Cationic emulsifier systems for sunscreens
Combining efficacy with cost advantage

ABSTRACT
Cationic emulsions have attracted increased interest during the last years due to their unique skin feel, that is more dry and powdery than that of anionic or nonionic emulsions. Cationic emulsions can also help to improve the moisturisation level of elderly skin. Due to their unique film forming efficacy, cationic emulsifiers allow to prepare 100 percent water resistant emulsions without any addition of a film former. They are compatible with all types of filter systems except for benzimidazole sulfonic acid derivatives. These properties turn them into a versatile and cost-efficient alternative to conventional emulsifiers in sunscreens.

INTRODUCTION
Since 1999, with the introduction of new cationic emulsions for skin, hand, and baby care in the United States, this market segment has expanded broadly into over 15 new products containing the cationic emulsifier Disteararylmonium Chloride in 2005 (1), (Picture 1). The application area first seen in the market was skin care for babies. Mennen marketed this line under the trade name Baby Magic™ using two cationic emulsifiers (2). S.C. Johnson & Son launched the second cationic emulsifier based product, Curel®, now sold under the name of Kao’s subsidiary, Andrew Jergens. The success of this product can be attributed to the unique sensory profile that cationic moieties offer. Cationic emulsions give a smooth powdery after-feel that allows high active loadings. Thus, they are broadening the range of aesthetics available to the formulator.

SUITABILITY OF USE
Cationic moieties have typically been associated with hair care for conditioning. In this application, they impart lubricity, antistatic properties and smoothness to the hair fibers (3). Given these facts, Cetrimonium Chloride and Behentrimonium Chloride have been widely used in conditioning rinses, although they have only been regulated as preservatives up to the 6th amendment of the EU cosmetics regulation. However, there was an exception for higher use levels in non-preservative applications which expired with the 7th amendment. The Scientific Committee for Cosmetic Products (SCCP) is now evaluating a dossier dealing with the safe use of these products as conditioners. Due to their eye irritation profile, it’s expected that concentration limits in the range of max. 0.5 percent (for leave-on products) up to 3 percent (for rinse-off products) will be fixed for the mentioned monoalkyl quats. However, as long chain dialkyl quaternaries are milder on the skin than long chain monoalkyl analogues (4) and as alkylamidoamine quats are also known to be less irritating than their amide and spacer group-free analogues, we will concentrate on the evaluation of the former product types (Table 1).

Picture 1. New skin care products containing distearylmonium chloride
SUNSCREENS

The choice of cationic emulsifiers in sunscreen formulations is crucial for sensory properties. In general, sensory properties for these emulsions are powdery, smooth and dry. The formulas in Figure 2 were used to characterize the sensory profiles for Distearyldimonium Chloride and Palmitamidopropyltrimonium Chloride.

Table 1. Toxicity

<table>
<thead>
<tr>
<th>Product</th>
<th>Type</th>
<th>Structure</th>
<th>Safety</th>
</tr>
</thead>
</table>
| Distearyldimonium Chloride | Dialkyl quat | CH₂(CH₂)₁₅CH₃ N – CH₂(CH₂)₁₅CH₃ | • Dialkyquats are milder than their monoketyl counterparts  
• Not orally toxic (rat)  
• Not irritant in diluted and undiluted concentrations (rabbit)  
• No sensitization potential observed |
| Palmitamidopropyltrimonium Chloride | Amidoamine quat | CH₂(CH₂)₁₄CH₃ – NH(CH₂)₁₄CH₃ | • Alkylamidooamine quats are known to be milder than monoketylquats  
• No oral or dermal toxicity  
• No irritations at 2.5 and 5 % use concentration in a HET CAM assay of a cosmetic test emulsion |

TEGO® Care CE 40 is a flaked form of Palmitamidopropyltrimonium Chloride that is Propylene Glycol free and offering better handling in processing.

SENSORY EVALUATION

The classic use of cationic products has been to impart lubricity, smoothness and antistatic properties to the hair fibre, properties that are also of interest in skin care (5,6). Cationic products may also be used as O/W emulsifiers for skin care. This functional transfer of properties from traditional hair to skin care applications provides an innovative and economical platform to the formulator. The consumer demographic shift over the next fifty years will more than double the 60+ segment, making this an attractive market for skin and sun care product manufacturers. A major concern for this segment of the market is maintaining the skin’s health and elasticity by protecting it from damage by UV-irradiation. Every day facial and décolleté care with UV shielding is one of the means to achieve this goal. With higher loads of UV filters, however the formula may impart an unpleasant oily or greasy and heavy skin feel. Cationic emulsifiers will mask these negative sensory properties, with the specific aesthetics determined by the choice of cationic emulsifier. In general, sensory properties for these emulsions are powdery, smooth and dry.

