

The use of x-ray fluorescent spectroscopy to study the influence of cationic polymers on silicone oil deposition from shampoo

JAMES V. GRUBER, BURTON R. LAMOUREUX,
NIRAJ JOSHI, and LUIS MORAL, *Amerchol Corporation, 136
Talmadge Rd., Edison, NJ 08818-4051 (J.V.G., N.J., L.M. {retired}),
and Union Carbide Corporation, 1 River Rd., Bound Brook, NJ 08876
(B.R.L.)*.

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Synopsis

In this study, x-ray fluorescent spectroscopy was employed, in a non-destructive way, to analyze the influence that water-soluble, cationic hydroxyethylcellulose (i.e., polyquaternium-10) has on the deposition of silicone oil (dimethicone) onto hair. Virgin brown hair tresses were washed with various model shampoos that contained emulsified dimethicone. The shampoos were modified only by the addition or absence of polyquaternium-10. The results indicate that the cationic polymers do influence silicone oil deposition onto hair during the shampooing process. In the absence of cationic polymer, the silicone oils deposit readily, but appear to show “build-up” phenomena upon repeated washings. When a cationic polymer is present in the continuous phase of the shampoo, the build-up phenomena is significantly diminished, and silicone oil deposition remains relatively constant in repeated washings. In addition, we have noted that the molecular weight of the cationic polymer can have a strong effect on silicone oil deposition. It appears that the higher the molecular weight of the polyquaternium-10, the greater the amount of silicone deposition onto the surface of the hair. To demonstrate that the analysis technique has potential applications in commercial shampoos, we examined a commercial “2-in-1” shampoo that contains dimethicone and polyquaternium-10 and found that the data for our simple model shampoos and the commercial shampoo correlated closely.

INTRODUCTION

The use of silicone polymers, especially non-ionic silicone polymers such as dimethicone, is prevalent in personal care (1). These unique oleaginous materials, because of their very low surface tension, have a remarkable ability to spread over both hydrophobic and hydrophilic surfaces. When applied to hair or skin they offer significant beneficial improvements in the sensory properties of skin and hair in both the wet and dry state. Cationic polymers likewise have enjoyed a healthy relationship with the personal care

James V. Gruber's present address is Arch Personal Care, 70 Tyler Place, South Plainfield, NJ 07080.

industry because of their natural ability to bind to the anionic surfaces of hair and skin (2). How this deposition takes place from surfactant-containing systems in which the cationic polymers find themselves in a broth of anionically charged surfactant molecules remains a topic of discussion (3–6).

Many shampoo and body wash products available today offer the consumer a blend of both cationic polymers and emulsified silicone oils as a conditioning package. However, little work has been conducted to address the influence that these two macromolecules have on one another when they are delivered simultaneously to the body via the washing process. Recently, we reported on the use of x-ray fluorescence spectroscopy to examine the influence of cationic polysaccharides on silicone oil deposition (7). The technique is unique for this application, as it allows us to examine a keratin surface, i.e., hair, in a non-destructive fashion to determine how a dissolved cationic polymer affects the deposition behavior of dispersed dimethicone. We wish to broaden our discussion to examine the influence that cationic polymer concentration has on silicone deposition. In addition, we will show that the results we have obtained using our model shampoos appear to correlate well with the silicone deposition we find for a commercially available “2-in-1” conditioning shampoo.

EXPERIMENTAL

The model shampoo formulations and cationic polymers employed in this study are shown in Table I. The testing protocol, shampooing protocol, and other information important to the technique can be found elsewhere (7). This referenced article goes into considerable detail to describe sources of potential error in the use of x-ray fluorescence for direct analysis of silicon on hair. These errors include such experimental details as the method of hair washing, particle size of the emulsified silicone oils, number of x-ray scans, and direction of the hair during scanning, among others. We elected, for this reason, to discuss only average relative silicon deposition without reference to error.

