A cosmetic ingredient innovation for the stabilization and delivery of volatile fluoroether with cosmetic applications

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Synopsis

Initially this work attempts to support, evaluate and identify the stabilization and release mechanism of volatile fluoroether (Cosmetic Fluid CF-61®*) in a self-assembling nanostructure in an external water phase (Phoenomulse CE-1®†) through evaporation rate analysis. The release mechanism is hypothesized to be a result of a dehydration process, a decrease in water efficiency due to evaporation of external water at the liquid-air interface, which results in destabilization of the nanostructure. This work further attempts to quantify the release mechanism of the same volatile fluroether (Cosmetic Fluid CF-61®) from the nanostructure in cosmetic formulations through a newly developed *in vitro* test method which measures initial foam generation rate. Finally, this work demonstrates the application of these newly developed test methods as a useful tool for product development, formulation navigation, and performance optimization.

INTRODUCTION

The more recent marketing trends in the personal care cleansing categories for super-mild, natural-based detergents have left many consumers and marketing professionals with growing disappointment, particularly with the foaming performance of these products. Poor foam quality and quantity during usage of natural-based shampoos may be the largest limiting factor and largest technical challenge to the formulating chemist. Consumer behavior continues to teach product development professionals that overall product performance is directly related to the foaming performance of the product (1).

"Foam boost technology (FBT)," an active foam boosting technology, may provide a solution to some of these inadequacies through its capabilities of enhancing the foaming performance of products. This powerful technology, via stabilization of volatile fluoroether, (Cosmetic Fluid, CF-61®), allows self-activated foaming products to be packaged in non-pressurized standard containers. The foaming action is activated when the product is exposed or open to the air, but remains stable in a closed container.

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* **Cosmetic Fluid CF-61®** (Methyl pefluorobutyl ether methyl perfluoroisobutyl ether), 3M Company St. Paul MN, 55144.
† **Phoenomulse CE-1®** (Polyhydroxystearic Acid (and) isononyl isononanoate (and) ethylhexyl isononanoate (and) sodium cocamidopropyl PG-dimonium chloride phosphate (and) methyl pefluorobutyl ether (and) methylperfluoroisobutyl ether), Phoenix Chemical Inc., Somerville NJ 08876.

Table I

Formulations Prepared with Varying Concentrations (% w/w) of Corn Syrup for Foam Rate Determination

Phase	Lot no.	Ingredient	ARL-8-1A	ARL-8-1B	ARL-8-1C	ARL-8-1D	ARL-8-1E	ARL-8-1F	ARL-8-1G
1	N/A	Deionized water	69.55	64.55	59.55	54.55	49.55	39.55	29.55
1	7040463	Steol® CS-130[1]	20.00	20.00	20.00	20.00	20.00	20.00	20.00
1	0506	Farmal HFS 2656[2]	0.00	5.00	10.00	15.00	20.00	30.00	40.00
1	5JK8665K	Keltrol CG-T[3]	0.15	0.15	0.15	0.15	0.15	0.15	0.15
1	10803040	Gelcarin PC379[4]	0.30	0.30	0.30	0.30	0.30	0.30	0.30
2	0540	Phoenomulse CE-1[5]	10.00	10.00	10.00	10.00	10.00	10.00	10.00
		Total %	100	100	100	100	100	100	100

[1] Sodium laureth sulfate (Steol® CS-130), Stepan Company Northfield IL 60093.
[2] Saccharide hydosalte (Farmal HFS 2656®), CornProducts, Bedford Park IL, 60501.
[3] Xanthan gum (Keltrol CG-T®), CP Kelco Chicago IL, 60606.
[4] Chondrus crispus (Carrageenan) (Gelcarin PC379®), FMC BioPolymer via Earth Supplied Products, Philadelphia PA, 19103.

Foaming products formulated with Phoenomulse CE-1® and FBT generate foam quality and quantity at levels which are unobtainable using any other past or current formulation technologies. Unlike traditional, passive, cleansing systems, FBT active systems are different in that they do not require outside mechanical action to generate foam.

