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

Allison Hunter and Melanie Trevino

New Phase Technologies, A Division of Baker Petrolite Corporation, Sugar Land, Texas USA

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 reapplication, 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[a] 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[b] and C20-40 alcohols[c] 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.[1,2] 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[d]. This instrument measures the amount of ultraviolet light coming

[a] *PERFORMA V 1608 Polymer is a product of New Phase Technologies, Sugar Land, TX USA. PERFORMA V is a registered trademark of Baker Hughes Incorporated.*

[b] *PERFORMALENE 400 Polyethylene is a product of New Phase Technologies. PERFORMALENE is a registered trademark of Baker Hughes Incorporated.*

[c] *PERFORMACOL 350 Alcohol is a product of New Phase Technologies. PERFORMACOL is a registered trademark of Baker Hughes Incorporated.*

[d] *The SPF-290S Analyzer System is a product of Optometrics LLC, Ayer, MA USA.*

Key words

SPF, sunscreen, water resistance, film formers

Abstract

At low formulating levels, film-forming polymers can increase water resistance and enhance SPF in sun care formulations, while also imparting improved aesthetics. In the case of C30-38 olefin/isopropyl maleate/MA copolymer, a synergistic SPF effect can be achieved with PVP/eicosene copolymer.

Formula 1. Sunscreen test formula

A.	Glyceryl stearate (and) PEG-100 stearate	4.00% w/w
	Polysorbate-20	2.00
	Octyl methoxycinnamate	7.50
	Benzophenone 3	4.00
	Octyl salicylate	5.00
	Cetearyl alcohol	0.75
	C12-15 alkyl benzoate	5.00
	Polymer chosen for evaluation	2.00
B.	Water (*aqua*)	52.15
	Disodium EDTA	0.10
	Carbomer, 2%	12.00
	Butylene glycol	4.00
C.	Triethanolamine, 99%	0.50
D.	Propylene glycol (and) diazolidinyl urea (and) methylparaben (and) propylparaben	1.00
		100.00

Table 1. In vitro SPF test conditions

Test parameter	Test condition or value
Substrate	Vitro-Skin Substrate* hydrated overnight in hydration chamber
Hydration chamber	Desiccator with 256 g water and 44 g glycerin in bottom of chamber
Amount of sunscreen on substrate	2 microliters/cm²
Dry-down time	15 min
Measurements per sample	6 (at different positions on same piece of substrate)
Immersion time	80 min
Water bath temperature	37°C
Agitation rate	190 rpm
Delay time*	1 hr

* Interval between time of removal from bath to time of SPF measurement

* Vitro-Skin Substrate is a product of Innovative Measurement Solutions (IMS) Inc., Milford, CT USA.

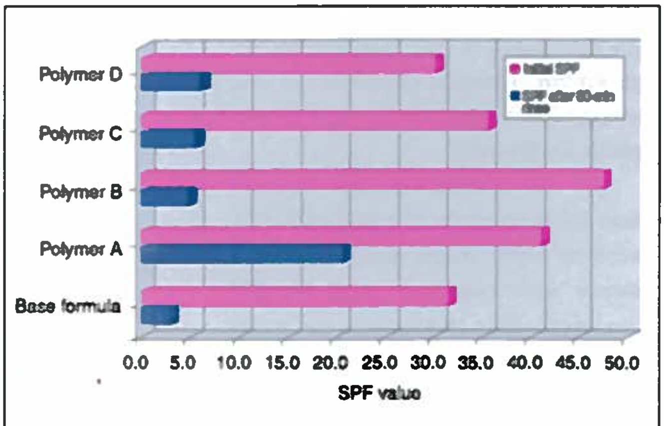

Figure 1. Comparison of water resistance and SPF; 2% polymer in test formula
Polymer A = C30-38 olefin/isopropyl maleate/MA copolymer
Polymer B = Polyethylene
Polymer C = C20-40 alcohols
Polymer D = PVP/eicosene copolymer

Formula 2. Water resistant sunscreen (SPF 32)

