Evaluation of relative shampoo detergency

D. THOMPSON, C. LEMASTER, R. ALLEN, and
J. WHITTAM, *Forrest C. Shaklee Research Center,*
1992 Alpine Way, Hayward, CA 94545.

Synopsis

An analytical protocol is described for the assessment of relative shampoo detergency on hair by which raw materials, prototype formulations, and competitive products can be objectively contrasted. Hair tresses are soiled with a standard nine-component synthetic sebum mixture using 2% and 10% sebum in hexane solutions. Soil removal is determined under three test conditions: bulk bath washer, traditional "finger squeeze," and controlled-pressure apparatus. Gas chromatography of the residual sebum components serves as the analytical basis for the investigations. Comparisons are based upon the "tracking" of 20 gas chromatograph peaks which are indicative of the various sebum fractions. An internal control sample is used to compensate for any sample-to-sample variation in soiling level. Solutions (10%) of different surfactant types, ammonium lauryl sulfate (ALS), sodium laureth 2-sulfate (AES) and sodium alpha olefin C14-C16 sulphonate (AOS), are evaluated with both single and multiple soiling and washing cycles to investigate sebum partitioning as a function of the active ingredient type.

Sebum fraction removal is seen to be dependent upon:

1. Washing technique—The finger squeeze method of sample treatment is the least reproducible of the sample treatments investigated due to the high degree of operator interaction required.
2. Surfactant system—The type of surfactant determines which sebum fractions are removed and to what extent.
3. Multiple cycles—Repeated washing and soiling cycles indicate that ALS leaves the least amount of residue with repeated use.

INTRODUCTION

The theory of detergency dates back over half a century (1–4). In essence, the theoretical principles and tenets of surface chemistry can be used to describe the removal of soil from a solid surface based upon molecular interactions at the solid-liquid and liquid-liquid interfaces (5–7). Experimental detergency evaluation of various surfactant solutions, on the other hand, has been more difficult. Part of this difficulty lies in agreement on a standard soil, a controlled substrate, a consistent and reproducible soiling process, a standard soil removal procedure and, finally, analytical methodology capable of measuring subtle changes in minor components from the soiled substrate.

Significant process has been made over the years in arriving at a standardized procedure

for soiling fabric and measuring the degree of soil removal (8,9) from the fabric after washing in a surfactant solution. This has not been the case with regard to the development of a widely accepted procedure for soiling and cleaning of hair. For any method to be accepted by others it must lend itself to the convenience of running a myriad number of test samples over a short period of time. It often is the case that this type of study is considered prohibitive due to the large number of variables beyond the control of the analyst. In addition, it usually requires a large number of samples to determine a significant difference between treatments. This quickly becomes impractical due to the laborious nature of the extraction and analytical procedure. As a result the investigator defers to other means of perceptual panel evaluation of the overall cleaning process. In our study every effort was made to limit the effect of extraneous variables and to develop a simple and consistent analytical procedure. This resulted in fewer samples for analysis, which extends the technology to even modestly equipped laboratories.

This paper summarizes a study on relative shampoo detergency and offers a method that will allow the researcher to:

1. Evaluate different shampoo solutions on a hair substrate.
2. Quantitatively determine the amount of soil removal in a reproducible manner.

EXPERIMENTAL

The evaluation procedure and our investigation of the soiling, cleaning, and analysis processes are detailed as follows.

HAIR SUBSTRATE

One of the most significant problems faced by analysts in the measurement of residual soiling levels on hair is reproducibility of the actual soiling level on the tress. To reduce this problem, we split the soiled samples prior to treatment with surfactant or prototype shampoo. This is done to compensate for tress-to-tress variation in soiling level by using the non-treated soiled sample as an internal control. In addition, this allows for the determination of residual sebum levels relative to the non-washed control.

DeMeo hair tresses (New York, N.Y.) of standard 8-inch length were used in all cases. In the single treatment assessments, 3-gram tresses were initially soiled. After soiling, the tress was split into two equal samples: one for surfactant treatment and the other to act as an internal control to compensate for sample-to-sample variances in soiling levels. In the case of repeated soiling and washing studies, single 1.5-gram tresses were soiled and treated. The cyclic nature of this portion of the experiment precluded the use of internal control samples due to the large amount of initial tress required. In this instance 5 replicate samples were soiled and left untreated to serve as experimental control samples. Only virgin tresses were evaluated, but the method is applicable to damaged/bleached/waved hair as well.