Once foam is produced, whether from an active FBT system, or a passive system, it can be analyzed. Traditional foam analysis models and methods, such as Ross Miles, cylinder shake, and the Hart-deGeorge blender method, which are designed to measure the foam quantity or stability of passive systems, are insufficient tools to guide product development professionals when optimizing formulations using FBT (2–4). A newly developed method for measuring foam quantity and stability, through analysis of a foam rate, provides a valuable tool for formulators who wish to use FBT to enhance the foam quality of otherwise poor-foaming detergents, such as decyl glucoside.

Decyl glucoside (Planteran 2000 N UP®‡), a natural-based detergent used in body washes and shampoos, has had minimal marketing impact in the cosmetic industry. This is due primarily to the consumer-perceived poor foam quality and quantity of this detergent (5). Using the test methods disclosed in this work, a starting formulation including Planteran 2000 N UP® as the primary surfactant has been identified. The foaming performance of this formulation is similar to sodium lauryl sulfate (SLS), demonstrating the improvement provided by FBT active systems.

EXPERIMENTAL

FOAM RATE DETERMINATION

Solutions of varying corn syrup concentration were prepared according to the formulations presented in Table I.

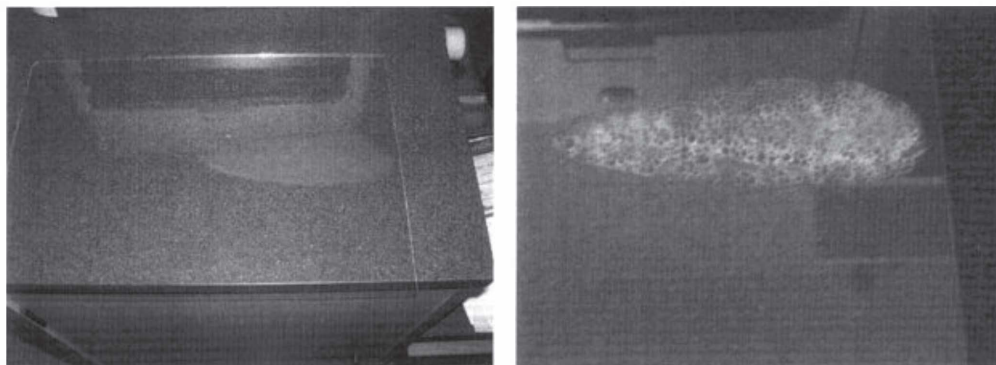‡ Planteran 2000 N UP® (decyl glucoside), Cognis Corporation, Cincinnati, OH, 45232.

Figure 1. Initial (right) versus end point (left).

Ingredients of phase 1 were combined in a 250-mL disposable beaker and heated to 85–90°C under medium-speed prop mixing. Contents were mixed until uniform, at which point they were allowed to cool back to room temperature. Once phase 1 was cool, phase 2 was added, and solution was hand-mixed until uniform.

The foam rate for the above solutions was determined by creating a film from 1g of the test solution on a standard 8x10 glass plate with a 10-micron draw-down bar. A film was drawn down on the plate and the time it took for the film to completely foam over was recorded using a standard stop watch with hours, minutes, and seconds (Figure 1). Three trials were run for each solution.

To calculate the foam rate constant the following equation was used:

$$T = \frac{\text{Time it takes for test solution (B-G) to foam}}{\text{Time it takes for standard (A) to foam}}$$

To normalize the rate constant and obtain the rate constant for foam, K_f the reciprocal of T was taken according to the equation:

$$K_f = 1/T$$

The effect of Phoenomulse CE-1® on the foam of a natural based decyl glucoside surfactant (Planteran 2000 N UP®, Cognis), was evaluated using the above method. Two stock solutions were prepared according to Table II.

Table II
Preparation of Stock Solutions (% w/w)

Phase	Lot no.	Ingredient	ARL-8-7A	ARL-8-7B
1	U6B13Z026	Plantaren 2000 N UP®[1]	10	—
1	7040463	Steol® CS-130	—	20
1	506	Farmal HFS 2656®	5	5
1	5JK8665K	Keltrol CG-T®	0.15	0.15
1	10803040	Gelcarin PC379®	0.3	0.3

[1] Decyl glucoside (Plantaren 2000 N UP®), Cognis Corporation, 5051 Estecreek Drive, Cincinnati, OH, 45232.