A.	Ethylhexyl salicylate	5.00% w/w
	C12-15 alkyl benzoate (Finsolv TN, Finetex)	4.50
	Isopropyl myristate	4.00
	Diethylhexyl 2,6-naphthalate (Corapan TQ, Symrise)	5.00
	PPG-2 myristyl ether propionate (Crodamol PMP, Croda)	0.50
	Benzophenone-3	4.00
B.	Butyl methoxydibenzoylmethane	3.00
C.	Stearyl alcohol	0.30
	Polyglyceryl-3 methylglucose distearate (Tego Care 450, Degussa)	3.00
	C30-80 olefin/isopropyl maleate/MA copolymer (PERFORMA V 1608, New Phase Technologies)	1.00
	Disodium EDTA	0.05
D.	Butylene glycol	2.00
	Glycerin (Glycerin, Procter & Gamble)	4.00
	Phenoxyethanol (and) methylparaben (and) propylparaben (and) butylparaben (Phenonip, Clariant)	0.70
E.	Water (*aqua*)	qs
F.	Carbomer (Carbopol Ultrez 10, Noveon)	0.20
G.	Triethanolamine, 99%	0.15

Procedure: Combine A and heat to 80°C with stirring. Add B and stir to dissolve. Increase heat to 90°C. Add C to AB, stirring after each addition until homogeneous. Heat water (less than 50 g) to 85°C. Preblend D and add to E. Predisperse F in 50 g water and set aside. With homogenization, add ABC to DE. Add F to batch. Maintain heat and homogenize for 10 min. Remove from heat. Stir with propeller while cooling. When temperature is below 40°C, slowly add G. Continue stirring to smooth, homogeneous lotion.

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.[3] 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[f]. 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

[f]Ganex V-220 alkylated polyvinylpyrrolidone is a product of International Specialty Products, Wayne, NJ USA.

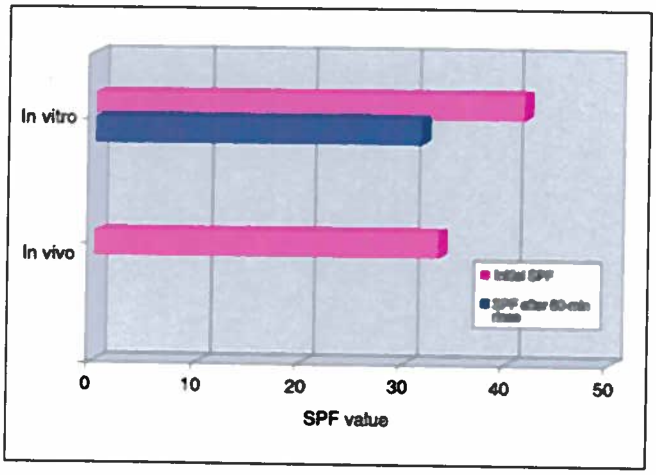

Figure 2. ***Water-resistant characteristics of prototype test formulation containing 1% C30-38 olefin/isopropyl maleate/MA copolymer***

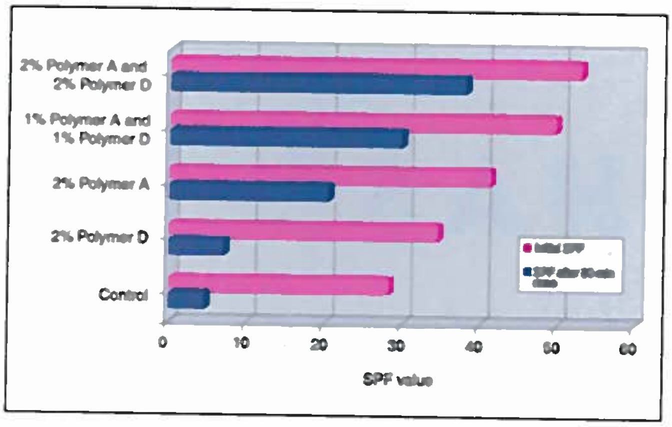

Figure 3. ***Synergistic water-resistance effect of C30-38 olefin/isopropyl maleate/MA copolymer (Polymer A) with PVP/eicosene copolymer (Polymer D)***

