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Linking enhanced deposition agent functionality with aesthetic performance

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Synopsis

This study examines the cationic polymers 1) guar hydroxypropyltrimonium chloride polymers (GHPTC), 2) acrylamidopropyltrimonium chloride/acrylamide copolymer (APTAC/Acm), 3) polyquaternium polymers (PQ-10, PQ-7, PQ-67), and 4) a new polymer system approach for their a) deposition efficiency (as measured by quantifying oils deposited on virgin hair) and b) ability to deliver good wet and dry lubricity to the hair from a cleansing formulation as measured by comb energy and friction characteristics of the hair samples. Conditioning polymer technology approaches 1) acrylamidopropyltrimonium chloride/acrylamide copolymer, 2) a guar hydroxypropyltrimonium chloride polymer, and 3) the new polymer system approach deliver superior deposition of natural conditioning oils and dimethicone materials from anionic/amphoteric surfactant cleansing formulations. These new polymer technologies offer formulators the ability to improve uniformity of deposition as well as deposition efficiency of conditioning agents onto hair, and target the desired hair lubricity.

INTRODUCTION

The function of conditioning shampoo is to cleanse the hair and to deposit active ingredients, conditioning agents, fragrances, and other materials onto the hair or scalp. Effective deposition of conditioning ingredients is associated with the formation of a polymer-surfactant coacervate complex formed from the shampoo on dilution with water (1). Acrylamidopropyltrimonium chloride/acrylamide copolymer and guar hydroxypropyltrimonium chloride polymers have been shown to enhance deposition of dimethicone and dimethicanol silicone oils onto hair (2). The deposition performance of these polymers for natural oils such as jojoba and meadowfoam seed oil is of interest given the movement in the marketplace towards natural ingredients.

OBJECTIVE

This study examined guar hydroxypropyltrimonium chloride(GHPTC) polymers, an acrylamidopropyltrimonium chloride/acrylamide copolymer(APTAC/Acm), polyquaternium-10, polyquaternium-67, and polyquaternium-7 polymers, and a new polymer system approach (DEV-1) under development at Ashland Inc. for their conditioning benefits. The conditioning polymers were formulated into a conditioning shampoo and compared with respect to their a) deposition efficiency for different oils onto hair and b) ability to deliver good wet and dry lubricity to the hair from a cleansing formulation.

EXPERIMENTAL

MATERIALS

1. INCI: guar hydroxypropyltrimonium chloride, GHPTC-1 (N-Hance™ 3196, Ashland Inc.)
2. INCI: guar hydroxypropyltrimonium chloride, GHPTC-2 (N-Hance™ 3215, Ashland Inc.)
3. INCI: acrylamidopropyltrimonium chloride/acrylamide copolymer, APTAC/Acm (N-Hance™ SP-100, Ashland, Inc.)
4. INCI: Polyquaternium-10, PQ-10 (Ucare* Polymer JR-30M, Dow Chemical Company)
5. INCI: Polyquaternium-7, PQ-7 (Merquat* 550, Nalco Company)
6. INCI: Polyquaternium-67, PQ-67 (SoftCAT* SX1300H, Dow Chemical Company)
7. DEV-1, guar hydroxypropyltrimonium chloride and acrylamidopropyltrimonium chloride/acrylamide copolymer (Ashland Inc.)
8. Sodium Laureth Sulfate (2EO) (Standapol* ES-2, Cognis Corporation)
9. Cocamidopropyl betaine (Amphosol* CA, Stepan Company)
10. Carbomer (Carbopol* 980, Lubrizol *Noveon*® Consumer Specialties)
11. Dimethicanol and TEA dodecylbenzene sulfonate microemuision (Dow Corning* 1784)
12. Jojoba oil (Lipoval* J, Lipo Chemicals, Inc.) Charkit Chemical Corp.
13. Meadowfoam seed oil(Natural Products, Inc.) Charkit Chemical Corp.

