Inverting the tables on emulsion sensory and performance

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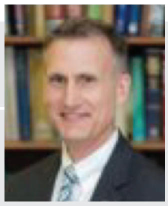

KEYWORDS: Emulsion, Invert emulsion, Silicone surfactant, Sensory modification, PEG free surfactant, PPG free surfactant, Emollient, Oil phase, Lauryl PEG 8 dimethicone, Lauryl TMP dimethicone, IPCE 2018.

ABSTRACT

For oil in water (O/W) emulsions, Appearance, Pick-up, and Rub-out (APR) aesthetic characteristics are all dictated by emulsifier selection; in After-feel evaluations, there is an equal influence of emulsifier and emollient(1). This was all laid out elegantly by Dr. Johann Wiechers and the team back in 2002. This current study demonstrates that invert (water-in-oil and water-in-silicone) emulsions made with PEG-free TMP Lauryl Dimethicone emulsifier had different aesthetic characteristics when compared to the same emulsions using the very similar Lauryl PEG-8 Dimethicone emulsifier. Overall, it was demonstrated that invert (water-in-oil) emulsions have similar properties from their oil-in-water counterparts in terms of APR and After-feel characteristics but the emulsion characteristics are also effected by the emollient in an invert emulsion.
This study was undertaken by Siltech and ACT Technologies and was presented by Mark Chandler of ACT Technologies at the IPCE in 2018 in Italy.

INTRODUCTION

It has been demonstrated that oil-in-water emulsion aesthetics, with Appearance, Pick-up, and Rub-out in particular, are controlled by the emulsifier selection, while After-feel characteristics show influence from both emulsifier and emollient choice (1). Water-in-oil and water-in-silicone emulsions, a platform not extensively evaluated by previous aesthetic studies (2), represented a new layer of exploration. The initial drive was to find differences in these systems with a change in emulsifier. Once an ideal emulsifier had been determined, the next step involved discerning the changes in aesthetic characteristics from varying emollients, all the while maintaining a constant emulsifier. The differences between the two emulsifiers tested was strictly in the nature of the hydrophilic portion, with TMP Lauryl Dimethicone being trimethylolpropane, and Lauryl PEG-8 Dimethicone, a polyethylene glycol (PEG) chain. The emollients tested included Heptyl Undecylenate, Ethylhexyl Palmitate, Diheptyl Succinate (and) Capryloyl Glycerin/Sebacic Acid Copolymer, and Diheptyl Succinate and Capryloyl Glycerin/Sebacic Acid Copolymer.

The main difference between a conventional and invert emulsion involves the phase that is continuous and the phase that is suspended. Oil-in-water (O/W) emulsions are comprised of oil droplets suspended in an aqueous continuous phase, while W/O emulsions involve water droplets suspended in a continuous oil phase. The varying properties of the two systems allow for the unique applications for each. The ability to manipulate the APR and After-feel characteristics of an invert emulsion could lead to fewer limitations and possible innovative applications for these oil-continuous products.

While the search for a contrast in aesthetics is a sound concept, there are some issues that could prevent a fully thorough analysis. The various emollients tested were compared to each other in terms of sensory analysis. There was no option of a control formulation to demonstrate the absence of a contribution to skin feel of an emulsifier or emollient. This is because the absence of one or the other would not allow for a proper emulsion. It has also been shown that skin characteristics of the same formulation made twice using the same ingredients and in the same quantities can be different due to processing and manufacturing variables (1). This further complicates the idea of a perfect benchmark formulation, which would be the same formulation with the same ingredients but without the emulsifier or emollient. Skin feel contribution is instead assessed here using isolated changes in either emulsifier or emollient but keeping all other ingredient and formulation variables constant.

CHEMISTRY

The PEG free emulsifier we developed has a structure shown in Figure 1. The molecule has (a) a silicone backbone, (b) an alkyl pendant group and (c) a hydrophilic dihydroxy pendant group. The balance between these groups allows for a molecule that has an outstanding ability to make invert emulsions of either oil or silicone as the external phase and water as the internal phase. The product is commercially available as Silube 316.

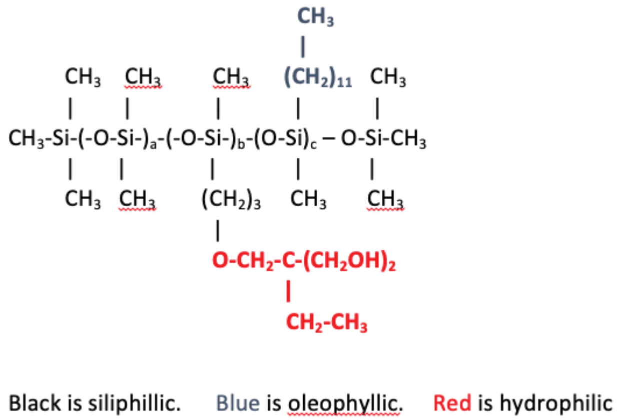

Figure 1. PEG Free Alkyl Dimethicone Emulsifiers
INCI: TMP Lauryl Dimethicone.

