Film-Formers Enhance Water Resistance and SPF in Sun Care Products

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With ever higher levels of awareness, consumers are putting greater demand on sun care products. Performance is a key issue: products are expected to remain on skin for an extended time without the need for reaplication, even in the presence of water. Good aesthetics also are a must: consumers want lotions and creams that leave the skin feeling soft and moisturized, without the greasy, oily feel traditionally associated with sun care products.

By capitalizing on new technologies for improved aesthetics, greater resistance to wash-off and enhanced SPF, formulators can create innovative sun care products to meet specialized global requirements and the needs of individual skin types.

Polymers That Enhance Water Resistance and SPF

Among materials that impart water resistance, C30-38 olefin/isopropyl maleate/MA copolymer is a low molecular weight, hydrophobic material that ensures a light feel. The MA in this INCI name refers to maleic anhydride. For convenience, we will refer to this polymer as the olefin/MA copolymer.

The maleic functionality of the olefin/MA copolymer makes it easy to disperse and helps it adhere to the skin. It does need to be neutralized for oil-in-water dispersions, but when neutralized, it disperses readily into water and also acts as an anionic emulsifier. The olefin/MA copolymer forms a water-resistant film that also enhances SPF. Because of the copolymer’s highly efficient film-forming properties, it may be possible to use lower levels of potentially irritating active ingredients in formulation.

Polyethylene and C20-40 alcohols also have hydrophobic properties that make them useful ingredients for offering water resistance to formulations. As with the olefin/MA copolymer, the low molecular weight of these ingredients imparts a light feel on the skin. The linear polymer backbone of the polyethylene provides a foundation for thickening and structuring the oil phase of formulations, while giving a matte appearance and a dry, non-oily feel. In the case of long-chain linear alcohols, the alcohol functionality offers compatibility with silicones, while helping to stabilize these ingredients in sun care formulations.

The film-forming properties of the polyethylene and alcohols improve the water resistance of formulations and minimize the levels of active ingredients. Their superior ability to thicken oils makes these ingredients especially useful for enhancing SPF.

In Vitro Tests Assess SPF

The studies described in this article involved in vitro evaluations of water resistance for several materials. They were developed based on several protocols. Water resistance was measured on the polymers at a use level of 2% by weight in an “easy-to-remove” prototype formula (Formula 1) that incorporates high levels of very hydrophilic surfactants.

For the control condition, water was substituted for the polymer. Sunscreens were coated onto a clear substrate and analyzed with an SPF analyzer. This instrument measures the amount of ultraviolet light coming.
through the sample compared to an uncoated substrate, then calculates the SPF value. Samples were then placed in a heated water bath with agitation. After immersion, a final SPF value was measured. Specific test conditions were as indicated in Table 1.

In vitro SPF measurements collected by this method appear to be higher than those obtained with in vivo tests, possibly because in vitro analyzers overestimate SPF by missing side scatter of UV rays. However, the approach used in this study is a useful screening tool for making relative comparisons among materials. Figure 1 summarizes in vitro data for the test sunscreen containing 2% of some commercially available water-resistant polymers, before and after immersion.

Initial SPF was boosted versus the base formula for all the test polymers, particularly the polyethylene. However, results for olefin/MA copolymer show significantly better water resistance than the other polymers or the commercial benchmark, PVP/eicosene copolymer. Not only is initial SPF enhanced with the olefin/MA copolymer, but it remains significantly higher after immersion compared to samples formulated with the other materials.

Although use levels of olefin/MA copolymer were 2% in the "easy to remove" prototype test formulation, lower levels may be sufficient in more optimized formulations. Figure 2 illustrates the water resistance that can be attained through the sample compared to an uncoated substrate, then calculates the SPF value. Samples were then placed in a heated water bath with agitation. After immersion, a final SPF value was measured. Specific test conditions were as indicated in Table 1.

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The olefin/MA copolymer can be used in oil-in-water systems (which we discuss in this article) or water-in-oil systems. The polymer should be added to the oil phase of the formula, which must be heated to 85-90°C to melt the polymer. To ensure proper incorporation, the water phase should also be heated to 85-90°C. An appropriate amount of base, such as triethanolamine or sodium hydroxide, must be added to oil-in-water formulations to neutralize the polymer.