SEBUM

The artificial sebum composition was based on a formulation used in previous work (10).

The rationale for using a synthetic sebum in the study was to obtain a reproducible soil composition and thus eliminate significant sources of variability (11).

The sebum formulation was chosen to have a composition with a variety of functional groups similar to that in actual sebum (12). Functional group composition was:

    1. Triglycerides—35%
    2. Fatty acids—30%
    3. Waxes, hydrocarbons—15%
    4. Esters—20%

The actual formula for the Spangler sebum (10) used in our study was:

Olive oil	20.0%
Coconut oil	15.0%
Palmitic acid	10.0%
Stearic Acid	5.0%
Oleic Acid	15.0%
Paraffin wax	10.0%
Squalene	5.0%
Spermaceti	15.0%
Cholesterol	5.0%
	100.0%

SOILING PROCESS

Soiling of the hair tress was accomplished by dipping the tress in a sebum in hexane solution at the concentration under study. The soiled sample was manually agitated every 5 minutes while exposed to the soiling solution and then removed after 20 minutes. The solvent was then allowed to evaporate from the tress at room temperature (approx. 23 degrees C) for a period of 30 minutes. In this study two different soiling levels (2% and 10% sebum in hexane) were contrasted. The 2% solution represented a perceived soiled hair as determined in a panel perception study. The 10% soiling was performed to represent an overload situation. Comparisons of sebum removal at both total and component levels were made.

CLEANING PROCESS

One of the greatest problems in a study of this type is the development of consistent methods which are representative of real-life conditions for sample soiling and treatment. In our efforts to be as "true to life" as possible, tap water was used for all rinsing. The tap water normally supplied in Hayward, California, is considered soft with an average hardness of 3 to 4 grains (about 60 ppm calcium carbonate). Formulations and single component actives were prepared using deionized water. Three different methods of sample cleaning were evaluated.

1. Bulk process. In this process the soiled hair tress is dipped into a surfactant solution and agitated for 5 minutes, rinsed, and the "clean" hair tress evaluated. In this study a 100-ml bath of 0.1% aqueous surfactant solution was used for each 1.5 grams of hair. Rinsing was accomplished by holding the hair swatch for 10 seconds per side in

running warm water (40 degrees C). The total rinse volume was approximately 500–600 ml. The hair was then dried using a hand-held dryer.

2. Finger method. This technique most accurately mimics the "real world" shampoo procedure in that the solution being tested is applied and agitated in a manner consistent with actual consumer use. A 1.5-gram soiled tress was wetted under running water for 5 seconds per side (about 250 ml of water). Next 0.1 gram of undiluted shampoo (approximately 10% surfactant) was applied to the length of the tress. The tress was rubbed 15 times between the fingers as evenly as possible. Then the tress was reversed and rubbed 15 more times. Next the tress was rinsed under warm (40 degree C) water for 10 seconds per side and dried as before using a hand-held dryer. This yielded a total rinse volume of approximately 500–600 ml.

3. Sponge method. This technique is a modification of the "finger method" described above. The procedure is modified to provide a more consistent pressure upon the hair tress during the rubbing portion of the sample treatment. A 1.5-gram soiled tress was held under warm (40 degrees C) running water for 5 seconds per side, and then 0.1 gram of 10% surfactant solution was applied to the length of the tress. The tress was drawn 15 times between two prewetted sponges. A 100-gram weight was placed on the top sponge to simulate the approximate pressure applied by the fingers in that method. The tress was rinsed under 40 degree C running water for 10 seconds on each side and dried as previously stated. The sponges were cleaned before each use to prevent any buildup of sebum on them. We felt that this procedure combined the optimum combination of realism and simplicity.

ANALYSIS

The samples were placed in a forced air draft oven at 60 degrees C for 4 hours. This was to provide a uniform moisture content throughout the sample set. Karl Fischer moisture determinations indicated a residual moisture level of approximately 0.2% after the oven drying step. After samples were allowed to cool to room temperature, they were weighed (about 1 gram of hair) into 50-ml borosilicate serum vials. At this time exactly 20 ml of hexane was pipeted into the vial. The sample vessel was then sealed with a teflon-faced silicone septum and shaken on a mechanical shaker for 30 minutes. Hexane was chosen as the extraction solvent based upon the evaluation of available literature (10,12,13,15) and on the basis of experimental data which indicates that it provides the best balance in extraction power, low toxicity, and relatively high boiling point compared with other nonpolar solvents. Other solvent systems which were investigated were methanol, isopropanol, methyl ethyl ketone, diethyl ether, carbon disulfide, chloroform, and isopropanol/hexane mixture (50:50). It was determined early on in the course of our study that the hexane solvent system removed >95% of the available sebum from the sample using this procedure. Chromatographic profiles of the hexane extract of soiled hair tresses were comparable to profiles of standard sebum in hexane solutions used for the determination of component retention time. After the samples had been shaken for the set amount of time, the solvent was decanted from the sample. A portion of this was poured directly into an auto-sample vial, while the remaining extract was placed into a sample bottle and sealed for possible later examination. The auto-sampler vials were placed into the sampler and the analysis begun.

