Introduction

Consumers are increasingly aware that there is a further need for broad spectrum sun protection, and particular protection during times of heavy sun exposure. Every day, broad spectrum UV protection is necessary to keep the skin looking youthful and healthy. The category is growing, but there continue to be concerns regarding the effectiveness, safety, and aesthetics of the sunscreen actives.

The United States (US) has far fewer approved sunscreen actives than the rest of the world. Of those available in the US, some are not used due to lack of effectiveness and perceived toxicity. While the industry continues to wait for the FDA approval of actives used in Europe and elsewhere, an evaluation of underutilized Category 1 actives is important. Two actives that should be considered are the organic, water-soluble materials, ensulizole and sulisobenzone. Neither of these actives will work on their own, but both can be part of building innovative sun protection packages that please formulators and consumers.

Adaptive Cosmetic Technology Solutions Corp. (ACT Solutions Corp.), assisted in the development of a new broad spectrum, water resistant, SPF 25+ daily facial moisturizer. Specific ingredient selection and innovative formulation techniques were completed to produce this new formulation.

Background

Previously, two broad spectrum daily facial moisturizer formulations were created; one oil-in-water system and one water-in-oil system. Each moisturizer contained ensulizole or sulisobenzone, both underutilized Category 1, organic, water-soluble sunscreen actives. Within 20 minutes after application, most cosmetic emulsions lose the majority of water in a formulation through evaporation. It is likely formulators have been disappointed with these sunscreen actives as they return to their crystalline state as they fall out of solution, ultimately becoming ineffective. Multiple studies have shown that the addition of Zemea propanediol provides a high-performing solvent with additional performance benefits. A study simulating an aqueous phase of ensulizole at 4% and Zemea propanediol at 10% showed that solubility can be maintained when 75% of the water in the aqueous phase has evaporated. In parallel, an aqueous phase of 10% sulisobenzone and 10% Zemea propanediol could also withstand the loss of water at 75%. This was successfully demonstrated in the two formulations created, ultimately increasing the efficacy of the sunscreen actives.

The utilization of the two organic, water-soluble sunscreen actives combined with Zemea propanediol generated market interest. Key learnings from the original formulations were taken and optimized into a new water-in-oil emulsion. Additional testing was completed on this formulation including critical wavelength/broad spectrum testing, in-vitro and in-vivo SPF testing, as well as, 40-minute and 80-minute water resistance testing. The formulating techniques and results are presented in this technical bulletin.
Materials and Methods
Leveraging the learnings from the original two formulations, one water-in-oil emulsion was created.

Table 1. W/O Broad Spectrum, Water Resistant, SPF 25+ Daily Facial Moisturizer

<table>
<thead>
<tr>
<th>Phase</th>
<th>Ingredient</th>
<th>INCI Name</th>
<th>Supplier</th>
<th>Function</th>
<th>Wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Water</td>
<td>Water</td>
<td>-</td>
<td>-</td>
<td>52.40%</td>
</tr>
<tr>
<td></td>
<td>Spectrastat™</td>
<td>Caprylhydroxamic Acid (and) Caprylyl Glycol (and) Glycerin</td>
<td>Inolex</td>
<td>Preservative</td>
<td>0.80%</td>
</tr>
<tr>
<td></td>
<td>AquaSul</td>
<td>Sulisobenzone (Benzophenone-4)</td>
<td>SandreamImpact</td>
<td>Active</td>
<td>2.00%</td>
</tr>
<tr>
<td>B</td>
<td>Zemea® Propanediol</td>
<td>Propanediol</td>
<td>DuPont Tate &amp; Lyle</td>
<td>Humectant</td>
<td>10.00%</td>
</tr>
<tr>
<td></td>
<td>Parsol HS</td>
<td>Ensulizole</td>
<td>DSM Active</td>
<td>Active</td>
<td>3.00%</td>
</tr>
<tr>
<td>C</td>
<td>Tris Amino Ultra PC</td>
<td>Tromethamine</td>
<td>Angus</td>
<td>Neutralizer</td>
<td>2.20%</td>
</tr>
<tr>
<td>D</td>
<td>Solaveil™ XT-40</td>
<td>Titanium Dioxide (and) Aqua (and) Polyglyceryl-2 Caprate (and) Sucrose Stearate (and) Simmondsia Chinensis (Jojoba) Seed Oil (and) Stearic Acid (and) Alumina (and) Glyceryl Caprylate (and) Squalane</td>
<td>Croda</td>
<td>Active</td>
<td>3.00%</td>
</tr>
<tr>
<td></td>
<td>KerrSoft AVG</td>
<td>Acetylated Hydrogenated Vegetable Glyceride</td>
<td>Kerry</td>
<td>Emollient</td>
<td>15.00%</td>
</tr>
<tr>
<td></td>
<td>KerrEmul PGPR</td>
<td>Polyglyceryl-3 Polyrinoleate</td>
<td>Kerry</td>
<td>Emulsion</td>
<td>2.50%</td>
</tr>
<tr>
<td></td>
<td>Solaveil™ AT-300</td>
<td>Caprylic/Capric Triglyceride (and) Titanium Dioxide (and) Polyhydroxystearic Acid (and) Stearic Acid (and) Alumina</td>
<td>Croda</td>
<td>Active</td>
<td>3.00%</td>
</tr>
<tr>
<td></td>
<td>Xperse® 201</td>
<td>Zinc Oxide, Caprylic/capric triglyceride, Polyhydroxystearic acid, Triethoxycaprylsilane</td>
<td>Umicore</td>
<td>Active</td>
<td>3.00%</td>
</tr>
<tr>
<td></td>
<td>CosmoSurf® CE-100</td>
<td>Octodecyl Citrate Crosspolymer</td>
<td>SurfaTech</td>
<td>Emollient</td>
<td>3.00%</td>
</tr>
<tr>
<td>F</td>
<td>CAB-O-SIL® TS-610</td>
<td>Silica Dimethyl Silylate</td>
<td>Cabot</td>
<td>Thickener</td>
<td>0.10%</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td></td>
<td></td>
<td></td>
<td>100.00%</td>
</tr>
</tbody>
</table>

