

Propanediol in a broad spectrum moisturiser

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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 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 underutilised 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 moisturiser. Specific ingredient selection and innovative formulation techniques were completed to produce this new formulation.

Abstract

Zemea® propanediol is a natural, preservative-boosting humectant for cosmetic formulations. A pure, petroleum-free diol, it offers high performance in a variety of applications and is certified 100% bio-based by the USDA BioPreferred programme.

Benefits include its high purity, lack of skin irritation or sensitisation, improved humectancy and excellent sensory characteristics. Studies also have shown that Zemea propanediol can boost the efficacy of preservatives and reduce the amount of preservatives needed in formulations.

The ingredient is certified natural by the Natural Products Association (NPA) and considered a derived organic ingredient under the definitions of ISO 16128-1.

It can replace petroleum-based glycols such as propylene glycol, butylene glycol, and glycerin in formulations, with functions including: humectant, solvent, emollient, hand-feel modifier, among others.

In this article, the efficacy of Zemea propanediol in providing a range of benefits to a sunscreen formulation was assessed.

Background

Previously, two broad spectrum daily facial moisturiser formulations were created; one oil-in-water system and one water-in-oil system. Each moisturiser contained ensulizole or sulisobenzone, both underutilised 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 high-performing solvency 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 (now referred to as 'bio-based 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 utilisation of the two organic, water-soluble sunscreen actives combined with bio-based propanediol generated market interest. Key learnings from the original formulations were taken and optimised into a new water-in-oil emulsion. Additional testing was completed on this formulation including critical wavelength/broad spectrum testing (Fig 1), *in vitro* and *in vivo* SPF testing, as well as, 40-minute and 80-minute water resistance testing (Table 2).

The formulating techniques and results are presented in this article.

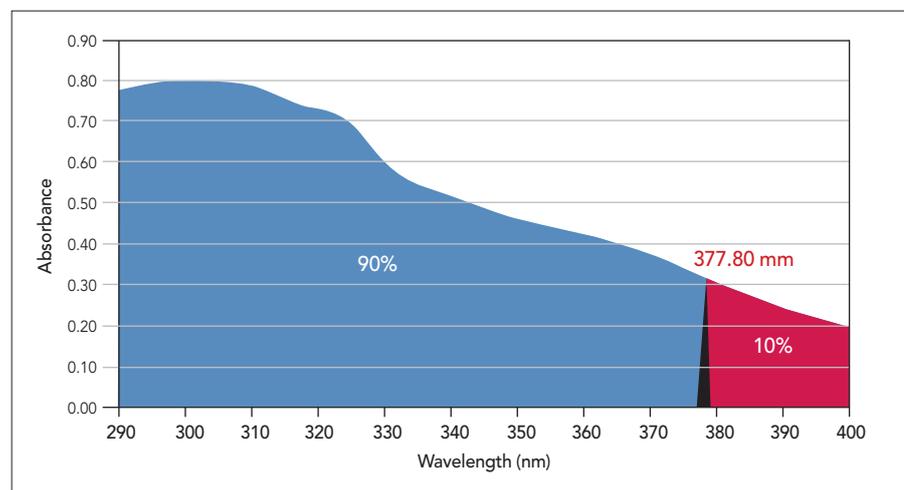


Figure 1: AMA Labs FDA Critical Wavelength.

