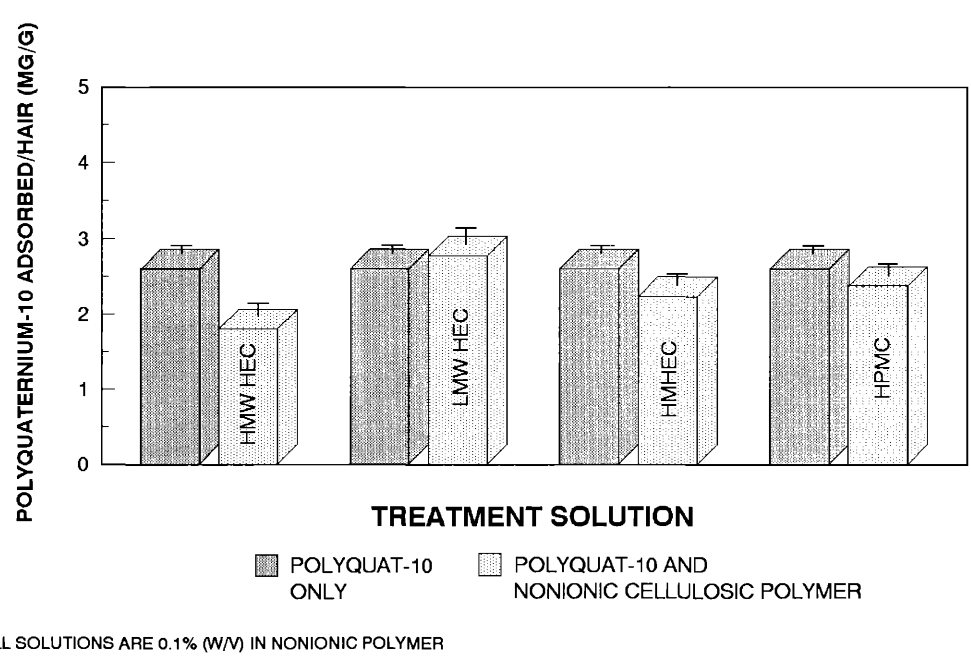

Figure 1. The effect of nonionic cellulosic polymers on polyquaternium-10 adsorption by mildly bleached hair.

Polyquaternium-10 adsorption by harshly bleached hair from solutions containing either HMW HEC or LMW HEC was not significantly different from that of cationic control solutions (Figure 2). In light of these results, the lower uptake by mildly bleached hair of cationic due to HMW HEC, HPMC, and HMHEC in the treatment solutions (Figure 1) at first seems anomalous. However, adsorption of cationic onto the less damaged surface of this hair is already low compared to that of the more harshly bleached hair (Figure 2). Small decreases caused by competitive adsorption of the nonionic would then be larger relative to the total amount of polyquaternium-10 adsorbed.

The increase in cationic uptake by harshly bleached hair (but not mildly bleached hair) in the presence of HPMC and HMHEC is noteworthy. The explanation may well be a rate effect occasioned by the surface activities specific to these two polymers rather than one involving direct interactions with the polyquaternium and/or hair. The surface activities of HPMC and HMHEC are 60–65 dynes/cm @ 0.1% (12) and 46–51 dynes/cm @ 0.1% (13), respectively.

As described previously (10), the contact time of bleached hair tresses with treatment solutions was standardized to 45 minutes. After 45 minutes, adsorption of polyquaternium-10 onto mildly bleached hair from 0.1% treatment solutions of the polyquaternium alone was largely complete at 2.6 mg/g; longer treatments of up to 180 minutes resulted in only a 0.9 mg/g increase to 3.5 mg/g. On the other hand, harshly bleached hair had adsorbed considerably more polyquaternium in the interval between 45 and 180 minutes (at 8.6 and 12.6 mg/g, respectively).

As such, HPMC and HMHEC may speed the approach of the polyquaternium to equilibrium adsorption by lowering the interfacial surface tension between the solution bulk and hair surface, and thus facilitate phase transfer of the polyquaternium-10 to the hair surfaces. This mechanism seems especially reasonable in light of earlier studies (7)

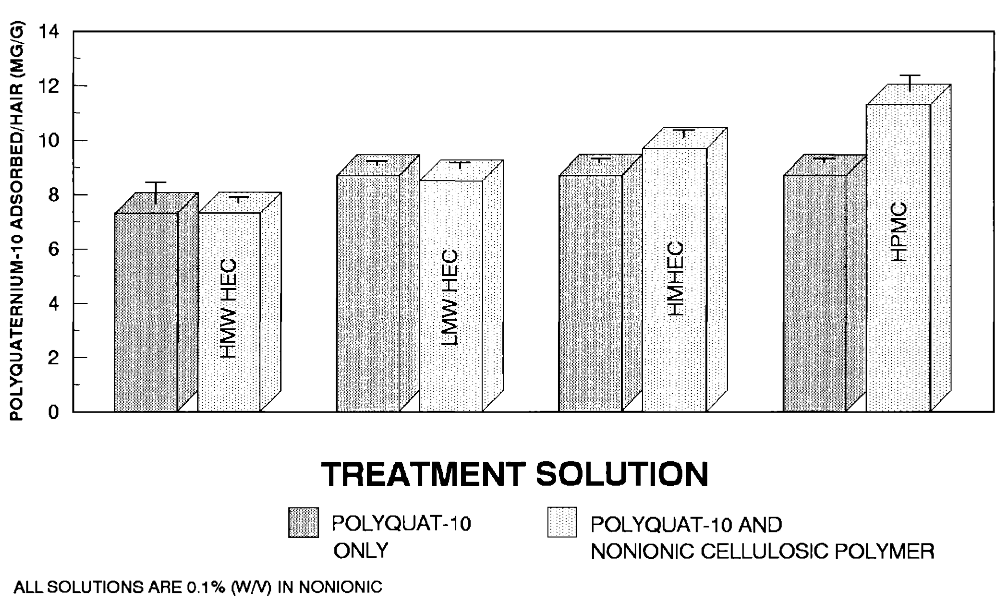

Figure 2. The effect of nonionic cellulosic polymers on polyquaternium-10 adsorption by harshly bleached hair.