The consumer demographic shift over the next fifty years will more than double the 60+ segment, making this an attractive market for skin and sun care product manufacturers. A major concern for this segment of the market is maintaining the skin’s health and elasticity by protecting it from damage by UV-irradiation. Every day facial and décolleté care with UV shielding is one of the means to achieve this goal. With higher loads of UV filters, however the formula may impart an unpleasant oily or greasy and heavy skin feel. Cationic emulsifiers will mask these negative sensory properties, with the specific aesthetics determined by the choice of cationic emulsifier. In general, sensory properties for these emulsions are powdery, smooth and dry.

The formulas in Figure 2 were used to characterize the sensory profiles for Distearyldimonium Chloride and Palmitamidopropyltrimonium Chloride.

FORMULATING WITH CATIONIC EMULSIFIERS

Formulating with cationic emulsifiers is straightforward and similar to the techniques employed with the traditional non-ionic emulsifiers. They can either be added to the oil or the water phase. Similar to other hydrophilic O/W emulsifiers, additional stabilization of the formulations is achieved by incorporating consistency enhancers such as Stearyl Alcohol, Cetyl Alcohol, Glyceryl Stearate or Stearic Acid. Cationic emulsifiers are incompatible with anionic moieties, such as Carbomers or anionic water soluble sunscreens such as Phenylbenzimidazole Sulfonic Acid. These materials should be avoided or their use minimized.

<table>
<thead>
<tr>
<th>Cationic Lotion with Dialkyl Quat ADP-5545-40</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distearyldimonium Chloride (VARISOFT® TA 100)</td>
<td>4.75</td>
</tr>
<tr>
<td>Petrolatum</td>
<td>4.55</td>
</tr>
<tr>
<td>Isopropyl Palmitate</td>
<td>4.25</td>
</tr>
<tr>
<td>Cetyl Alcohol</td>
<td>3.75</td>
</tr>
<tr>
<td>Dimethicone</td>
<td>0.40</td>
</tr>
<tr>
<td>Water</td>
<td>74.60</td>
</tr>
<tr>
<td>Sodium Chloride</td>
<td>0.05</td>
</tr>
<tr>
<td>Glycerin</td>
<td>7.65</td>
</tr>
<tr>
<td>Preservative, Parfum</td>
<td>q.s.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Cationic Lotion with Amid amine Quat ADP-5553-140*</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Palmitamidopropyltrimonium Chloride (and) Cetearyl Alcohol (TEGO® Care CE 40*)</td>
<td>7.20</td>
</tr>
<tr>
<td>Petrolatum</td>
<td>4.55</td>
</tr>
<tr>
<td>Isopropyl Palmitate</td>
<td>4.25</td>
</tr>
<tr>
<td>Dimethicone</td>
<td>0.40</td>
</tr>
<tr>
<td>Water</td>
<td>75.90</td>
</tr>
<tr>
<td>Sodium Chloride</td>
<td>0.05</td>
</tr>
<tr>
<td>Glycerin</td>
<td>7.65</td>
</tr>
<tr>
<td>Preservative, Parfum</td>
<td>q.s.</td>
</tr>
</tbody>
</table>

*TEGO® Care CE 40 contains Cetearyl Alcohol. The formula was adjusted from the original to compensate for this component.

Figure 2. Two cationic emulsions differing only in the type of emulsifier.
MOISTURIZATION
A comparison of the moisturizing properties of a non-ionic versus a cationic emulsifier was conducted by an outside laboratory. The data below outlines the results from a moisturization study comparing Glyceryl Stearate SE against Distearyldimonium Chloride. The moisture measurements were taken in May 2005 on 11 panellists over a 12 hour period using a Corneometer by Khourage & Khazaka. The formula in Figure 3 was used as the test formulation in this study.

Corneometer readings were taken hourly. The results as presented in Fig. 4 indicate that during the initial 8 hours of the study the cationic emulsifier did not show an increased performance versus the Glyceryl Stearate SE regarding moisturization. After 8 hours the cationic film showed superior performance versus the Glyceryl Stearate SE. The slopes of the moisture loss curves were -0.4384 and -1.1545 respectively, thus the improvement of long time moisture retention in the skin is 38 percent with the cationic emulsifier. This result is most likely due to the ability of Distearyldimonium Chloride to form a substantive durable film on the skin in which the hydrophobic moieties of the emulsifier are directed to the outside.

