

## Consistency development and destabilization of a model cream

LORRAINE E. PENA, BARBARA L. LEE, and  
JAMES F. STEARNS, *Drug Delivery R&D—Specialty Products*,  
*The Upjohn Company, Kalamazoo, MI 49007.*

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### Synopsis

Emulsions are thermodynamically unstable and with time show progressive signs of this instability with eventual phase separation. It is also an established fact that creams based on nonionic emulsifier systems exhibit an initial period of delayed consistency development prior to the destabilization process. To illustrate these phenomena, a cream having a nonionic emulsifier system is destabilized by a surface-active ingredient that also exaggerates the period of retarded consistency development. Using rheologic and microscopic techniques, this study presents a systematic approach by which consistency development and destabilization can be monitored. Characteristic patterns in the rheograms upon aging are correlated with changes seen microscopically, and specific changes signaling the beginning of the destabilization process are identified. Rheologically, destabilization becomes apparent through formation of additional spurs and inflections at low shear rates, a decrease in hysteresis, and a shift to lower maximum shear stress values. Microscopically, polarized light shows formation of diffuse, weakly birefringent structures while ordinary light shows an increase in droplet size. Thermal optical videomicroscopy and trace substance analysis have identified the structures as segments of agglomerated oil phase and verify the photomicroscopy observation that the oil and wax components phase separate as distinct entities.

### INTRODUCTION

All emulsion systems undergo a process of destabilization and phase separation. However, creams based on nonionic emulsifier systems first undergo an initial period in which their consistency slowly develops. The gel network theory has shown that the consistency of a cream is due to structuring of the continuous phase via penetration and swelling of the fatty amphiphile component by the aqueous surfactant phase to form a viscoelastic, lamellar liquid crystalline gel network (1–6). In the case of nonionic surfactants, this penetration is delayed, and therefore consistency development is also delayed (3). This paper presents a systematic approach by which consistency development and destabilization can be monitored.

A cetearyl alcohol/cetareth-20 cream is destabilized by the addition of a surface-active ingredient that also exaggerates the period of delayed consistency development. Rheology and microscopy are used to monitor consistency development and destabilization

of the cream. Thermal optical videomicroscopy and trace substance analysis are used to characterize the cream and to identify the composition of the structures observed in the photomicrographs.

## EXPERIMENTAL

### FORMULA

The cream is based on a commercially available blend of cetearyl alcohol and cetareth-20 in a 75/25% (w/w) ratio. The cetareth-20 is the surfactant that penetrates the fatty amphiphile, cetearyl alcohol, to provide body to the cream in accordance with the gel network theory (1–6). Cetyl palmitate is a wax used to assist in adding body to the cream via formation of a secondary network structure (7). Isopropyl myristate is the liquid internal phase. The identity of the destabilizing ingredient is proprietary, but it can be described as an anionic surfactant. The cream was manufactured using a variable speed mixer with a marine propeller. Emulsification was via the water-to-oil phase inversion technique. A water ring was used to force cool the cream to room temperature.

### RHEOLOGY AND MICROSCOPY

A Ferranti-Shirley cone and plate viscometer was used to determine the rheology of the cream. Samples were tested at 25°C with the instrument in low gear using the 7-cm truncated cone, a 60-sec sweep time, and the 1× scale expansion on the recorder. A shear rate range of 0–164  $\text{sec}^{-1}$  was achieved with these instrument settings. Photomicrographs were obtained with a Zeiss Universal microscope at 500× magnification using both ordinary and polarized light on the same sample.

### THERMAL OPTICAL VIDEOMICROSCOPY

Thermal optical videomicroscopy was performed using polarized light and a 250× magnification. The melting behavior of the cream and its raw materials was studied using a Mettler FP 82 hot stage equipped with photomonitor at a heating rate of 5°/minute over the range of 25°C to slightly above the melting point. Samples were also studied by videotaping the melting transition. The melting point was defined as the temperature at which a thermal arrest appears in the photomonitor recording and/or the temperature at which the cream or crystals liquefied and flow began. In order to obtain a thin film suitable for microscopy, raw materials were premelted on the slide prior to monitoring their behavior. Cream samples were monitored directly from the initial slide preparation since a thin film was easily produced and because preliminary heating destroyed the sample.