Each stock solution was diluted with 1, 5, 10, 15, and 20% Phoenomulse CE-1® and adjusted to 100% with deionized water.

RATE OF EVAPORATION

The rate of evaporation for the following systems was determined by weight loss over a period of ten minutes using a standard analytical balance and conventional convection lab oven. 100g of each solution was placed in a 250-mL disposable beaker and weighed on the balance. The mass of the solution was recorded every minute for ten minutes. Data was recorded at standard conditions (25°C, 50–60% RH) and elevated conditions (40°C, 50–60% RH).

SYSTEMS TESTED
● 100% Deionized water
● 100% Cosmetic fluid CF-61® (3M Company)
● 100% Phoenomulse CE-1® (Phoenix Chemical, 60 Fourth Street Somerville NJ, 08876)
● 20% Phoenomulse CE-1® and 80% Deionized water

To calculate the rate of evaporation, K_{evap}, mass vs. time was graphed for each system, and the negative slope of the line was recorded. The slope of the line for water was set equal to 1. To calculate the K_{evap} of each subsequent system the following equation was used.

$$K_{evap} = \frac{\text{slope of test system}}{\text{slope of water}}$$

RESULTS AND DISCUSSION

STABILIZATION AND RELEASE MECHANISM OF COSMETIC FLUID CF-61®

Evaporation Rate (K_{evap}) of Cosmetic Fluid CF-61® was determined and found to be significantly higher than K_{evap} of Phoenomulse CE-1®. The K_{evap} for Phoenomulse CE-1 was approximately 60% higher than that of water. Considering the external phase of Phoenomulse CE-1® is water, and contains 52.5% Cosmetic Fluid CF-61® in its internal phase, a higher K_{evap} is expected verses water. The difference in K_{evap} between Cosmetic Fluid CF-61® and Phoenomulse CE-1® is about 175%. This trend is also observed at an elevated temperature, with the exception of Phoenomulse CE-1® and deionized water, which only differs by 108%. The K_{evap} of the Phoenomulse CE-1®/deionized water system was lower than K_{evap} of deionized water at 25°C. However, at 40°C, the K_{evap} of the Phoenomulse CE-1®/deionized water system was 196% greater compared to deionized water. No bubbling was observed in the solutions at room temperature or at elevated temperature during the test phase. All weight loss is assumed to be due to evaporation at the surface.
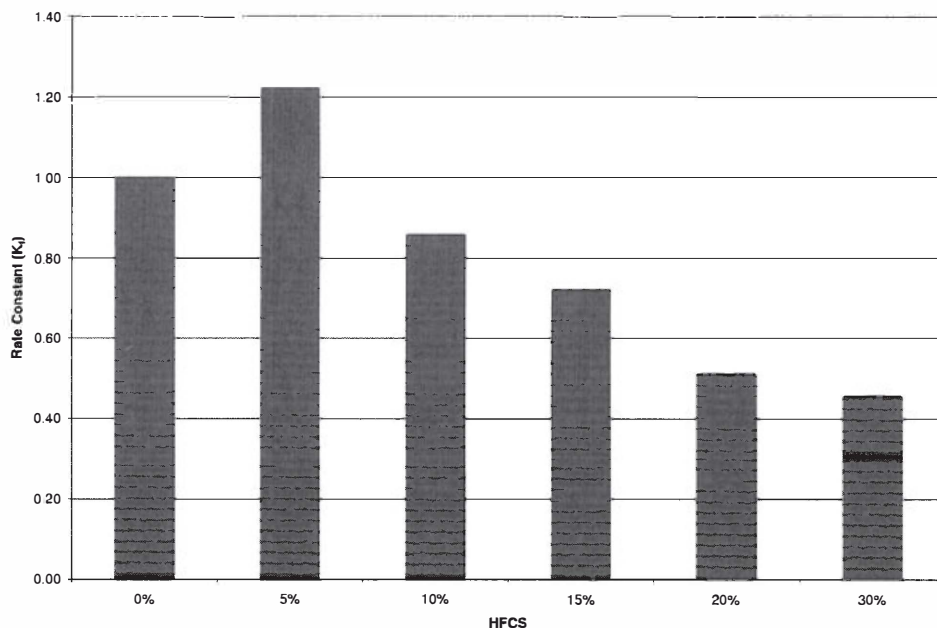
Figure 2. Effect of Farmal HFS 2656 on foam rate of 10% Phoenomulse CE-⅓% SLES (20–25°C, 50–60% RH).