Table I
Shampoo Formulation and Cationic Polymers

Ingredients	A	B	C	D	E	F	G
Ammonium lauryl sulfate	14.0	14.0	14.0	14.0	14.0	14.0	—
Ammonium laureth sulfate	3.9	3.9	3.9	3.9	3.9	3.9	—
Cocamidopropyl-betaine	3.0	3.0	3.0	3.0	3.0	3.0	—
Ethylene glycol distearate	2.0	2.0	2.0	2.0	2.0	2.0	—
Dimethicone ¹	1.5	1.5	1.5	1.5	1.5	—	—
Cationic polymer	0.5	0.3	0.1	0.5	—	—	—
	Polymer 1 ²	Polymer 1	Polymer 1	Polymer 2 ³			
Preservative	0.4	0.4	0.4	0.4	0.4	0.4	—
Water	74.7	74.9	75.1	74.7	75.2	76.7	—
15-Pareth-9							100.0

¹ Dimethicone is a blend of a high-molecular-weight gum, and a low-molecular-weight fluid in the ratio of 60:40.

² Polymer 1: Polyquaternium-10 of approximate molecular weight 400,000 and approximate percent cationic nitrogen of 1.0.

³ Polymer 2: Polyquaternium-10 of approximate molecular weight 900,000 and approximate percent cationic nitrogen of 1.0.

Readers who wish to understand the error and sources of error inherent in the technique are directed to the more detailed article.

We wish, at this time, to describe in a general fashion how the x-ray fluorescent spectrometer works in our particular application and some of the important sources of error that can affect the measurements. We have employed both a Kevex energy dispersive instrument and a Philips Electronic P2400 wavelength dispersive instrument. The terms *energy dispersive* and *wavelength dispersive* relate to the method of wavelength discrimination, and for those interested in a more thorough description of these terms, we suggest a recent review by Torok *et al.* (8). The Philips instrument is more modern and is equipped to spin the sample during analysis. We have found that due to the directionality of hair, it is essential to spin the fibers during analysis, but with the Kevex instrument, this rotation can be done manually in 90° steps and the results obtained correlate very well with measurements taken on the instrument that rotates the samples during analysis (7). We have found that the greatest source of error in the analysis technique occurs in the preparation of the shampoos and the washing of the tresses, and we have outlined our steps to minimize these sources of error as much as possible (7). Within our discussion, references to differences in relative silicon deposition can be considered statistically significant.

Figure 1 shows a schematic representation of the x-ray spectrophotometer. Very simply, the device is a direct excitation mode instrument in which the sample, i.e., the treated tress, is directly excited by the primary radiation from the x-ray tube. The x-rays from the source strike the hair tress, covering a sample size of approximately one inch in diameter. The x-rays cause various atoms to emit excess energy at specific energies to afford fluorescence. This technique measures the signal from the atoms (i.e., silicon), without regard to their attributes inside a compound. The characteristic silicon fluorescence occurs at 1.74 KeV, and is called the $K\alpha$ band.

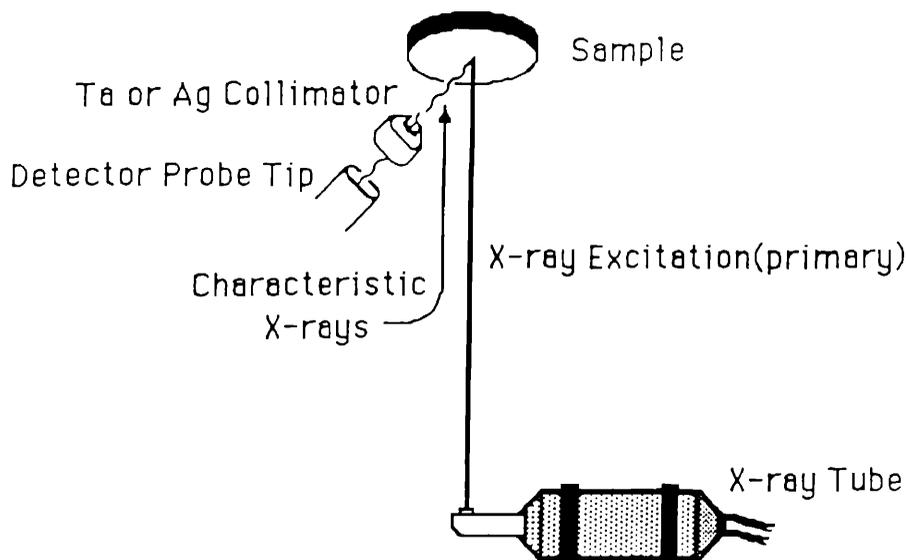


Figure 1. Schematic of x-ray fluorescent spectrophotometer.