The product was compared to a commonly used invert emulsifier, Lauryl PEG 8 dimethicone (Figure 2)

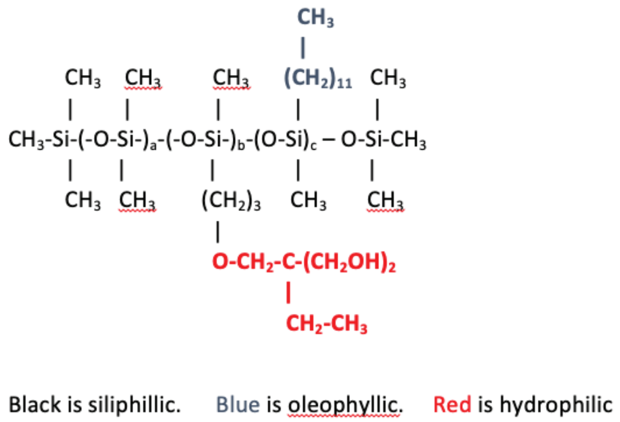

Figure 2. Standard Alkyl PEG Dimethicone Emulsifier
INCI Lauryl PEG 8 dimethicone.

MATERIALS AND METHODS

The first portion of this study explored water-in-oil and water-in-silicone emulsions that differed only in the emulsifier system. All other ingredients and concentrations were kept the same within each emulsion type, and emulsifier concentration changed accordingly. Four different formulations were utilized for comparison (1524, 1529, 1903, and 1909), as seen in Table 1.

Formulation Identities	
1524	Water-in-Silicone, TMP Lauryl Dimethicone
1529	Water-in-Silicone, Lauryl PEG-8 Dimethicone
1903	'Natural' Water-in-Oil, TMP Lauryl Dimethicone
1909	'Natural' Water in Oil, Lauryl PEG-8 dimethicone
2106	70% Internal Phase w/ Heptyl Undecylenate and TMP Lauryl Dimethicone
2108	70% Internal Phase w/Ethylhexyl Palmitate and TMP Lauryl Dimethicone
2112	70% Internal w/ Diheptyl Succinate (and) Capryloyl Glycerin/Sebacic Acid Copolymer and TMP Lauryl Dimethicone
2113	70% Internal w/ Diheptyl Succinate and Capryloyl Glycerin/Sebacic Acid Copolymer and TMP Lauryl Dimethicone

Table 1. Properties and Identities of Formulations Analyzed.

The second phase of the study involved water in oil emulsions with a change in emollient. All other ingredients and concentrations remained constant, and four different emollient types were utilized Table 1: 2106, 2108, 2112, 2113).

TMP Lauryl Dimethicone was chosen as the constant emulsifier for these systems.

All sensory analyses were performed as comparisons against the new emulsifier or emollient system. The descriptions were based on the Spectrum Descriptive Analysis™ method (Sensory Spectrum, Chatham, NJ, USA) (3). This sensory technique relies on obtaining an accurate score on a set number of attributes with a fixed meaning. The attributes were divided and subdivided into groups to gauge Appearance (2 attributes), Pick-up (2), Rub-out (3), and Immediate After-feel (2). Panelists evaluated on a 1 to 5 scale, with 1 being the low and 5 being the high, each of the aesthetic characteristics for each formulation.

Data obtained from these comparisons were subjected to statistical analysis to identify significant differences between formulations. These were verified using a two-sample t-test assuming equal variances at p=0.05.

RESULTS

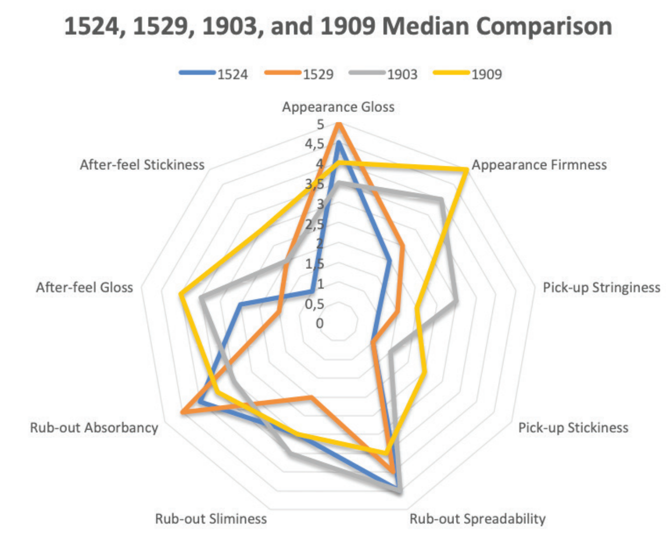

Figure 3. Sensory Results of Water in Oil and Water in Silicone Emulsions with Varying Emollient.