Table 1: W/O Broad Spectrum, Water Resistant, SPF 25+ Daily Facial Moisturiser

Phase	Ingredient	INCI Name	Supplier	Function	Wt.%
A	Water	Water			54.6%
	Spectrastat™	Caprylhydroxamic Acid (and) Caprylyl Glycol (and) Glycerin	Inolex	Preservative	0.80%
	Aqua Sul	Sulisobenzene	SandreamImpact	Active	2.00%
B	Zemea®	Propanediol	DuPont Tate & Lyle	Solvent	10.00%
	Eusolex® 232	Ensulizole	EMD Performance Materials	Active	3.00%
C	TEA	Triethanolamine		Neutralizer	qs%
D	Solaveil™ XT-40	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	Croda	Active	3.00%
E	KerrSoft AVG	Acetylated Hydrogenated Vegetable Glyceride	Kerry	Emollient	15.00%
	KerrEmul PGPR	Polyglyceryl-3 Polyricinoleate	Kerry	Emulsifier	2.50%
	Solaveil™ AT-300	Caprylic/Capric Triglyceride (and) Titanium Dioxide (and) Polyhydroxystearic Acid (and) Stearic Acid (and) Alumina	Croda	Active	3.00%
	Xperse® 201	Zinc Oxide, Caprylic/capric triglyceride, Polyhydroxystearic acid, Triethoxycaprylylsilane	EverZinc	Active	3.00%
	CosmoSurf® CE-100	Octododecyl Citrate Crosspolymer	SurfTech	Emollient	3.00%
F	CAB-O-SIL® TS-610	Silica Dimethyl Silylate	Cabot Corporation	Thickener	0.10%
	Total				100.00%

Procedure:
 1) Add (B) to (A). 2) Add (C) until (AB) is clear. 3) Add (D) with propeller stirring. 4) Add (ABCD) to (E) VERY SLOWLY with propeller stirring. 5) Add (F) with propeller stirring. 6) Homogenize until glossy.

Materials and methods

Leveraging the learnings from the original two formulations, one water-in-oil emulsion was created (See Table 1).

Formulating for success

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

Bio-based propanediol

Bio-based 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 sulisobenzene, would stay in solution and protect through the duration of the SPF testing and beyond. This proved to be a processing challenge, but was overcome by blending the ensulizole and bio-based 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 moisturisers is to keep the skin moisturised and healthy.

The use of bio-based propanediol helps build moisturisation. 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 seen as organic (chemical) absorbers or inorganic (physical) blockers based on the mechanism of action. Sunscreens containing inorganics like titanium dioxide and zinc oxide provide a good option for individuals with sensitive skin. These actives are not associated with sensitisation and irritation and can provide full spectrum UV light protection. Similarly, water-soluble organic actives, ensulizole and sulisobenzene, 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 maximising SPF and overall sun protection. The two water-soluble actives, ensulizole and sulisobenzene, 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 377.8 nm.

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 maximisation 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 SPFs and inherent water resistance. The formulation also contains CosmoSurf® CE-100, a water resistant emollient based on bio-based 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

Table 2: Evaluation of sun protection by SPF determination (FDA) - 40 and 80 minute water immersion.

Subject	Sex	MED/ Hr	I (Amps)	Skin Type	MED I J/M ²	MED II J/M ²	STD (7%PadO/ 3%Oxyb)	WR Control	SPF Static	Values WR
40 minute Immersion										
58 2460	F	128.5	6.0	III	35.55	35.55	16.30	18.00	28.75	28.75
42 0311	F	125.9	6.0	II	35.55	35.55	18.75	18.00	28.75	25.00
80 minute Immersion										
62 1831	F	127.8	6.4	I	28.44	28.44	16.30	18.00	28.75	25.00
84 5462	M	126.9	6.2	II	28.44	28.44	16.30	18.00	25.00	25.00

when using the less-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-panellist static *in vivo* SPF testing including a two-panellist 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 optimised for formulations containing inorganic sunscreen actives was completed at

Heliosciences in France.

The final broad spectrum daily facial moisturiser 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 377.8 nm, well above the 370 nm necessary for the broad spectrum claim. The *in vitro* SPF test showed to be above 30, reinforcing the confidence that a full 10-panellists SPF testing would have the desired level of protection.

Conclusion

Zemea propanediol is useful in formulating effective, innovative sun protection products,

primarily daily facial moisturisers 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.

Formulation strategies for maximising sun protection efficiently included combining organic and inorganic actives, placing actives in both phases, and going water-in-oil.

The addition of Zemea propanediol in a daily facial moisturiser with SPF improves aesthetics. Zemea propanediol is non-irritating and provides increased moisturisation and excellent sensory characteristics, eliminating stickiness and greasiness in the formulation. PC