## RESULTS AND DISCUSSION

### CONSISTENCY DEVELOPMENT

The model cream was a white lotion at the time of manufacture, but it slowly developed

a semisolid consistency. The rheograms in Figure 1 reflect the structural development of the cream by an increase in hysteresis and a shift toward higher shear stress values. The narrow hysteresis loop and low yield value at day 1 are very characteristic of a lotion consistency, while the broad hysteresis loop and high yield values at days 15 and 34 are characteristic of creams. Note that the overall shapes of the rheograms at days 15 and 34 remain the same while the yield value increases in response to the structural development.

Photomicrographs of the cream corresponding to the rheogram time intervals are presented in Figure 2. An overall grainy texture appears in both ordinary and polarized light at day 1 and corresponds to the "coagel" or "lipophilic gel" phase described by Eccleston (1) and Junginger (8), respectively. This phase consists of partially hydrated, crystalline fatty amphiphiles with no surfactant penetration. Photos at days 15 and 34 show a gradual replacement of the grainy texture with emulsion droplets. As the consistency develops, ordinary light shows better definition of the emulsion droplets and polarized light shows formation of birefringent lamellar structures. Patel *et al.* (9) referred to these birefringent structures as "onion ring" lamellar phase and correlated them to the liquid crystalline gel phase of the gel network theory. Successive increases in lamellar thickness correspond to increased surfactant penetration of the fatty amphiphile with consequential gel phase formation and subsequent consistency development as demonstrated by the rheograms.

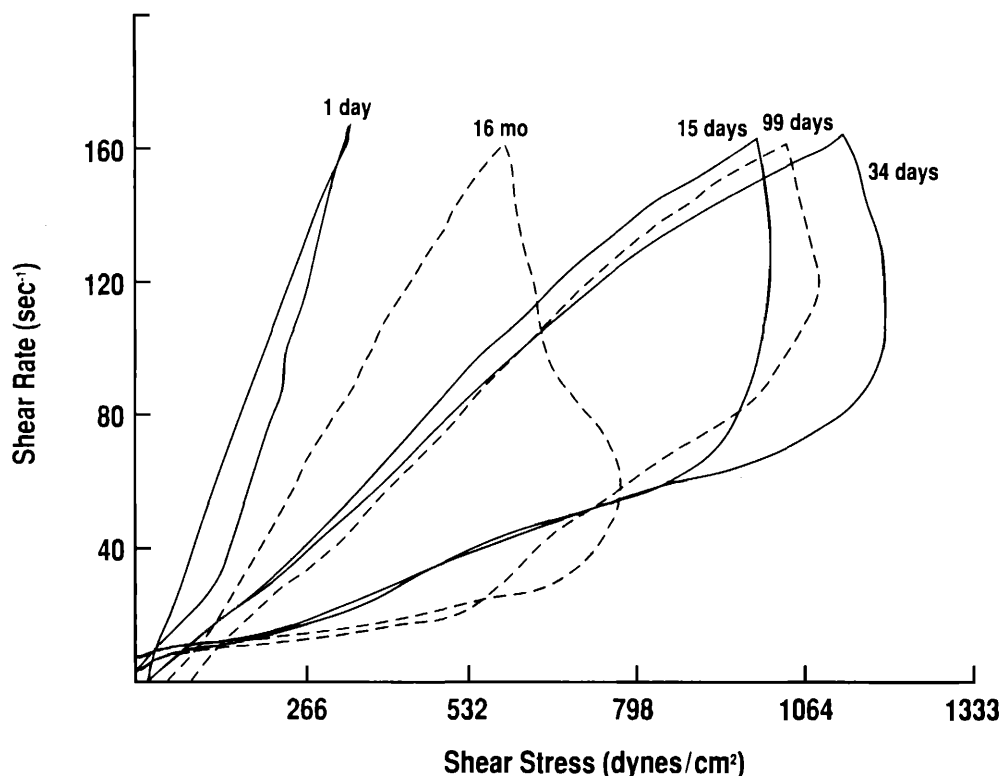


Figure 1. Rheograms of the aging model cream. Consistency development——. Destabilization ---.