In the early phases of this project, residual sebum was determined by gas chromatography using a packed-glass column which contained a high temperature liquid phase (3% Dexsil 300 on Suplecoport). This column provided for the resolution of most of the major sebum components with the exception of spermaceti and cholesterol and some of the minor paraffinic compounds. The column produced some tailing of the acidic sebum components.

In order to improve the resolution of the chromatographic system the use of capillary columns (Supelco SPB-1) was investigated. This resulted in the baseline separation of the squalene/cholesterol peaks and the minor paraffinic compounds. The overall reactivity of the chromatographic system was also improved so that the acidic components no longer produced tailing peaks.

Analyses were conducted on a Hewlett Packard model 5840 equipped with a dual FID and setup for on-column injection. The chromatographic conditions for packed and capillary techniques are listed in Table I.

In the normal course of sample analysis 20 characteristic peaks were identified and tracked as a function of sample treatment. Identification was done through the matching of retention times between sample peaks and corresponding peaks in individual sebum fraction standards. This matching technique allowed for the tracking of the various sub-components present in the various sebum formula constituents. This resulted in the collection of more than 15,000 data points in the course of our evaluation. The volume of data which had to be reduced required the use of a micro-computer using Visi-Calc and Lotus 1-2-3 for weight correction and normalization with control samples. Lotus 1-2-3 also provided the ability to prepare visual representations of the data.
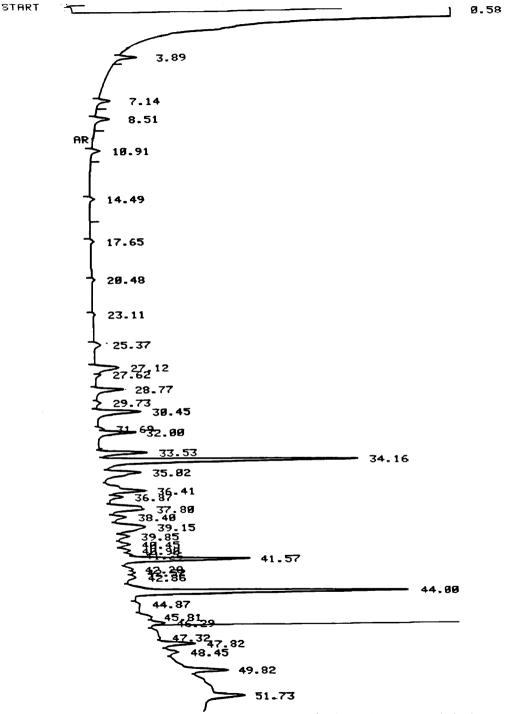
SINGLE SURFACTANT SYSTEMS

The investigation was conducted with three surfactants which represent some of the major actives used in commercial shampoos. The surfactants used were ammonium lauryl sulfate (ALS), sodium alpha olefin C14-C16 sulphonate (AOS), and sodium laureth 2-sulphate (alkyl ethoxy sulfate or AES containing 2 moles ethylene oxide). Each surfactant was evaluated at a use level of 10%.

Table I
Gas Chromatographic Operating Conditions for Sebum Analysis on Both Packed and Capillary Columns

	Packed	Capillary
Liquid phase	3% Dexsil 300	Supelco SPB1
Column length (meters)	2	60
Helium flow rate (ml/min)	30	12
Makeup gas flow (ml/min)	not required	40
Injection temperature	320 deg. C	280 deg. C
FID Detector temperature	320 deg. C	320 deg. C
Initial oven temperature	100 deg. C	180 deg. C
Initial temperature hold	4 minutes	8 minutes
Oven temperature rate	5 deg./min.	4 deg./min.
Final oven temperature	320 deg. C	320 deg. C
Attenuation	2/\8	2/\3
On-column injection Volume (microliters)	4	4