WATER RESISTANCE
With the increasing concern about sun induced skin damage, consumers are using sunscreens at the beach and throughout the year to protect their skin from premature aging. Although an oily feel is acceptable for the beach, it is not acceptable for daily wear - the challenge to formulators is to develop high SPF formulas that protect the skin and wear well, but do not feel oily. Cationic emulsifiers can offer the formulator a means to achieve the aesthetics along with the additional benefit of water resistance.

Water resistance is an important factor in sun care formulas, especially those intended to be used at the pool or on the beach. Data from an in-vitro water resistance study conducted according to a protocol that is under preparation by a scientific collaboration between different industrial laboratories and testing institutes in Europe were gathered with sunscreens containing the identical filter combination as well as the identical emulsion base only varying the emulsifier. The tests are performed featuring the following:

- PMMA Hélioplates as substrate
- Stirring method in a water-filled beaker
- In-vitro testing by the Optometrics SPF-290S

The study evaluated the water resistance of four emulsifiers: Ceteareth-25, Polyglyceryl-3 Methylglucose Distearate, Distearyldimonium Chloride (all three O/W) and Polyglyceryl-4 Diisostearate/Polyhydroxystearate/Sebacate (W/O for comparison reasons). The filter combination was in all cases a mixture of 5 percent Ethylhexyl Methoxycinnamate, 4 percent Menthyl Anthranilate, and 4 percent Ethylhexyl Salicylate.

The following measurements were made and the results are indicated in Table 2 and Figure 5. The result for the pure non-ionic emulsifier Ceteareth-25 is in this test somewhat higher than

<table>
<thead>
<tr>
<th>Code</th>
<th>Emulsifier</th>
<th>Emulsion type</th>
<th>WR* [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>MK 68/1</td>
<td>Ceteareth-25</td>
<td>O/W</td>
<td>70</td>
</tr>
<tr>
<td>MK 67/1</td>
<td>Polyglycerol-3 Methylglucose Distearate</td>
<td>O/W</td>
<td>60</td>
</tr>
<tr>
<td>Ma 48/04-3</td>
<td>Distearyldimonium Chloride</td>
<td>O/W</td>
<td>100</td>
</tr>
<tr>
<td>MK 68/1</td>
<td>Polyglyceryl-4 Diisostearate/Polyhydroxyesterate/Sebacate</td>
<td>W/O</td>
<td>100</td>
</tr>
</tbody>
</table>

* Water resistance (in-vitro water-resistance test, Optometrics SPF-290S, 1 mg/cm², on PMMA slide)

Table 2. Choice of emulsifiers and results for the in-vitro water resistance test

Figure 5. Results for the in-vitro water resistance test

Sunscreen combination:
- Ethylhexyl Methoxycinnamate 5.0 %
- Menthyl Anthranilate 4.0 %
- Ethylhexyl Salicylate 4.0 %

Emulsifiers and consistency enhancers:
- Emulsifier 3.5 %
- Glyceryl Stearate 1.5 %
- Stearyl Alcohol 1.0 %

Figure 5. Results for the in-vitro water resistance test
CATIONIC SUNSCREENS

SUNSCREENS

expected. Usually the in-vivo results for this emulsifier are below 50 percent water resistance.

Figure 6. This formulation utilizes Titanium Dioxide in combination with BMDM and Octocrylene to achieve a high SPF with good UVA protection. It complies with EU regulations.

CONCLUSION

Cationic emulsifiers offer the formulator a new tool in developing products which meet consumer demands. The unique properties of cationic emulsifiers enable the development of high lipophilic systems that offer enhanced consumer benefits without sacrificing aesthetics. Cationic emulsions lend a smooth powdery skin feel that non-ionic and anionic emulsions do not. Applications which benefit from this technology include facial, hand and body, baby and foot care, sunscreens, and other systems where a non-oily, high lipophilic system is an advantage. Cationic emulsifiers offer these benefits for sun products:

- Excellent emulsification
- Various possibilities to combine them with co-emulsifiers thus influencing skin feel and absorption behaviour
- Long-lasting skin moisturization
- High water resistance properties with no need for film forming polymers
- Excellent cost/performance ratio

REFERENCES AND NOTES