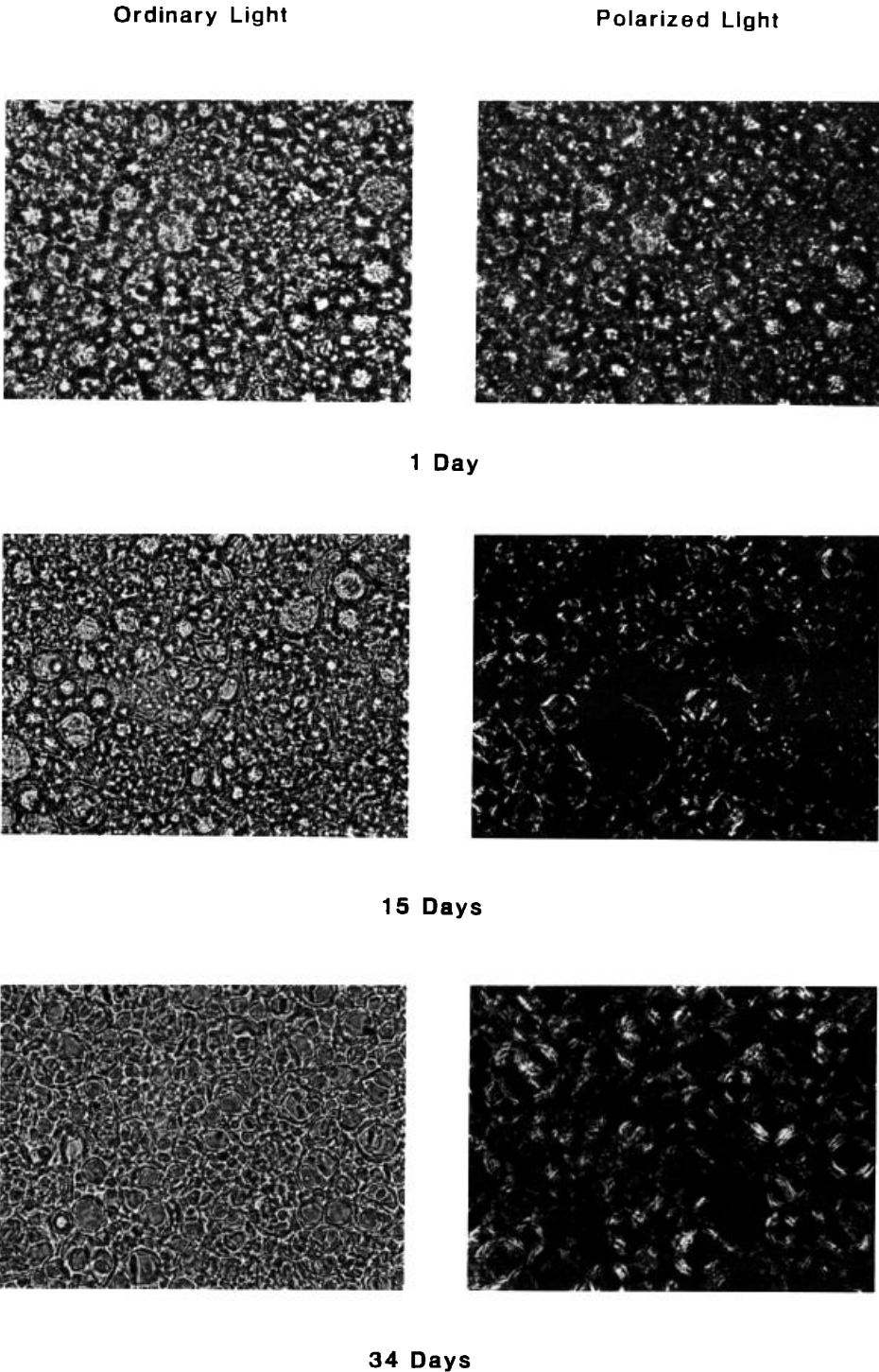


Figure 2. Consistency development of the model cream.