START ————————————————————————————— 0.58

3.89

7.14
8.51
AR
10.91

14.49

17.65

20.48

23.11

25.37

27.12
27.62
28.77
29.73
30.45
31.69
32.00
33.53   34.16
35.02
36.41
36.87
37.80
38.40
39.15
39.85
40.45
40.90
41.57
42.29
42.86
                                         44.00
44.87
45.81
46.29
47.32
47.82
48.45
49.82

51.73

Figure 1a. Representative chromatogram of a dilute (85 μg ml^{-1}) sebum solution on a packed column. Retention times of major components: palmitic acid, 7.14; stearic acid, 8.51; oleic acid, 10.91; paraffin 1, 14.49; paraffin 2, 17.65; paraffin 3, 20.48; paraffin 4, 23.11; paraffin 5, 25.37; paraffin 6, 27.62; paraffin 7, 29.73; squalene, 34.16; cholesterol, 41.57; not resolved from spermaceti: spermaceti 1, lost in baseline; spermaceti 2, 41.57; not resolved from cholesterol: spermaceti 3, 44.00; triglyceride 1, 47.82; triglyceride 2, 49.82; triglyceride 3, 51.73.

IFS
ARE
Z

0.54 0.72
1.15
1.65
1.55 1.35
2.26 2.68 2.78
3.75
3.78
4.77 4.89
5.37
6.43
6.78
7.43
8.44
9.33 9.44
10.09
11.45
13.78
15.91
17.21
17.91
19.12
19.79
20.95
21.59
21.93
22.34
22.67
23.30
24.31
24.93
25.31
25.70
26.49
27.00
27.50
28.00
28.69
29.45
29.76
30.13
30.63
31.50
32.23
32.81
33.32
34.32
35.51
36.62
37.49
38.73
41.30
42.89
46.01
48.23
49.69

Figure 1b. Representative chromatogram of a dilute (85 μg ml^{-1}) sebum solution on a capillary column. Retention times of major components: palmitic acid, 7.43; stearic acid, 11.98; oleic acid, 12.67; paraffin 1, 14.06; paraffin 2, 16.33; paraffin 3, 18.45; paraffin 4, 20.44; paraffin 5, 22.32; paraffin 6, 24.10; paraffin 7, 28.19; squalene, 25.85; cholesterol, 31.20; spermaceti 1, 27.42; spermaceti 2, 29.58; spermaceti 3, 34.03; triglyceride 1, 40.07; triglyceride 2, 45.77; triglyceride 3, 54.08.

CYCLIC RESOILING AND CLEANING

In the course of this investigation an attempt was made to evaluate repeat treatment effects as would occur with cyclic soiling and cleaning of the same hair substrate by actual product. This evaluation was conducted using single-model surfactants and virgin hair tresses which were evaluated at 1, 10, and 20 soiling and washing cycles.

In order to model a cyclic soiling/washing system, 20 sample tresses were prepared for each formula to be investigated. A single set of 5 soiled tresses were prepared and left unwashed to act as soiling control samples. The tresses were then washed using the sponge method, with sets of five samples withdrawn at intervals of 1, 10 and 20 cycles. The remaining samples were withheld in the event that additional cycles would be required.

RESULTS AND DISCUSSION

GC COLUMN COMPARISON

It became evident as we progressed in the study that we needed a better separation than our packed glass column could yield. At this point suitable alternatives were examined. The most obvious solution to our program was to extend our analysis to capillary gas chromatography. There are several problems which are normally encountered with this technology. Primary among these is the requirement for either splitting the sample injection or limiting the amount of sample placed at the head of the column. This is due to the limited sample capacity of the column and introduces the possibility that sample discrimination may occur in the sample injection step (13). The solution we found was to use wide-bore glass capillary columns which contained a non-polar methyl silicone bonded to the glass surface. These columns provide high sample capacity, are highly inert, have extended operating temperatures compared to static coated columns, and may be easily adapted for use in any chromatograph with a commercially available adapter kit (Supelco). This allows the analyst to use a column with better than 37,000 effective theoretical plates rather than the 6000 plates normally available with a packed column. This column allows for the separation of characteristic compounds from each of the sebum ingredients.