QUANTIFYING FOAM

Initial Foam rate determinations were made using formulations containing a constant active level of sodium lauryl sulfate (SLS) and varying saccharide hydrosalate§ levels from 0 to 30% (Figure 2). This work focuses only on initial foam quantity, or the amount of foam produced in the first few minutes of activation. Total foam would include the initial quantity plus the quantity produced over the length of time foaming occurs. Since total foam cannot be measured, this has been identified as an area for further research. When observing the effects of saccharide hydrosalate concentration on foam rate, an ideal concentration is defined at about 6–8% for maximum foam rate. As the concentration of saccharide hydrosalate increases beyond 8%, the foam rate decreases, as shown in Figure 1.

Foam rate comparison of sodium lauryl sulfate (SLS) vs. Planteran 2000 N UP® at Varying Concentrations of Phoenomulse CE-1® and a constant surfactant level resulted in Figure 3. The slope of each line was drastically different. The slope of the line representing SLS was much higher. Also, SLS foam rate was consistently higher at equal concentrations of Phoenomulse CE-1®, about five times higher on average.

The lower foam performance, represented by a slower foam rate in equivalent formulations of SLS vs. Planteran 2000 N IP® is not surprising. Foam measurements acquired by traditional test methods for passive systems conclude decyl glucosides have somewhat lower foaming performance verses anionic sulfate systems such as SLS (5). Perceived

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§ Saccharide hydrosalate (Farmal HFS 2656®, Corn Products, Bedford Park IL, 60501).
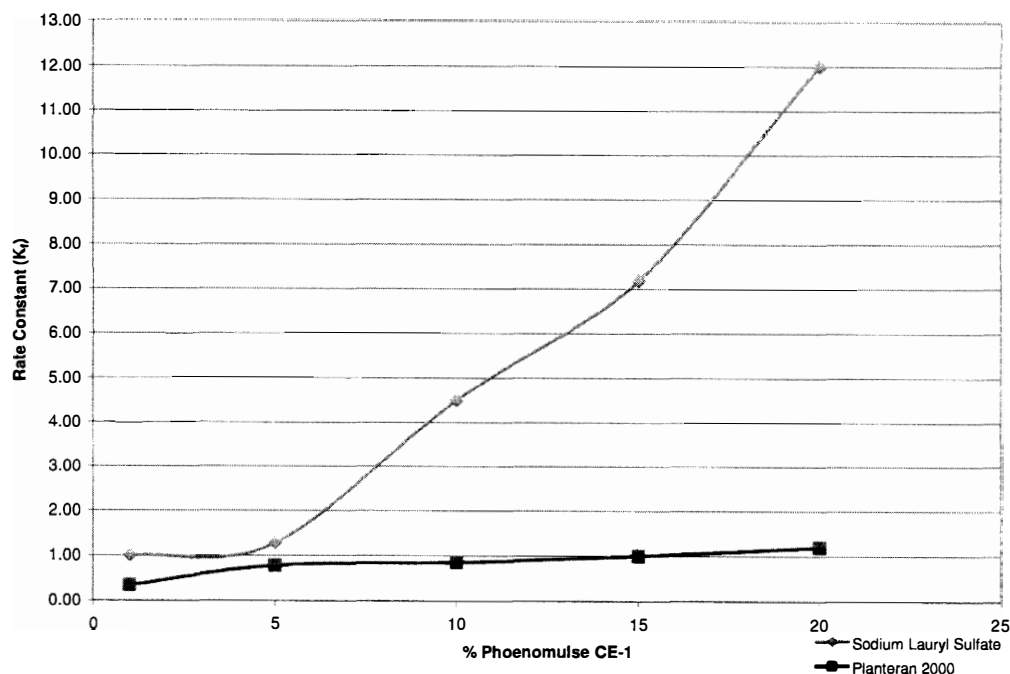
Figure 3. Sodium lauryl sulfate vs Planteran 2000 N UP®.

results from subjective evaluations of the formulations tested for foam rate agree with the measured foam rate results.