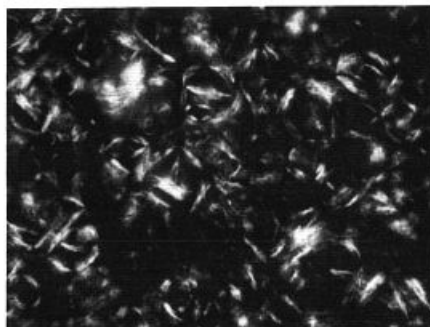
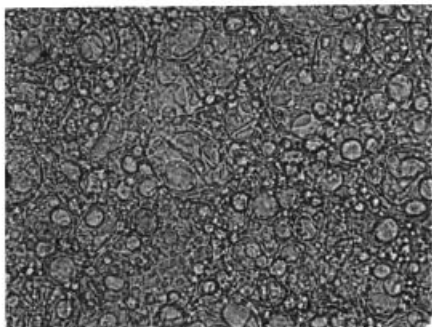
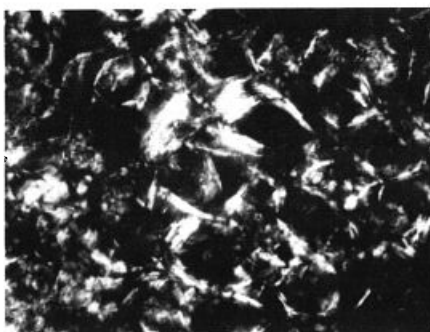
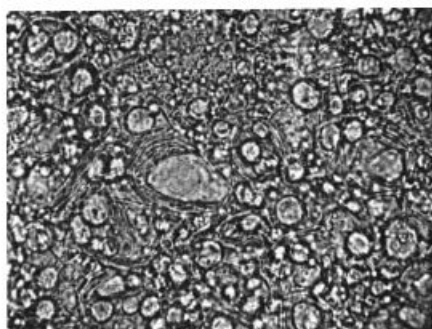
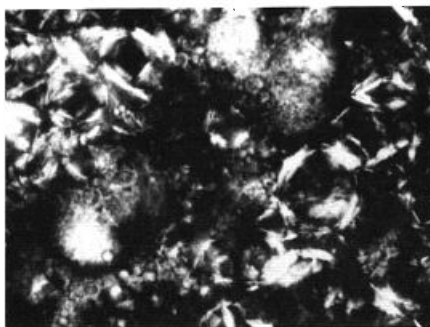
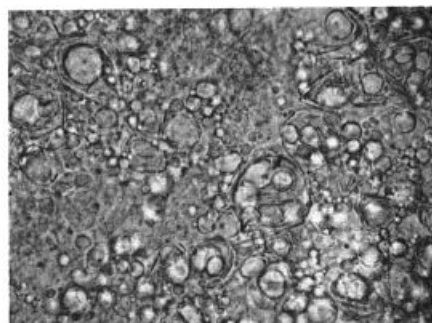
## DESTABILIZATION

As Figure 1 indicates, destabilization becomes apparent in the rheogram at 99 days. This instability is characterized by formation of additional spurs and inflections at low shear rates, a shift to lower maximum shear stress values, and a change in the size and shape of the hysteresis loop. In the 99-day rheogram, the low shear rate inflection occurs at 560 dynes/cm<sup>2</sup>, while the maximum shear stress value reduces to 1080 dynes/cm<sup>2</sup>. An intermediate inflection also occurs at 1000 dynes/cm<sup>2</sup>. The rheogram of the 16-month-old sample shows a dramatic growth in the spur. The rapid recoil of the rheogram after the yield value of 770 dynes/cm<sup>2</sup> suggests a weakly associated sample structure that is very unstable to shear. Hints of instability were present in the 34-day rheogram by a slight low shear rate inflection at 400 dynes/cm<sup>2</sup> and a slight recoil after the maximum shear stress value at 1184 dynes/cm<sup>2</sup>.

Cumulative examination of the rheograms 34 days through 16 months reveals a general trend in the rheogram characteristics as destabilization progresses. The low shear rate inflection shifts toward higher shear stress values and ultimately becomes the maximum shear stress value while the recoil following the maximum shear stress value shifts to lower shear rates. Overall, the maximum shear stress value decreases. As was discussed in a previous work, these secondary inflections can be correlated with three-dimensional network structures (7). The rheogram changes occurring as destabilization progresses indicate successive destruction of a shear-resistant network structure and formation of a network with less shear resistance. As will be proven later, this corresponds to destruction of the liquid crystalline gel network, particle coalescence, and agglomerate formation. The rheogram behavior is consistent with the physical changes in the cream. As destabilization progressed, the cream became softer and grainier. At 16 months, the cream had developed a highly pearlescent, soft texture which, as will be seen later, can be attributed to agglomerated oil phase components.