The resulting profiles allow for the tracking of the various sebum fractions as a function of treatment. Representative chromatograms from both types of columns appear in Figure 1a and 1b. The peaks are labeled as to their identity so that the two columns may be easily contrasted. It is readily apparent that the resolution achieved with the packed column does not allow the clean separation of all the components of interest. In comparison, it is obvious that the capillary column provides resolution which allows for the tracking of every sebum component of interest. The relatively high capacity of the capillary column, coupled with the low baseline background, allows for improved levels of detection compared to the packed column.

CONTRAST OF WASHING TREATMENTS

Of the three washing techniques evaluated the finger method technique most closely mimicked the "real life" use situation. Unfortunately, it also experienced the greatest degree of variability due to the high degree of operator dependence found in the

Table II
Precision of the Finger, Bulk and Sponge Washing Techniques

	Method		
Replicate	Finger*	Bulk*	Sponge*
1	25	42	37
2	42	37	50
3	23	34	56
4	41	33	54
5	38	34	49
Average	34	36	50
% R.S.D.	27	10	15

* These figures represent the % residue of a specific paraffin fraction across five individual replicates. The numbers for the finger and bulk data were derived through the analysis of finished-product-treated samples, while the sponge data comes from samples treated with single-surfactant-model system.

procedure. The bulk process method produced the most uniform results but also is the most removed from real life or actual use-type conditions and resulted in higher overall sebum levels. This is thought to be due to the fact that the samples experienced significantly less agitation in this technique compared with the other two methods. The method of choice became the sponge method procedure. It provides the highest
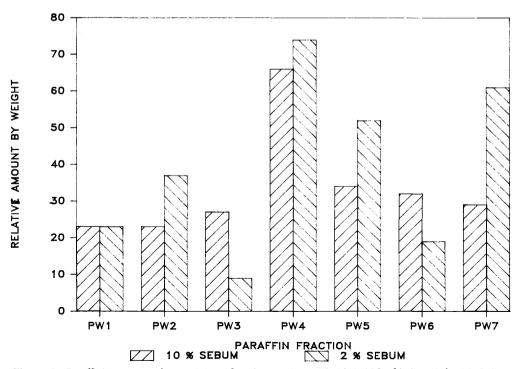

Figure 2. Paraffinic compounds remaining after shampooing with 10% ALS of hair soiled with 2% or 10% sebum solutions.

degree of "realism" combined with good precision. This improvement in precision is due to the elimination of the operator-dependent pressure portion of the finger method.

The precision of the three techniques as demonstrated by the relative standard deviation for a specific sebum fraction is tabulated in Table II. One can clearly see that the precision of the individual treatments, as judged by residues from a specific paraffinic fraction across five replicate samples improves in the following order:

Finger (27% RSD) > Sponge (15% RSD) > Bulk (10% RSD)

SOILING CONCENTRATION

Two different soiling levels (2% and 10% sebum in hexane) were investigated. At the 10% soiling level the actual amount of sebum removed was greater relative to the 2% soiled samples on both a weight and percentage basis. This is strictly due to the fact that more sebum is physically available for removal. However, when the detergency is compared on a residue weight basis, the amount remaining is essentially the same for both cases. For example, in the paraffinic fraction one sees about 95% removal for the 10% loaded samples and 60% removal for the 2% loaded samples. On a weight basis this corresponds to residue amount of 0.5 in both cases. This is presented in Figure 2.
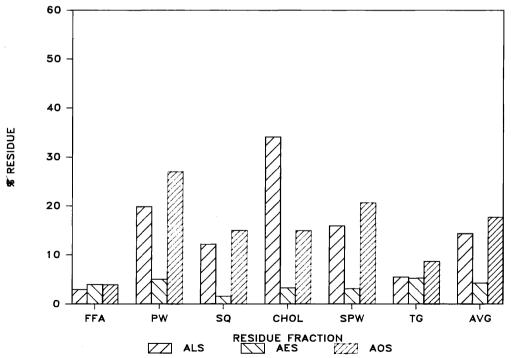