Figure 3 depicts an overview of the first portion of this study, with blue and orange lines representing the water-in-silicone emulsions, while the yellow and silver lines represent the water in oil emulsions (Table 1). The differences in median comparisons for emulsions made with PEG-free TMP Lauryl Dimethicone emulsifier when compared to the same emulsions using ethoxylated Lauryl PEG-8 Dimethicone emulsifier revealed variances in aesthetic characteristics (Figure 3). These changes show that Rub-out spreadability was higher and After-feel stickiness was lower with TMP Lauryl Dimethicone emulsifier. More subtle differences can be seen in Appearance gloss, Appearance firmness, and Rub-out absorbency; where the TMP Lauryl Dimethicone emulsions are lower in each category. Rub-out sliminess can be seen to have a slight variation as well, with TMP Lauryl Dimethicone being higher rated in this instance.

Attribute	Frequency of Significant Differences
Appearance:	
Gloss	1
Firmness	5
Pickup:	
Stringiness	2
Stickiness	0
Rub Out:	
Spreadability	1
Sliminess	3
Absorbency	1
After feel:	
Gloss	2
Stickiness	4
Sum:	19

Table 2. *Frequency of Significant Differences of Attribute Comparisons.*

Paired Comparison	Frequency of Significant Differences
2106 vs. 2108	3
2106 vs. 2112	2
2106 vs. 2113	4
2108 vs. 2112	5
2108 vs. 2113	3
2112 vs. 2113	2
Sum:	19

Table 3. *Frequency of Significant Differences of Formulation Comparisons.*

Once TMP Lauryl Dimethicone was established as the choice emulsifier for this study, comparison work began to distinguish whether a change in emollient with a consistent emulsifier would lead to a change in aesthetic characteristics. This was an unexplored area of prior studies, and lead to some unforeseen results. Table 2 represents the frequency of statistical significance in each attribute. Appearance and After-feel were shown to have the highest amount of significant differences with 6 each. The variable emollients also had a large effect on Rub-out characteristics with 5 total differences. The least affected aesthetic was demonstrated to be Pick-up, with only 2 total differences (table 2).

The pattern of aesthetic characteristics could also be viewed from a formulation comparison standpoint. Table 3 represents the statistically significant differences between each formulation of variable emollient. The largest discrepancy involving 2108 and 2112. Utilizing Ethylhexyl Palmitate (2108) versus Diheptyl Succinate (and) Capryloyl Glycerin/Sebacic Acid Copolymer (2112) leads to 5 differences in aesthetic comparisons, with the next highest variation being 4 differences (2016 vs 2113). These divergences suggest that the structure of the emollient does influence sensory feel.

It was predicted that there would be less variation seen with comparisons between 2016/2108 and 2112/2113, and more when comparing the groups against each other. This was due to notable structural similarities between the two pairs, as well as a similar molecular weight. Heptyl Undecylenate (2106), and Ethylhexyl Palmitate (2108) both share an ester base structure with alkyl chain side groups. The only variation being the length of each chain, a branched group with 2018, and an alkene on the end of the chain of 2016. Diheptyl Succinate (and) Capryloyl Glycerin/Sebacic Acid Copolymer (2112) and Diheptyl Succinate and Capryloyl Glycerin/Sebacic Acid Copolymer (2113) are even more similar, with 2113 being a longer copolymer of diheptyl succinate and capryloyl glycerin/sebacic acid. While this prediction was supported by most of the results in Table 2, there were also less expected differences with a frequency of 3 and 2 when comparing 2106/2018 and 2112/2113, respectively. This goes to demonstrate that even a mild change in the structure of an ester side chain (2106 vs 2018), or a change in only the length of the copolymer (2112 vs 2113) can lead to changes in aesthetic with a W/O emulsion.

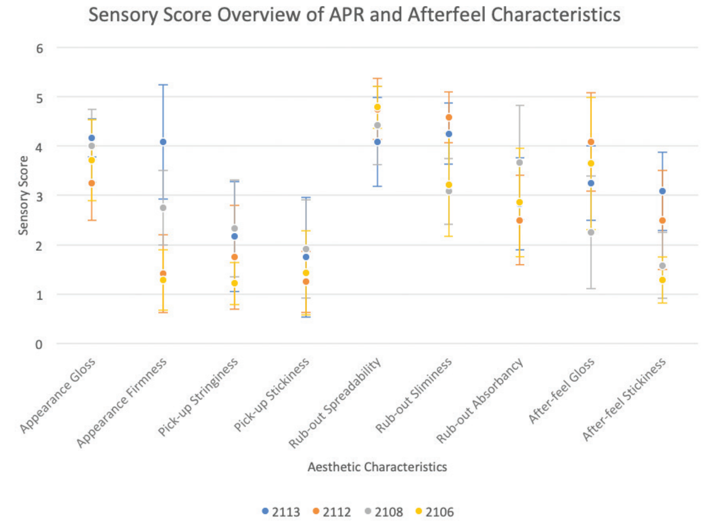

Figure 4. Sensory Results of Water in Oil Emulsions using Silube 316 and Varying Emollient.