Figure 3 presents photomicrographs of the destabilized creams. Polarized light indicates that instability can be associated with formation of diffuse, weakly birefringent structures that are devoid of a surrounding lamellar liquid crystalline gel network. Ordinary light photomicrographs show that areas corresponding to these weakly birefringent structures are also diffuse. Additionally, ordinary light shows a general increase in droplet size in the remaining liquid crystalline areas. It will be shown that these diffuse, weakly birefringent structures are actually agglomerated oil phase components.

At 99 days, instability is not visually apparent in the cream, and the diffuse, weakly birefringent structures are present in a relatively low concentration. However, at 16 months, the cream develops a pearlescent sheen, and distinct areas of lamellar liquid crystalline structures and agglomerates can be identified microscopically when scanning the slide preparation. Examples of these distinct areas from a slide preparation of the 16-month-old sample are shown in Figure 3. Comparison of the photomicrographs of the 99-day-old sample and the area of the 16-month-old sample with no agglomerates shows few differences. However, the photomicrograph of the area of the 16-month-old sample with agglomerates shows numerous small droplets associated with the agglomerates when viewed with polarized light. These droplets are also devoid of a lamellar surrounding structure and are presumed to be phase-separated isopropyl myristate. These observations are consistent with the phase separation process described by Junginger (8). According to this process, the lamellar gel structure breaks down and the

**Ordinary Light****Polarized Light****99 Days****16 Months****No Agglomerates****16 Months With Agglomerates****Figure 3.** Destabilization of the model cream.

cream transforms into the unstable state of an emulsion droplet suspension. Further, after this transition to the suspension state, the lipophilic gel phase (also known as coagel) still surrounds the dispersed internal phase. The agglomerates and oil droplets in the photomicrographs of Figure 3 indicate that the wax and oil components of the internal phase form distinct entities when phase-separated. According to both Eccleston (1) and Junginger (8), pearlescence in creams is attributable to crystallization in the continuous phase in the form of light-refracting platelets. Junginger (8) further states that these platelets are structurally similar to lipophilic gel phase (i.e., coagel). In the case of the model cream discussed here, the phase-separated wax components are responsible for the pearlescence in the 16-month-old sample.

#### IDENTIFICATION OF PHASE-SEPARATED COMPONENTS

In order to further identify the phase-separated components, thermal optical videomicroscopy was performed on the 16-month-old cream using slides specifically selected to have minimal or extensive agglomeration. Figure 4 shows the photomonitor recordings of the melting transitions of 16-month-old cream samples from slides with and without extensive agglomeration. The slide with relatively few agglomerates forms a smooth transition to an initial arrest at 45°C followed by a final arrest at 48.5°C. The videotape of the melting transition indicated that these arrests correspond to the melting point of the cream matrix and trace amounts of agglomerate, respectively. The initial arrest in the slide with extensive agglomeration occurs at the same temperature as the slide with trace agglomerates and, according to the videotape, also corresponds to the melting point of the cream matrix. A broad transition in the photomonitor recording occurs over the range from 47°C to 58.5°C. The videotape indicates that this corresponds to the agglomerate melting transition. Examination of the formula indicates that the agglomerates could be cetyl alcohol, cetyl palmitate, and/or stearyl alcohol, which have literature melting points at 49°C, 54°C, and 56–60°C, respectively (10). The values at the