Figure 3. Sebum fraction remaining after shampooing with 10% ALS, AES, or AOS of hair soiled with 2% sebum solution. FFA = average of palmitic, stearic, and oleic acid components; PW = average of paraffin components; SQ = squalene component; CHOL = cholesterol component; SPW = average of synthetic spermaceti wax components; TG = average of triglyceride components; AVG = average of all of the above fractions.
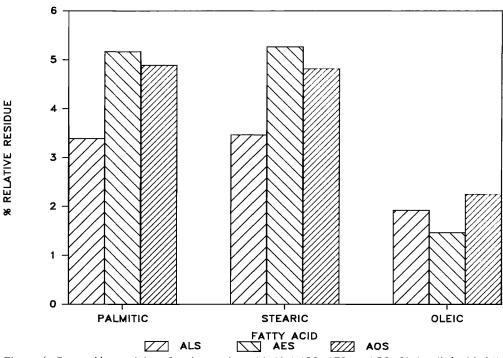
Figure 4. Fatty acids remaining after shampooing with 10% ALS, AES, or AOS of hair soiled with 2% sebum solution.
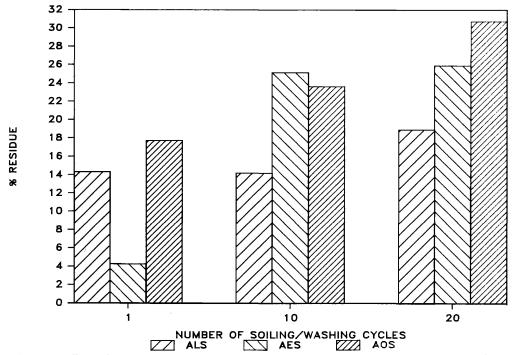
Figure 5. Effects of multiple soiling/shampooing treatments on average (across all components) sebum residues on hair. Hair soiled with 2% sebum solution and shampooed with 10% ALS, AES, or AOS. Soiling/shampooing carried through one, ten, and twenty cycles.
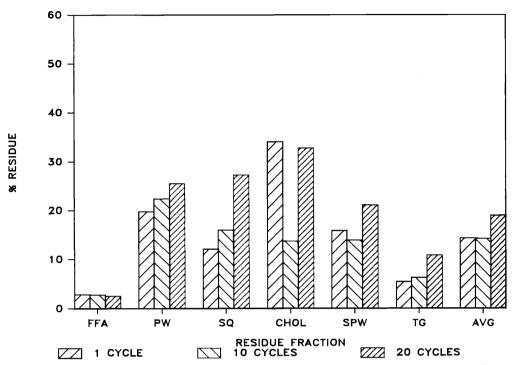
Figure 6. Effects of multiple soiling/shampooing treatments on average (by chemical fraction) sebum residues on hair. Hair soiled with 2% sebum solution and shampooed with 10% ALS. Soiling/shampooing carried through one, ten, and twenty cycles. FFA = average of palmitic, stearic, and oleic acid components; PW = average of paraffin components; SQ = squalene component; CHOL = cholesterol component; SPW = average of synthetic spermaceti wax components; TG = average of triglyceride components; AVG = average of all of the above fractions.

These observations are explained by the fact that at the highly soiled tress levels, the bulk removal of sebum is most likely a rollback mechanism (5) in which surfactant solution comes in contact mainly with the sebum matrix. In this type of sebum removal, principal effects are most likely liquid-liquid (detergent—sebum) in nature, with the actual surface effects of the hair playing only a minor role. As the soiling level decreases during the cleaning process, more of the hair surface is available for surfactant-sebum-substrate interactions. This results in a relatively constant amount of fraction residue on the substrate.

COMPARISON OF THE VARIOUS SURFACTANT SYSTEMS

As previously mentioned, certain sebum fractions were more effectively removed from the hair tress than others. Component removal is manifested by two key observations for the single-cycle treatments:

1. The polar sebum fractions were more easily removed from the substrate than the nonpolar fractions.
2. The degree of non-polar fraction removed is determined by the surfactant.

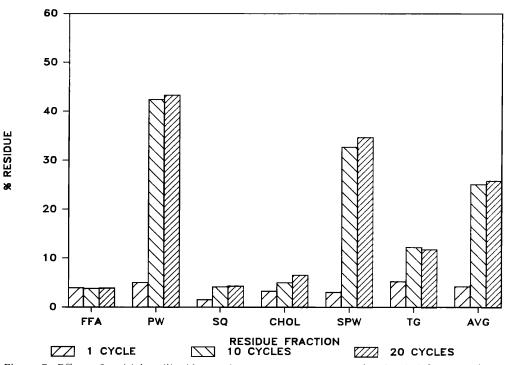For every surfactant system studied, the most difficult fraction to remove appears to

Figure 7. Effects of multiple soiling/shampooing treatments on average (by chemical fraction) sebum residues on hair. Hair soiled with 2% sebum solution and shampooed with 10% AES. Soiling/shampooing carried through one, ten, and twenty cycles. FFA = average of palmitic, stearic, and oleic acid components; PW = average of paraffin components; SQ = squalene component; CHOL = cholesterol component; SPW = average of synthetic spermaceti wax components; TG = average of triglyceride components; AVG = average of all of the above fractions.

be the paraffinic wax compounds illustrated in Figure 3. The easiest fraction to remove from the hair is the fatty acid components. All of the single-component surfactant systems investigated removed essentially the same amount of the free fatty acids from the sebum as seen in Figure 4. The actual residue level is normally below 5% relative to the amount originally applied. This same observation generally held true for the triglycerides with greater than 90% removal.