in which the adsorption of polyquaternium-10 by harshly bleached hair continued over a week's time. This latter study served to demonstrate the porous nature of this damaged hair type and the slower diffusion into and adsorption of polymer within the fiber after quick initial adsorption at the immediate outer fiber surfaces.

The influence of polyquaternium concentration was also studied by examining 0.10% HMW HEC on cationic adsorption from 0.05% and 0.20% solutions of the polyquaternium (Figure 3). Cationic uptake was less from 0.05% polyquaternium-10 solutions when 0.10% HMW HEC was included for both mildly and harshly bleached hair ($p = 0.001$ and $p = 0.062$, respectively). There were no differences in adsorbance relative to controls from 0.20% polyquaternium-10 solutions containing HMW HEC for either bleached hair type. Data for these results are found in Table II.

Within the 45-minute time frame allowed for adsorption, polyquaternium-10 uptake depends on treatment solution concentration. Compare 2.8 vs 3.5 mg/g hair and 8.6 vs 9.1 mg/g hair in going from 0.05% to 0.20% in polyquaternium-10 (Table II). High-molecular-weight HEC can compete to some degree for adsorption sites with polyquaternium-10 when the latter is at low concentration, i.e. at 0.10% and less, but not at the higher 0.20% concentration. The degree of hair damage also influences competitive uptake.

SUMMARY

Nonionic cellulosic polymers influence the uptake of polyquaternium-10 by bleached hair. The direction and magnitude of this influence is dependent on both the severity of the bleach treatment and the type of nonionic cellulosic included.

Mildly bleached hair shows decreased cationic uptake when high-molecular-weight

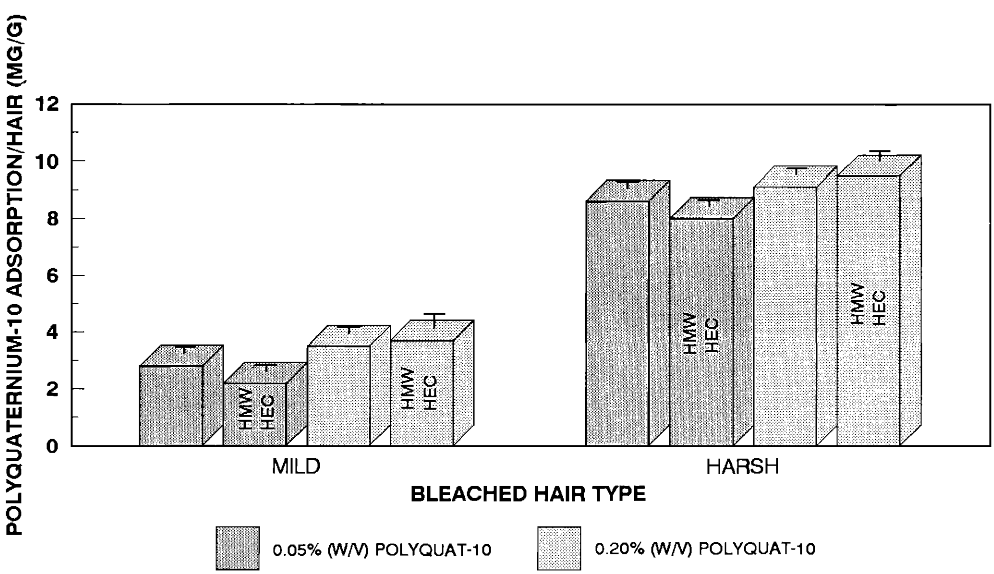

Figure 3. The effect of polyquaternium-10 concentration and 0.10% HMW HEC on cationic adsorption by bleached hair.

Table II
Effect of Polyquaternium-10 Concentration and Addition of 0.10% HMW HEC on Polyquaternium-10 Uptake by Bleached Hair (Average N = 3)

	Mildly bleached hair (mg/g)	Harshly bleached hair (mg/g)
0.05% Polyquaternium-10 control	2.8 (0.1)[a]	8.6 (0.2)
0.05% Polyquaternium-10/0.10% HMW HEC	2.2 (0.1)	8.0 (0.2)
0.20% Polyquaternium-10	3.5 (0.2)	9.1 (0.3)
0.20% Polyquaternium-10/0.10% HMW HEC	3.7 (0.4)	9.5 (0.3)

[a] Numbers in parentheses indicate standard deviation.

HEC, HPMC, and HMHEC are included in a cationic treatment solution. This decrease is most likely a result of limited competitive adsorption of the nonionic cellulosic by the hair surface.

Harshly bleached hair shows increased cationic adsorption when HPMC or HMHEC are included in cationic treatment solutions.

High-molecular-weight HEC reduced polyquaternium-10 uptake for both hair bleach types when included in 0.05% cationic polymer solutions. There was no difference in cationic adsorption from 0.20% solutions containing HMW HEC for either hair bleach type.

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