METHODS

Virgin European medium brown hair was supplied as 12-inch tresses from International Hair Importers. Tresses were washed with a 4.5% sodium lauryl sulfate solution prior to applying the shampoo treatment:

A) *Shampoos compositions* used in this study contained 0.25 wt% cationic conditioning polymer and the following ingredients: 12 wt% SLES (sodium laureth sulfate (2EO), 2 wt% CAPB (cocamidopropyl betaine), 1 wt% sodium cloride, 1.5 wt% conditioning oil, and carbomer added for emulsion stabilization.

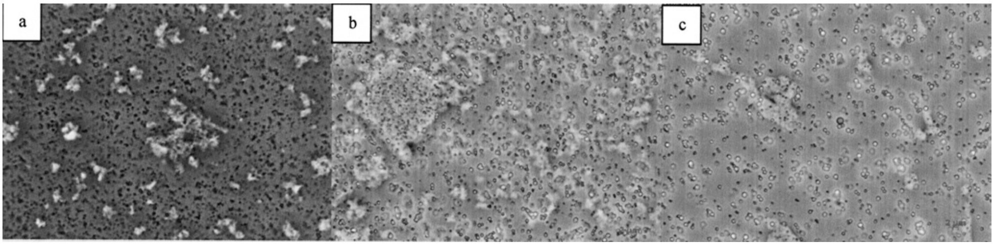
B) *Wet and dry combing performance measurements.* Combing performance was measured on an Instron* 5542 testing system, equipped with a double comb fixture. Eight combs were performed per tress, at 23°C and 50% relative humidity. Hair tresses were then allowed to dry overnight at 23°C and 50% relative humidity.

*Trademark owned by a third party.

C) *Coefficient of friction measurements on dry hair*. Friction measurements were obtained on a CETR UMT* M0 tribometer using a sledge friction test with a silicon wafer countersurface at 23°C and 50% relative humidity after air drying the hair overnight at 23°C and 50% relative humidity.

D) *Microscopy.* The microstructure of shampoo samples was examined under an Olympus* BH-2 Phase Contrast Light Microscope (LM). All of the samples contained two particle phases as shown in Figure 1(a–c), with the oil phase appearing as round particles and small agglomerates (generally appearing as blue spots in the phase contrast images).

E) *Natural oil deposition measurements.* Virgin brown (VB) hair tresses were extracted with hexane to recover the soluble hair extract. Solutions of hair extracts were run on a gas chromatograph (GC) with a flame ionization detector. For jojoba oil, the area of the four major peaks, identified by GC/Mass Spectrometry as ester forms, were summed and compared to a standard. Figure 2a shows a chromatogram for the jojoba oil standard. The four major peaks present a unique pattern of the jojoba ester components that was used to quantify the jojoba oil in the hair extracts (3). The limit of quantitation (LOQ) is considered to be approximately 11 mg/kg. Figure 2b shows a chromatogram for the meadowfoam oil standard. The five major triglyceride peaks present a unique pattern that was used to quantify the meadowfoam seed oil in the hair extracts. The limit of quantitation (LOQ) is considered to be approximately 100 mg/kg.



Figure(1a–c). Light photomicrographs of shampoo containing acrylamidopropyltrimonium chloride/acrylamide copolymer (APTAC/Acm) and (a) dimethicanol, (b) jojoba, and (c) meadowfoam seed oils.