Since the x-ray energy penetrates only a few microns into the hair tress, it only measures the silicone oils that have deposited onto the surface of the hair tress, i.e., onto the hair cuticle. Because we do not know the absolute value for the amount of silicone deposited onto the hair [although methods exist to measure these absolute amounts (9,10)], we are looking instead at qualitative values of silicone deposition that are taken as counts/second. Therefore, only tresses washed using carefully controlled model shampoo formulations treated under similar washing conditions on the same type of hair can be evaluated, and the use of specific control tresses is critical for relating data.

RESULTS AND DISCUSSION

In our original discussion, we noted a surprising result that we show graphically in Figure 2. When virgin brown tresses (DeMeo Brothers) are washed with a model shampoo that contains a silicone emulsion but does not contain a cationic polymer (Formulation E), the silicone not only deposits, but after multiple washings continues to deposit, showing indications of a build-up phenomena. The control tresses in this case are also shown and include tresses washed one time with a non-ionic surfactant, 15-Pareth-9 (Formulation G) and tresses washed one and ten times with our model shampoo base without silicone or cationic polymer (Formulation F). However, when we examined the data for our formulation containing a low-molecular-weight polyquaternium-10 at 0.5 wt%, (Formulation A), we noted that while initial single-wash silicone deposition was slightly depressed compared to the silicone-only shampoo, after multiple washes the presence of the cationic polymer appears to modulate the silicone deposition and the build-up phenomena is suppressed.

This suggests to us that in the washing process, the two polymers must interact with one another in some fashion that is not presently understood due to the complexity of the application process, which includes high shear, foaming, and dilution effects. While the influence of the cationic polymer on the silicone oil deposition is readily apparent from

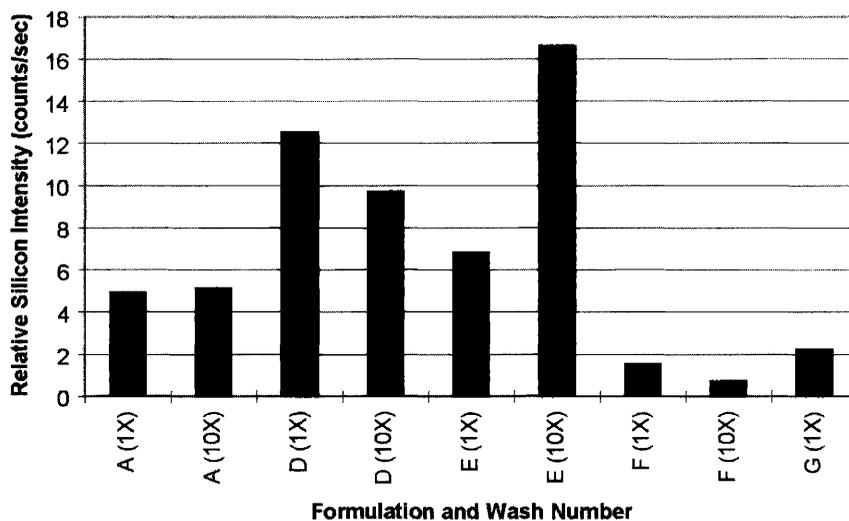


Figure 2. Relative silicon x-ray fluorescent intensities for hair tresses treated with various shampoo formulations including data for single (1×) and multiple (10×) washing experiments (except as noted).

these experiments, the juxtaposed influence of the silicone oil on the cationic polymer deposition is not, and this aspect is currently a topic of investigation in our laboratories.

The effect of cationic polymer molecular weight can also be seen from the data in Figure 2. It appears that as the molecular weight of the cationic polymer increases (compare Formulation A with Formulation D), the amount of silicone oil that deposits on the hair increases as well. We note that in a single washing experiment, the higher-molecular-weight polyquaternium-10 polymer deposits nearly 60% more silicone than the comparable lower-molecular-weight polymer of equal charge. This further suggests to us that perhaps factors such as the rheology of the shampoo during application and rinsing, or the hydrodynamic volume of the cationic polymer, can also play an important role in modulating the oil deposition.