Formulations were chosen for statistical analysis based on the results shown in Figure 4. Error bar analysis was conducted for each aesthetic characteristic, with the selection process for significance limited to p=0.05. The largest spread and discrepancy can be attributed to appearance (firmness), which is further reflected in Table 2 with 5 differences. Comparatively, Pick-up (stickiness) had a tighter cluster, which is again reflected in Table 2 with 0 differences for this characteristic. The exact formulation comparisons tested can be seen on SI Table 5.

Overall, the W/O emulsions with TMP Lauryl Dimethicone and varying emollients revealed a total of 19 significant aesthetic differences (Table 2, Table 3). Emollient was found to have a large influence on APR characteristics including firmness and sliminess, as well as After-feel stickiness. Less substantial differences involved APR characteristics such as gloss, stringiness, spreadability, absorbency, and After-feel gloss. The only APR characteristic with no significant differences between formulations was Pick-up stickiness.

DISCUSSION

O/W emulsions represent the largest share of cosmetic skin care systems. W/O emulsions, on the other hand, are used for high-performance applications. Water-in-silicone emulsions represent the bulk of liquid foundation makeup products. The milder nature, superior coverage, and ability to leave the skin's lipid bilayer intact make a W/O emulsions ideal for dry/sensitive skin treatment and sunscreen applications. The ability to favorably alter the properties of these emulsions toward a more aesthetically appealing product will be an important asset to pharmaceutical and cosmetic companies looking to design higher performance products with lasting consumer appeal.

It had been previously demonstrated that for O/W emulsions, Appearance, Pick-up, and Rub-out (APR) characteristics are all controlled by emulsifier, with equal influence of emulsifier and emollient in After-feel(1). Here it was proven that APR and After-feel characteristics of W/O emulsions can be influenced by both changes in emulsifier and emollient (Table 2, Table 3). It is advisable to first vary emulsifier while keeping the emollient constant, determining the W/O emulsifier that provides the primary aesthetic characteristics that would have the most appeal for the target audience. Second, vary the emollient to further refine the aesthetics, knowing that for a W/O system, both APR and After-feel characteristics will vary. Not formally part of the study but of particular interest was that it was noticed that differences in the neat feel of the emollient did not translate into differences in formulation aesthetics. Once again, the "oh doesn't that feel nice" technical/sales pitch for emollients has little credence. Differences in aesthetics of W/O emulsions brought on by varying emollient must be due to emulsion structural changes brought on by the interaction of emulsifier and emollient. This thought is made most evident by the fact that the only aesthetic quality that did not show differences when emollient was varied was stickiness.

CONCLUSION

Systems with oil as the external phase represent an understudied area of cosmetic science(2). For O/W systems, it had been established that APR is controlled by the emulsifier, and After-feel characteristics are influenced by both emulsifier and emollient in roughly equal measure (1). This study concludes that varying the emulsifier in W/O systems shows the same influence, but that varying the emollient can lead to changes in APR as well as After-feel characteristics.

TMP Lauryl Dimethicone emulsifier revealed different aesthetic characteristics when compared to the same emulsions using ethoxylated Lauryl PEG-8 Dimethicone emulsifier. Rub-out spreadability was higher in the TMP Lauryl Dimethicone emulsions, and After-feel stickiness was lower. Water-in-oil (W/O) emulsions using TMP Lauryl Dimethicone and varying emollients revealed a total of 19 significant aesthetic differences. Emollient was found to have a large influence on APR characteristics including firmness and sliminess, as well as After-feel stickiness. Less substantial differences involved APR characteristics such as gloss, stringiness, spreadability, absorbency, and After-feel gloss.

Overall, W/O emulsions have beneficial therapeutic and performance properties when compared to their O/W counterparts. Emulsifiers in these systems had a similar effect in terms of APR and After-feel characteristics; however, new characteristics were found to change when varying the emollient in the W/O system. This discovery leads to more possibilities when looking to formulate for aesthetics that resonate with the target audience for particular product, while providing the therapeutic effects that are demanded in the skin care area. What Dr. Wiechers has told us through his work that is being built upon in these studies is that as formulators we need to be looking at new materials and combinations to find that right mix that provide the aesthetics, stability, and performance to reach the target audience.

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