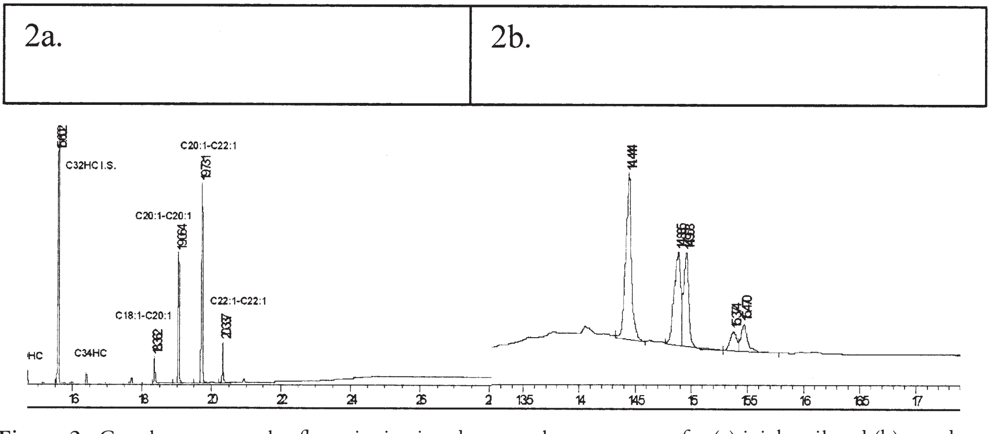


Figure 2. Gas chromatography-flame ionization detector chromatograms for (a) jojoba oil and (b) meadowfoam seed oil.

F) *Silicone deposition measurement.* The hair tress samples were double extracted with methylene chloride, and the silicone content was quantified in the infrared by measuring the $SiCH_3$ band near 1261 cm^{-1} using a Thermo-Nicolet MAGNA* 560 FTIR with a fixed path liquid cell (2).

RESULTS AND DISCUSSION

Jojoba oil has been used as a hair and skin moisturizer for many years. Considered a liquid wax, it is composed primarily of mono-unsaturated long chain fatty acid/fatty alcohol esters, mainly with a carbon chain length of C18 to C22. Meadowfoam oil has been used as a hair and skin moisturizer for many years. The oil is composed primarily of mono-unsaturated long chain triglycerides, mainly with a carbon chain length of C20 to C22. Virgin hair was treated with shampoos containing various additives to measure their effectiveness in retaining jojoba or meadowfoam oil after rinsing.

TOTAL DEPOSIT ON HAIR

Figure 3 shows the total weight of dried extract recovered per tress for both jojoba and meadowfoam seed oil shampoos. This extract contains the oil deposited on the tress in addition to other components. The relative weight of dried extract for each shampoo system gives a relative trend of deposition effectiveness for each polymer. Guar hydroxypropyl trimonium chloride polymers GHPTC-1 and 2, acrylamidopropyltrimonium chloride/acrylamide copolymer APTAC/Acm, and the polymer system DEV-1 enhance deposition onto hair from both jojoba oil and meadowfoam seed oil shampoos. PQ-7 and PQ-10 polymers deposit some material onto hair from the meadowfoam oil shampoos.