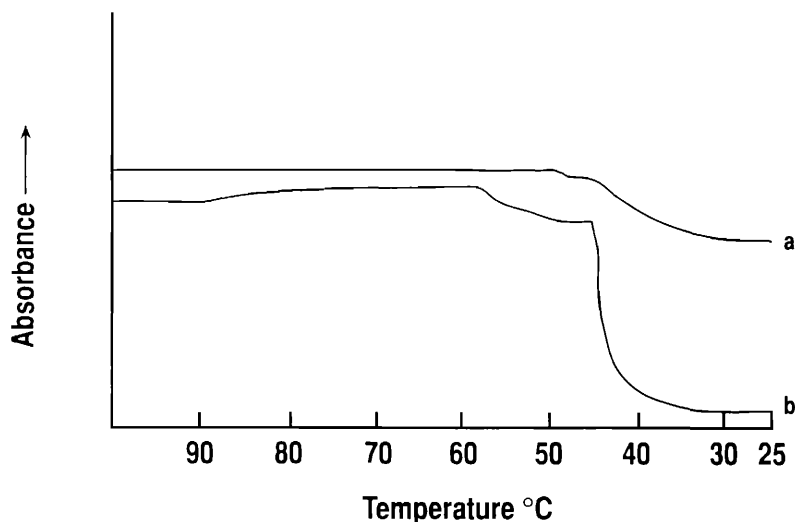


Figure 4. Photomonitor recordings of the model cream: (a) model cream with few agglomerates; (b) model cream with agglomerates.

thermal arrests of the photomonitor recordings are sufficiently consistent with these values to verify the suspected identity of the agglomerates. Thermal and infrared trace substance analysis of an isolated agglomerate indicated cetyl palmitate to be the major component and stearyl and cetyl alcohol to be the minor components (11). The absence of isopropyl myristate in the trace substance analysis verifies the photomicroscopy observation that the oil and wax components phase separate as distinct entities.

## CONCLUSIONS

The model cream was a white lotion at the time of manufacture that slowly converted to a semisolid consistency and subsequently became softer again as aging and the phase separation process progressed. The consistency development and destabilization were both associated with phase changes in the surfactant/fatty amphiphile systems. In the former case, surfactant interpenetrates the fatty amphiphiles in a semihydrate crystalline arrangement to form a fully hydrated, lamellar liquid crystalline gel network. In the latter case, the lamellar liquid crystal breaks down, expelling the fatty amphiphiles, which revert back to the crystalline semihydrate arrangement. The consistency changes reflect the integrity of the gel network since it is a highly viscoelastic system. The extent of destabilization is apparent in the degree of pearlescence, since the phase-separated fatty amphiphiles and waxes of the internal phase form light-refracting platelets.

The consistency development and destabilization process can be monitored using rheology and microscopy. Structural development is apparent in the rheograms by an increase in hysteresis and a shift toward higher yield values. However, once a semisolid consistency is established, the overall shape of the rheogram remains basically unchanged except for the shift to higher shear stress values. Destabilization appears in the rheograms through formation of spurs and secondary inflections, shifts to lower maximum shear stress values, and changes in the size and shape of the hysteresis loop. General trends in the destabilization process show a low shear rate inflection, which gradually becomes more pronounced and shifts to higher shear stress values, and a recoil following the maximum shear stress, which shifts to lower shear rates. These changes reflect the destruction of a shear-resistant network and formation of a less shear-resistant network and can be correlated with breakdown of the lamellar liquid crystalline gel network, droplet coalescence, and agglomerate formation.

The phase changes apparent in photomicrographs support the rheological findings. As the cream consistency develops, polarized light photomicrographs show a decreased presence of grainy textures (coagel or lipophilic gel) and increased formation and thickness of birefringent, lamellar structures (lamellar liquid crystalline gel phase or hydrophilic gel). Ordinary light shows gradual replacement of the grainy textures with emulsion droplets and improved definition of the droplets. These changes have been attributed to increased surfactant penetration of the fatty amphiphiles. Destabilization has been associated with formation of diffuse, weakly birefringent structures when viewed with polarized light. These areas also appear diffuse in ordinary light. The concentration of the diffuse, weakly birefringent structures has been found to increase as phase separation progresses. The pearlescence apparent in phase-separated creams has been attributed to these agglomerates that, according to theory (1,8), are structurally similar to coagel (i.e., lipophilic gel). The small oil droplets associated with the ag-



glomerates suggest that the waxes and oils of the internal phase separate as distinct entities. Thermal optical videomicroscopy and trace substance analysis have identified the phase-separated components of the agglomerates as cetyl alcohol, stearyl alcohol, and cetyl palmitate. The absence of isopropyl myristate in the trace substance analysis has verified the conclusion that the oil and wax components phase separate as distinct entities.

## ACKNOWLEDGMENTS

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