Distinctions between surfactant systems became more apparent with the comparison of the removal of the cholesterol, paraffins, squalene, and spermaceti fractions. In every case AES removed more of each particular sebum fraction than ALS or AOS. The greatest difference is found for the paraffin fraction. AES had an average residue of 10% and the other two surfactants had average residues of 45%. The difference between ALS and AOS was primarily manifested in the removal of the cholesterol fraction. The AOS removed 85% of this fraction, while the ALS removed only 65%.

SHAMPOOING CYCLES

One of the most interesting sets of questions posed by consumers is:

1. Does my shampoo become "tired" with regular use?
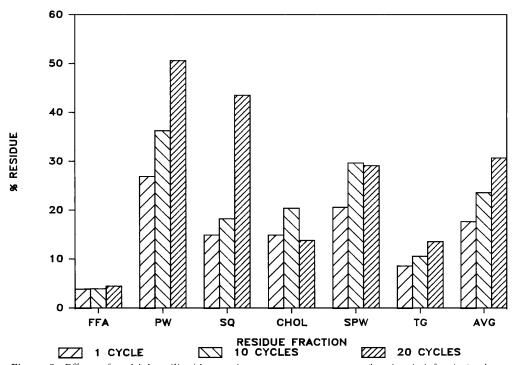2. Do I need to regularly change shampoos to keep my hair clean?

Figure 8. Effects of multiple soiling/shampooing treatments on average (by chemical fraction) sebum residues on hair. Hair soiled with 2% sebum solution and shampooed with 10% AOS. Soiling/shampooing carried through one, ten, and twenty cycles. FFA = average of palmitic, stearic, and oleic acid components; PW = average of paraffin components; SQ = squalene component; CHOL = cholesterol component; SPW = average of synthetic spermaceti wax components; TG = average of triglyceride components; AVG = average of all of the above fractions.

The question we decided to address was: Is there a difference in the amount of total sebum or sebum fraction left on the hair between the 1st and the nth soil/shampoo cycle?

In an attempt to analyze sebum removal as well as to determine if there may be a change or a build-up of one sebum fraction in comparison to another, we repeatedly soiled and washed hair tresses. Single-surfactant systems only were tested. This was done in an effort to isolate the effects of the actual active ingredient and to prevent coformulated ingredients from masking the desired observations. Data was collected for 1, 10, and 20 soiling and washing cycles for the 2% soiling samples and 1 and 10 cycles for the 10% soiled samples. This could represent a period of one or two months of regular shampooing for an individual, depending upon washing intervals.

Figures 5–8 represent the data obtained in this portion of the study. It is striking to note that there appears to be data supporting the notion that "shampoo fatigue" takes place in as few as 10 cycles. Of particular interest is the accumulation of the paraffinic compounds on the hair substrate. In almost every case the paraffinic and squalene residues were higher after 20 washing cycles than those observed after a single cycle. There did not appear to be an accumulation of the triglyceride, cholesterol, or fatty acid fractions after 20 cycles.
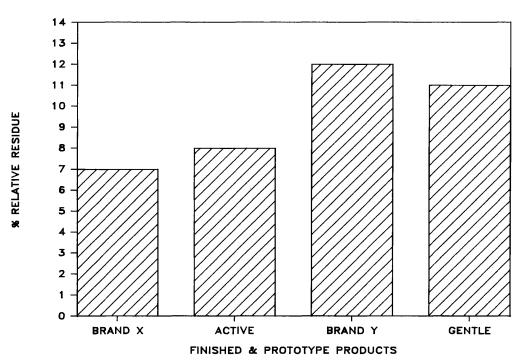
Figure 9. Average (across all components) sebum residues remaining after shampooing with commercial or prototype "active" and "gentle" shampoos of hair soiled with 2% sebum solutions.