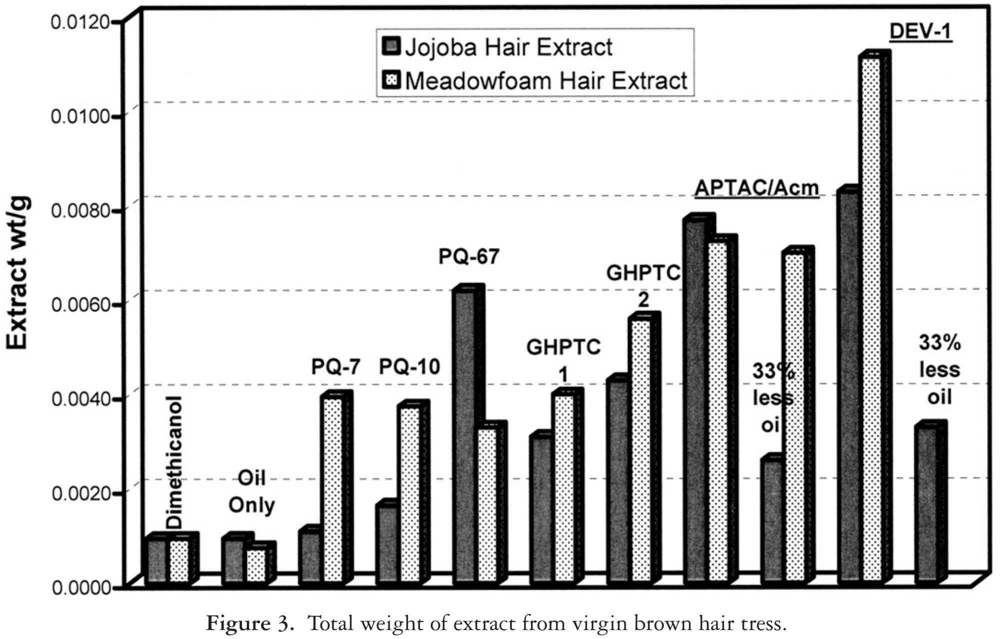


Figure 3. Total weight of extract from virgin brown hair tress.

AMOUNT OF OIL DEPOSIT ON HAIR

To determine the amount of oil present in the hair deposits, the dried extracts were redissolved in heptane and run on a GC with a flame ionization detector. Figure 4 shows the amount of oil recovered in the extract as measured by GC. The following polymers, listed in decreasing effectiveness of deposition, enhance deposition of both jojoba and meadowfoam seed oil onto hair relative to the shampoo containing oil without cationic conditioning polymer. PQ-10 polymer enhances deposition of meadowfoam seed oil, but not jojoba oil.

APTAC/Acm~DEV-1>>GHPTC-2 ~PQ-67>GHPTC-1 (jojoba oil)>PQ-10>PQ-7

As shown by comparing Figure 4 with Figure 5, the polymers depositing the most jojoba and meadowfoam oil from shampoos are also good deposition agents for dimethicanol, with the exception of the PQ-67 polymer. PQ-67 polymer shows poor silicone oil deposition from this formulation. Acrylamidopropyltrimonium chloride/acrylamide copolymer APTAC/Acm, DEV-1 developmental polymer system, and guar hydroxypropltrimonium chloride polymer GHPTC-2 enhance jojoba, meadowfoam and silicone oil deposition. The PQ-67 polymer enhances jojoba and meadowfoam oil deposition, but not silicone oil deposition. As shown in Figure 5, the acrylamidopropyltrimonium chloride/acrylamide copolymer APTAC/Acm effectively deposits the same amount of silicone oil onto the virgin brown hair, even at 33% reduced dimethicanol silicone oil levels in the shampoo. This enhanced deposition effectiveness at reduced oil levels, however, does not translate to the natural oils in this formulation, as shown in Figure 5.

The relative order of deposition effectiveness for jojoba and meadowfoam seed oil from the quantified oil graph in Figure 5 is in the order:

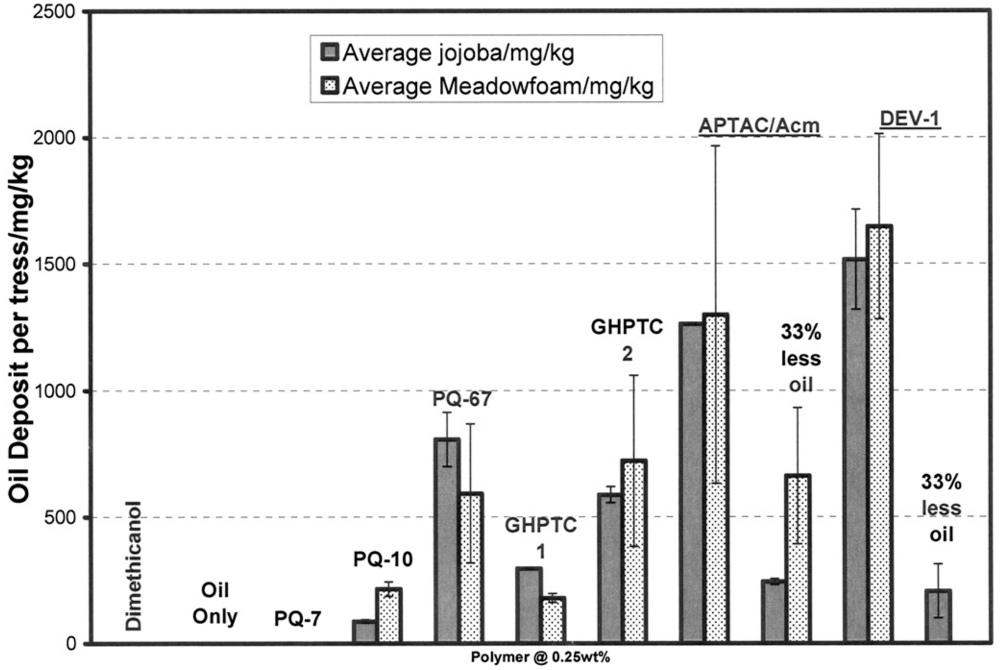


Figure 4. Amount of oil deposit on virgin brown hair tress.

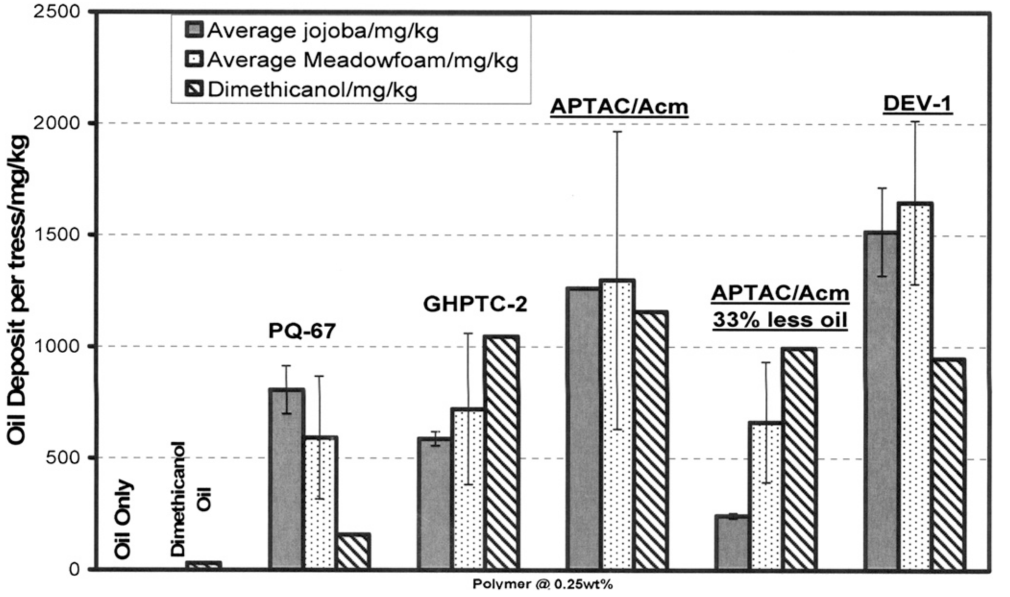


Figure 5. Comparison of deposition polymer effectiveness across oil types.

APTAC/Acm~DEV-1 >> GHPTC-2~PQ-67

The relative order of deposition effectiveness for dimethicanol microemulsion from the quantified oil graph in Figure 5 is:

APTAC/Acm ~ GHPTC-2 ~ DEV-1 >> PQ-67

HAIR PERFORMANCE AFTER SHAMPOO TREATMENT

Wet comb energy reduction. As shown in Figure 6, shampoos containing the dimethicanol microemulsion deliver slightly lower wet comb energies relative to shampoos containing jojoba and meadowfoam seed oil. The relative order of wet comb energy reduction performance for the series of polymers follows a similar order to deposition efficiency:

APTAC/Acm ~ GHPTC-2 ~ DEV-1> GHPTC-1>PQ-67 ~ PQ-10>PQ-7

The shampoos delivering lower comb energy also deliver more oil phase and extracted material to the tresses. Acrylamidopropyltrimonium chloride/acrylamide copolymer APTAC/Acm, guar hydroxypropyltrimonium chloride polymer GHPTC-2, and DEV-1 polymer system consistently deliver the lowest wet comb energies and the most oil deposit onto the tress. In addition, the wet comb performance of the shampoos containing acrylamidopropyltrimonium chloride/acrylamide copolymer APTAC/Acm and DEV-1 developmental system do not significantly change after reducing the oil content of the formulations by 33%.