CONCLUSIONS

The release of some Cosmetic Fluid CF-61® at the surface is hypothesized to be the result of a dehydration process or a decrease in water efficiency due to evaporation of external water at the liquid-air interface. In this state of dehydration, the nanostructures may invert, releasing the internal phase, comprised of Cosmetic Fluid CF-61® into the external water phase. The small amounts of Cosmetic Fluid CF-61® released from the nanostructure by this mechanism will evaporate at the rate of unstabalized Cosmetic Fluid CF-61®.

The stabilization effect of Cosmetic Fluid CF-61® in the nanostructure is apparent when comparing the differences in the individual evaporation rates of Cosmetic Fluid CF-61® verses Phoenomulse CE-1®. Comparing the evaporation rates of Cosmetic Fluid CF-61® to Phoenomulse CE-1® clearly supports a stabilization of Cosmetic Fluid CF-61® through nanostructure encapsulation.

The differences seen in the Phoenomulse CE-1®/deionized water system, at least at room temperature, may support the dehydration release mechanism hypothesis. Some settling of the nanostructures was observed in the Phoenomusle CE-1®/deinonized water system, allowing the excess water to act as a dehydration shield, therefore increasing the water efficiency at the liquid-air interface. There are currently no supporting experiments that attempt to explain why the K_{evap} of this system is lower than just a system of dein-

ionized water. A probable hypothesis may be that the Phoenomulse CE-1® is responsible for some hydrogen bonding which may be lowering the K_{evap} of the external phase. This phenomenon provides an opportunity for continued research.

Once the Cosmetic Fluid CF-61® from FBT formulations containing surfactant evaporates at the surface, foam is produced, creating an active foaming product. Since the release of the cosmetic fluid occurs only at the liquid-air interface, only a fraction of Cosmetic Fluid CF-61® is released at any given time. While this certainly enhances the positive foam attributes of the formulation, it also creates challenges when quantifying the foam of any given formulation.

Formulation modifications which affect the water efficiency at the liquid-air interface, will also affect initial foam quantity, and ultimately foaming performance. This is supported when observing the changes in foam rates at different saccharide hydrosalate levels (Figure 2). Foam rate increase observations in formulations with lower water efficiency at the liquid-air interface may also support the release mechanism hypothesis. The rate of nanostructure disruption directly affects foam rate, and ultimately, foam performance.

Foam rate measurements utilizing the *in vitro* test method developed for the use of this work can be a valuable aid when determining Phoenomulse CE-1® levels during FBT formulation navigation and formulation performance optimization. Determination of Phoenomulse CE-1® levels in formulations which contain naturally-based detergents whose foaming performance must equal that of SLS can be achieved with good accuracy. An example is demonstrated when observing similar initial foam generation rates of 5% SLS with 1–5% Phoenomulse CE-1® to formulations containing 5% Planteran 2000 N UP® with 15% Phoenomulse CE-1® (Figure 3). Subjective evaluations of these two formulations suggest similar foaming performance.

REFERENCES

(1) T. Harding, Perception of foam: Are there alternatives to SLES? *Proceedings of the Australian Society of Cosmetic Chemists (ASCC), 37th Annual Conference* (Cosmetics on a New Horizon), March 13–16, 2003, Hamilton Island, Queensland, Australia, CD-ROM, paper 11, pages 1–6.
(2) C. M. Persson, P. M. Claesson, and I. Johansson, Interfacial behavior of n-octyl beta-D-glucopyranoside compared to that of a technical mixture consisting of octyl glucosides, *Langmuir,* **16,** (26) (2000).
(3) K. Klein, Evaluating shampoo foam, *Cosmet. Toiletr.* 119 (10), 32–35 (2004).
(4) M. Krzan, K. Lunkenheimer, and K. Malysa, Surfactant's polar group on the local and terminal velocities of bubbles, *Colloids Suf. A: Physicochem,* 250 (1–3), 431–441 (2004).
(5) B. Salka, Polyglycosides properties and applications, *Cosmet. Toiletr.,* **108**(3), 89–94 (1993).