The olefin/MA copolymer can be used alone or in combination with other polymers that impart water resistance. Figure 3 shows the synergistic effect when olefin/MA copolymer and PVP/eicosene copolymer are used together in the test sunscreen formula (Formula 1). In this formula, 2% PVP/eicosene copolymer did not enhance SPF or provide good water resistance. The olefin/MA copolymer alone performed very well in SPF enhancement and water resistance. However, the combination

Figure 2. Water-resistant characteristics of prototype test formulation containing 1% C30-38 olefin/isopropyl maleate/MA copolymer

using 1% olefin/MA copolymer. Data in Figure 2 are based on Formula 2, a broad-spectrum sunscreen. This evaluation was based on a lower substrate coating level (1 microliter/cm²) than previous study conditions, to obtain SPF values closer to in vivo results.

The in vivo test was performed at a level of 2 mg/cm² according to the FDA Sunscreen Monograph. Note that an in vivo water resistance test was not conducted in this portion of the study.
of 1% of each copolymer outperformed 2% of either used alone. SPF was enhanced by more than 75% compared to the base formula. The combination also maintains a high SPF value even after an 80-minute warm water immersion. Doubling the level of each resulted in further improvement in both SPF enhancement and post-water immersion SPF value.

The Link Between Viscosity and SPF

Polyethylene and C20-40 alcohols can significantly improve the SPF of sunscreen formulas. Figure 4 shows that by adding 2.5% by weight — an amount selected so the oil phase will viscosify, but not solidify as it does at around 3% — of these film-forming polymers, the SPF of a prototype base formula used in the test more than doubled. Figure 4 also indicates the improvement in water resistance.

The property of enhanced SPF may be related to the viscosity-building properties of the material. When added to the oil phase, waxes or other viscosity-building materials can enhance SPF through their ability to act as good film formers and provide increased viscosity. Without their added benefit, the sunscreen formulation may flow downward into the wrinkles of the skin. The higher skin surface may be left without an adequate coating of sunscreen, and therefore more prone to damage from the sun. This proposed mechanism, illustrated in Figure 5, suggests why initial SPF may be higher with polyethylene and C20-40 alcohols, because they increase the viscosity of the oil phase.

Polyethylene and C20-40 alcohols can be used in oil-in-water or water-in-oil systems, and they should be added to the oil phase. Because these polymers are highly effective in building viscosity of the oil phase, use levels of 3% or less are recommended. The oil phase containing the polymers and the water phase should both be heated to 90-95ºC to ensure complete incorporation.

If the resulting system appears grainy or if incompatibility is observed, addition of a small amount of C20-40 pareth-40 is recommended. The optimal ratio, on a weight basis, is 1 part C20-40 pareth-40 to 10 parts polyethylene or C20-40 alcohols. A higher proportion of C20-40 pareth-40 negatively impacts water resistance.

Figure 6 compares SPF values and stability in a prototype sunscreen using concentrations of 0.25% and 1.0% C20-40 pareth-40 and the same formula without the polymer. Notice that in both cases, the control formulation was grainy (in the case of polyethylene) or separated (when formulated with C20-40 alcohols), while the addition of C20-40 pareth-40 produced stable formulations with varying SPF levels.

As Figure 6 indicates, just a small amount (0.25%) of C20-40 pareth-40 is effective in stabilizing the polyethylene and alcohols. Even though C20-40 pareth-40 is an emulsifier,
which could be considered an ingredient that would encourage wash-off, at its optimum level in the formulation there is an increase in water resistance compared to a control formulation without this ingredient. By achieving a better emulsion at the optimal level, it is possible to get better SPF protection.

Formula 3 illustrates a nongreasy sport formula. Polyethylene provides water resistance, enhanced SPF and a dry feel. C20-40 pareth-40 acts as a secondary emulsifier to produce a smooth, creamy formula.

Conclusions

Tests of water resistance showed that C30-38 olefin/isopropyl maleate/MA copolymer provided significantly better water resistance than the competitive benchmark or the polyethylene or C20-40 alcohol polymers evaluated in this study. However, combining PVP/eicosene copolymer with C30-38 olefin/isopropyl maleate/MA copolymer had a synergistic effect that provided much better water resistance than either polymer alone. Other products were evaluated together and no synergistic results were seen, so the phenomenon appears distinctive for this particular combination.

Because of their viscosity-building properties, polyethylenes and long-chain linear alcohols showed the best SPF enhancing characteristics in this study. These ingredients as well as the C30-38 olefin/isopropyl maleate/MA copolymer have highly efficient film-forming properties, which can allow formulators to use lower levels of potentially irritating active ingredients in sun care products.

These versatile and multifunctional properties, combined with excellent aesthetics, present formulators with broader choices for creating high performance, distinctive sun care products to meet the needs of today’s global consumers.

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