Procedure:
1. Premix Phase A, add Phase B to Phase A.
2. Add Phase C until (AB) is clear.
3. Add Phase D to (ABC) while mixing with propeller stirring.
4. Premix Phase E.
5. Add (ABCD) to Phase E very slowly while mixing with propeller stirring.
6. Add Phase F while mixing with propeller stirring.
Formulating for Success

Many formulation steps were taken to maximize the SPF, broad spectrum protection, and water resistance of the formulation.

Zemea® Propanediol

Zemea® propanediol was used at 10% so that upon evaporation of the water in the formulation when applied to the skin, the powdered water-soluble actives, ensulizole and sulisobenzone, would stay in solution and protect though the duration of the SPF testing and beyond. This proved to be a processing challenge, but was overcome by blending the ensulizole and Zemea® propanediol prior to adding to the aqueous phase. The two water-soluble actives absorb mainly in the UVB spectra, but offer different absorbance profiles when overlaid and can increase the SPF.

One of the main reasons for using sun protecting daily facial moisturizers is to keep the skin moisturized and healthy. The use of Zemea® propanediol helps build moisturization. It also provides additional benefits including lack of skin irritation and excellent sensory characteristics, ultimately improving the aesthetics of the formulation.

Combining Organic and Inorganic Actives

Sunscreens have traditionally been divided into chemical absorbers and physical blockers based on the mechanism of action. Sunscreens containing metal oxides like titanium dioxide and zinc oxide provide a good option for individuals with sensitive skin. These actives are not associated with sensitization and irritation and provide full spectrum UV light protection. Similarly, water-soluble actives, ensulizole and sulisobenzone, typically do not cause irritation or sensitivity. Water-soluble materials have a difficult time penetrating the hydrophobic barrier of the skin, the stratum corneum.

Combining organic and inorganic sunscreen actives is an effective strategy for maximizing SPF and overall sun protection. The two water-soluble actives, ensulizole and sulisobenzone, absorb mainly in the UVB, whereas the grades of inorganic sunscreen actives act across the UV spectrum. In total, the formulation attains both a high SPF and a high level of UVA protection, with an SPF of above 25 and a critical wavelength of 377.8nm.

Phase Formulation

Placing sunscreen actives in both the aqueous phase and the oil phase can have an additive effect and be an effective tool for formulating higher SPF products. Along with the organic sunscreen actives, a portion of the inorganic sunscreen actives were placed in the aqueous phase. The blending of titanium dioxide and zinc oxide done in this formulation can also work to increase overall sun protection. The particular grades of titanium dioxide were chosen for broad spectrum protection maximization rather than SPF heightening. Dispersions of the inorganic sunscreen actives were used, a move which works toward higher sun protection and lower whitening.

Water Resistance

A water-in-oil emulsion platform was chosen for the knowledge that these systems provide excellent coverage on the skin, yielding higher SPF’s and inherent water resistance. The formulation also contains Cosmosurf® CE-100, a water resistant emollient based off of Zemea® propanediol.

Achieving the combination of high SPF and high critical wavelength is rare. Achieving an SPF which is 3 times the level of sunscreen active used is not common when using the lesser-efficient sunscreen actives employed, especially in a formulation that can claim broad spectrum protection and beyond. Achieving all this in a water resistant formulation that looks and feels appealing is exceptional.
Testing and Results

Four-panelist static in-vivo SPF testing including a two-panelist 40-minute and 80-minute water resistance evaluation was performed at AMA Laboratories. Critical wavelength/broad spectrum testing was also completed there. An additional in-vitro SPF test, using a method optimized for formulations containing inorganic sunscreen actives was completed at Heliosciences in France.

The final broad spectrum daily facial moisturizer spreads well, absorbs quickly, and leaves the skin feeling soft and smooth. The in-vivo SPF results were between 25 and 28.75, before and after water resistance testing. The critical wavelength was 377.8nm, well above the 370nm necessary for the broad spectrum claim. The in-vitro SPF test showed to be above 30, reinforcing the confidence that a full 10-panelists SPF testing would have the desired level of protection.

Conclusion

- Zemea® propanediol is useful in formulating effective, innovative sun protection products, primarily daily facial moisturizers with SPF.
- Zemea® propanediol is a high performing solvent for both ensulizole and sulisobenzone, keeping these actives in solution through the evaporation process on the skin, leading to greater efficacy for these actives.
- Two formulation strategies for maximizing sun protection efficiently are combining organic and inorganic actives and placing actives in both the aqueous and emollient phase.
- The addition of Zemea® propanediol in a daily facial moisturizer with SPF improves aesthetics. Zemea® propanediol is non-irritating and provides increased moisturization and excellent sensory characteristics, eliminating stickiness and greasiness in the formulation.

For additional information or samples:

DuPont Tate & Lyle Bio Products
Customer Service
198 Blair Bend Drive
Loudon, TN 37774
Tel: +1-866-404-7933
www.duponttateandlyle.com