The tresses treated with the shampoo containing PQ-67 polymer show some of the highest wet comb energies in this study. This result was expected for the shampoo containing dimethicanol, because of low levels of silicone oil deposition by the PQ-67 polymer. The

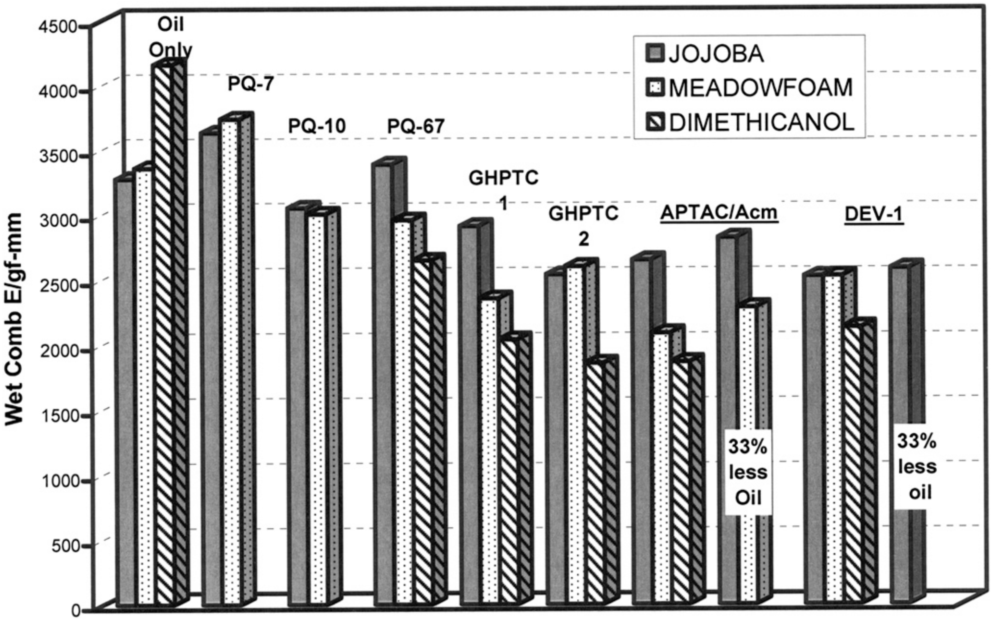


Figure 6. Wet comb energies for virgin brown hair treated with conditioning oil shampoos.

higher wet comb energies for tresses treated with the shampoos containing PQ-67 and jojoba and meadowfoam seed oil were unexpected.

Coefficient of friction reduction. Coefficient of friction measurements were performed on dry hair after treatment with the shampoo. The friction results are shown in Figure 7. The results in Figure 7 show that guar hydroxypropyltrimonium chloride polymer GHPTC-2 and the DEV-1 developmental system deliver the lowest friction to VB hair from jojoba shampoos, consistent with their high level of oil deposition from this shampoo.

For tresses treated with shampoos containing meadowfoam seed oil, shampoos containing either PQ-67 polymer or the DEV-1 developmental system were found to deliver the lowest friction to VB hair. As shown in Figure 7, the coefficient of friction measured on hair treated with shampoos containing dimethicanol.

SUMMARY

The results of this study show that acrylamidopropyltrimonium chloride/acrylamide copolymer APTAC/Acm, DEV-1 developmental polymer system, and guar hydroxypropyltrimonium choride polymer GHPTC-2:

1. significantly enhance deposition of jojoba, meadowfoam and dimethicanol oils from the shampoo formulation used in this study, relative to a control shampoo formulation containing no cationic polymer.
2. deliver the greatest reduction in wet comb energy when applied to virgin brown hair of all the polymers included in this study.