As previously stated, AES appears to exhibit the greatest detergency when the single-cycle data is examined. This did not prove to be the case when multiple soiling and cleaning cycles were performed. The data indicate that AES demonstrated the highest degree of sebum buildup with repeated application when compared to the other two surfactants. The data from the 5 sample replicates were examined in an effort to determine if this was an anomaly or a valid effect. The precision of the data appears to be consistent with respect to all of the other sample sets. A more extensive study will have to be conducted to develop a possible mechanism to explain this effect. AOS is similar in that it tended to leave higher residues regardless of cycle. ALS appears to exhibit the least amount of residue buildup of the three surfactants tested.

The data indicate that the surfactant type determines the detergency of the formulation. To further test this premise, several prototype shampoo formulations were prepared using these surfactant types and evaluated using this technique. Shampoo formulations prepared to reflect what would normally be perceived as "gentle" were found to leave higher sebum residues than those formulated as "active"-type shampoos. These prototype formulations were contrasted to existing finished product formulations which are generally recognized as active (Brand X) and gentle (Brand Y). This data is represented in Figure 9. The data from this portion of the experiment may indicate an apparent concentration effect. "Built" finished product formulations exhibit slightly different detergency than would be predicted strictly from the single-surfactant models. This could either be a concentration effect or some sort of enhancement between blended surfactants. This question will require additional work to fully develop a working predictive model for finished products.

CONCLUSIONS

This paper has described an approach to evaluating shampoo efficacy on a hair substrate. The technique is reproducible and practical. It can be ultimately extended to the evaluation of prototype formulations and to the evaluation of commercial products. It can be used to provide information about product effectiveness prior to conducting extensive and expensive *in vivo* use testing. The techniques described not only allow for the determination of sebum residue but can be used to profile residual sebum components as a function of treatment.

The experimental data collected indicate that shampoo effectiveness can be moderated or determined by the surfactant. The inclusion of certain surfactants will reduce the residue of the non-polar sebum fractions which seem to be more tenaciously bound to the substrate surface. The implication of this result should not be interpreted as some surfactants being "bad" or ineffective. On the contrary, these may be the surfactants of choice when a mild detergency is required, such as the case with "dry" hair.

The study also describes our findings which indicate that repeated soil/wash cycles can affect the perceived cleaning ability. Repeated soiling and washing cycles accentuate the accumulation of sebum residue remaining on the hair surface. It seems quite feasible that product effectiveness could be perceived as diminishing with use. Additional work will be required to determine how this situation may be remedied or controlled.

REFERENCES

 (1) A. M. Schwartz and J. W. Perry, *Surface Active Agents,* (Wiley-Interscience, 1949).
 (2) E. W. Washburn, *Phys. Rev. Ser.,* 2, 17, 273 (1921).
 (3) J. W. McBain, *Trans. Farady Soc.,* 9, 99 (1913).
 (4) S. K. Durham, *Surface Activity and Detergency,* (Macmillian, New York, 1961).
 (5) A. M. Schwartz, Recent advances in detergency theory, *J. Amer. Oil Chem. Soc.,* 48, 566–569, (1971).
 (6) N. K. Adam, *J. Soc. Dyes Colour,* 53, 121, (1937).
 (7) H. L. Rosano and M. Weil, *Am. Dyestuff Rep.,* 2, 53–56, (1953).
 (8) A.S.T.M., *Annual Book of ASTM Standards,* ASTM, 15, 15,04, D3050 (1983).
 (9) J. C. Harris, *Detergency Evaluation and Testing,* (Wiley-Interscience, 1954).
(10) Spangler, Cross, and Schoafsma, A laboratory method for testing laundry products for detergency, *J. Amer. Oil Chem. Soc.,* 42, 723–727 (1965).
(11) M. M. Breuer, Cleaning of hair, *J. Soc. Cosmet. Chem.,* 32, 437–458 (1981).
(12) M. Gloor, *Determination and Analysis of Sebum on Skin and Hair, Cosmetic Science Volume 1,* (Academic Press, London, 1978).
(13) L. S. Ettre, *Introduction to Open Tubular Columns* (Perkin-Elmer Corporation, Norwalk, Conn. 1976).
(14) J. Koch, K. Aitzetmuller, G. Bittorf, and J. Waibel, Hair lipids and their contribution to the perception of hair oiliness: Parts I & II, *J. Soc. Cosmet. Chem.,* 33, 317–343 (1982).
(15) H. J. O'Neill and L. L. Gershbein, Analysis of fatty acid and alcholic compounds of sebaceous lipid type, *J. Chrom. Sci.,* 14, 28–36 (1976).