Looking at the effect of cationic polymer concentration, we note that for the medium-molecular-weight cationic polymer (Polymer 1) there is little change in the amount of silicone depositing on the hair even after repeated washings down to a concentration of 0.3 wt% (compare Formulations A and B) (Figure 3). However, when the cationic polymer concentration drops to 0.1% (Formulation C), the effect on silicone oil deposition is quite dramatic and the shampoo behaves more like a formulation that does not contain cationic polymer, i.e., the silicone build-up phenomena is noted again. It appears that when the cationic polymer concentration falls below a certain level, its ability to interact with the silicone emulsion and influence the silicone deposition diminishes.

We were curious as to whether or not our analysis technique was providing results that might have significance to the behavior of commercial shampoos. For this reason, we elected to examine a commercial shampoo that we knew to contain a surfactant platform similar to our own model platform containing polyquaternium-10. However, we do not

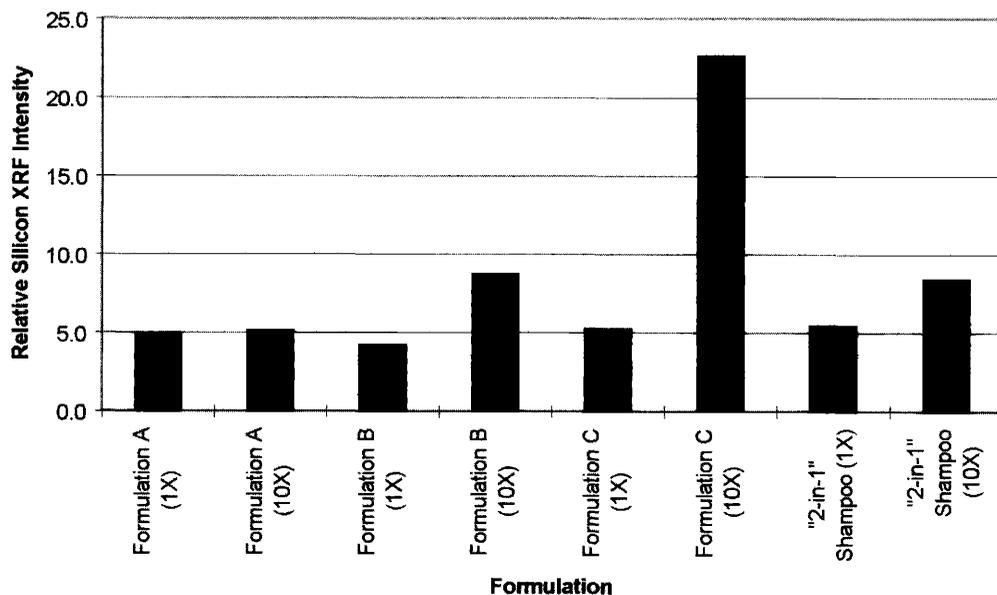


Figure 3. Effect of cationic polymer concentration (0.5, 0.3, and 0.1 wt%) on relative silicon XRF intensities for hair tresses treated with cationic Polymer 1 and data for a commercially available "2-in-1" shampoo containing dimethicone and polyquaternium-10 (1 and 10 washes).

know the exact composition of the shampoo or the concentrations of the ingredients in the commercial shampoo. The commercial shampoo also contains other ancillary ingredients that we have excluded in our simple model formula. The data for the commercial shampoo is provided in Figure 3. From this data, we note that the relative amount of silicone deposited from the shampoo and the amount of deposition we noted from our model shampoo containing 0.3% cationic polymer are essentially identical, even after multiple washing steps (compare Formulation B and the labeled "2-in-1" shampoo). We feel comfortable, therefore, in suggesting that the use of x-ray fluorescence in the fashion we have described can be predictive of real-world shampoo use.

CONCLUSIONS

We have demonstrated that x-ray fluorescent spectroscopy can be a useful tool for analyzing the behavior of ingredients delivered from emulsified surfactant systems. While we have focused in this study on the deposition of silicone oil onto hair, and have examined the role dissolved cationic polymers can play in potentiating the deposition, it seems very likely that this technique can be expanded to a wide variety of colloidal systems including, perhaps, the study of antidandruff agents (e.g., pyrithione zinc) and physical sun screens such as TiO_2 . Likewise, while we conducted our studies on hair tresses that are readily available, there does not appear to be any reason why this technique could not work on other types of fibers, or membranes such as skin.

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