The polyquaternium-67 polymer enhances jojoba and meadowfoam oil deposition relative to the control shampoo that contained no polymer, but PQ-67 shows only minor

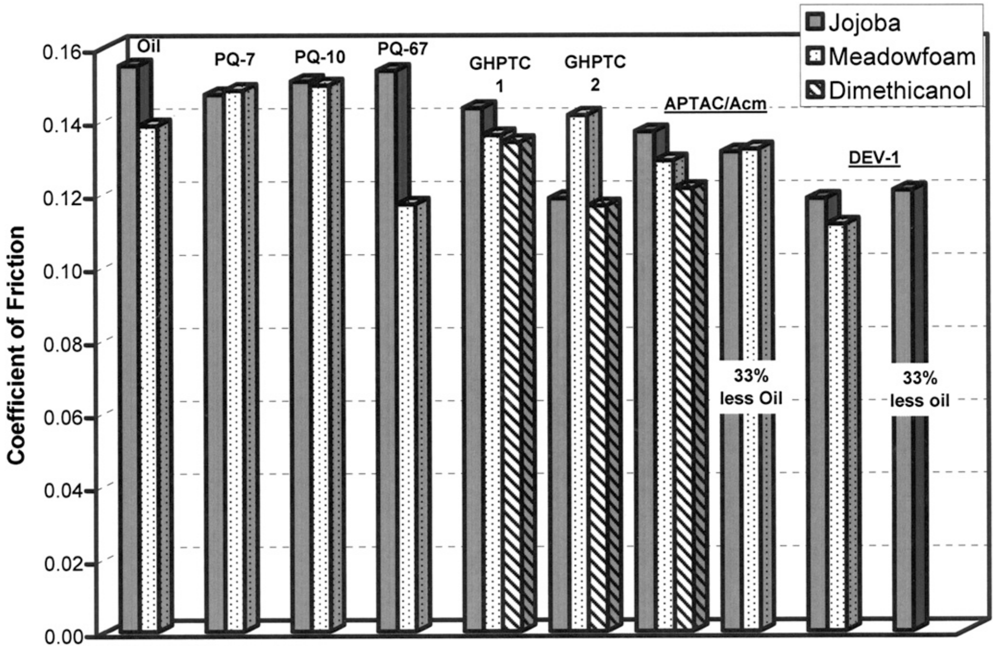


Figure 7. Coefficient of friction for shampoo-treated virgin brown hair.

enhancements in dimethicanol microemulsion deposition. Shampoos containing polyquaternium-10 polymer and guar hydroxypropyltrimonium chloride GHPTC-1 enhance deposition of jojoba and meadowfoam oil on to virgin brown hair, but less efficiently than shampoos containing the acrylamidopropyltrimonium chloride/acrylamide copolymer APTAC/Acm, DEV-1 developmental system, or guar hydroxypropyltrimonium chloride polymer GHPTC-2.

The conditioning polymer technology approaches 1) acrylamidopropyltrimonium chloride/acrylamide copolymer, 2) guar hydroxypropyltrimonium chloride polymer, and 3) the new developmental polymer system approach, deliver superior deposition of natural conditioning oils and dimethicone materials from anionic/amphoteric surfactant cleansing formulations as well as good conditioning performance. These new polymer technologies offer formulators the ability to improve uniformity of deposition (2) as well as deposition efficiency of conditioning agents onto hair.

REFERENCES

(1) R. Y. Lochhead and L. R. Huisinga, "Advances in Polymers for Hair Conditioning Shampoos," in *Hair Care: From Physiology to Formulation,* Angela C. Kozlowski, Ed. (Allured Business Media, Carol Stream, IL, 2008) pp. 123–136.

(2) P. E. Erazo-Majewicz, J. A. Graham, and C. R. Usher, Assessing the targeted conditioning performance of cationic polymers, *Cosmet. Toiletr.,* **125**, 24–30 (2010).

(3) T. K. Miwa, Structural determination and uses of jojoba oil, *J. Amer. Oil Chemists Soc.,* **61**, 407–410 (1984).