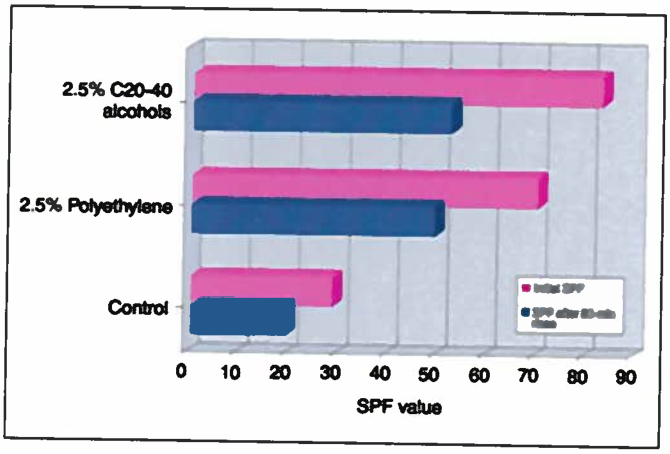

Figure 4. ***Water resistance of 2.5% polyethylene and 2.5% C20-40 alcohols***

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.[4] Note that an in vivo water resistance test was not conducted in this portion of the study.

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 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.[5] When added to

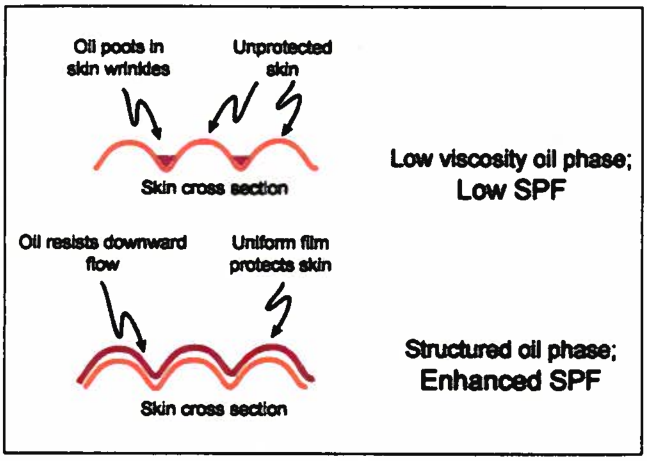

Figure 5. A structured oil phase of higher viscosity can optimize film formation to provide a uniform coating on the skin and enhanced SPF

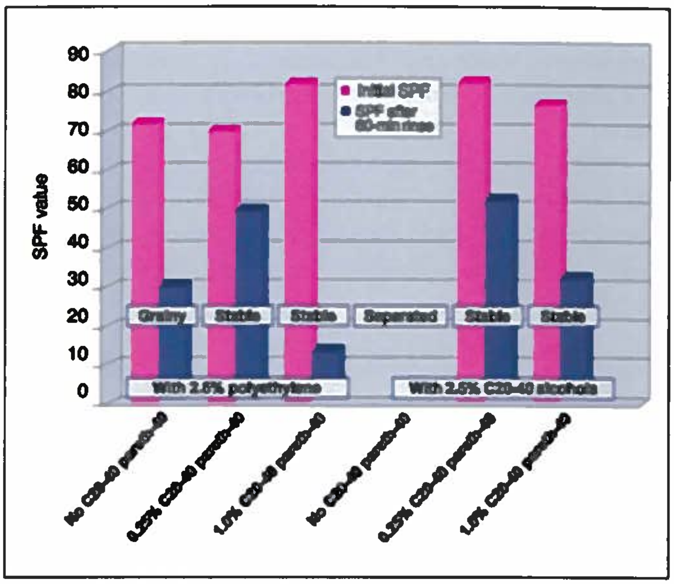

Figure 6. Optimal amount of C20-40 pareth-40 in sunscreen test formula with 2.5% polyethylene or 2.5% C20-40 alcohols

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 90-95°C 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[g] 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

[g] PERFORMATHOX 480 Ethoxylate is a product of New Phase Technologies. PERFORMATHOX is a registered trademark of Baker Hughes Incorporated.

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.

References

Address correspondence to Allison Hunter, c/o Editor, *Cosmetics & Toiletries* magazine, 362 South Schmale Road, Carol Stream, IL 60188-2787 USA.

1. SPF-290S Users Manual, Version 2.1, Optometrics LLC (Revised October 2002)
2. Developing next generation suncare products: A unified model of sunscreen performance on skin, a presentation by IMS Testing Group at the 2001 SCC Florida Chapter Sunscreen Symposium (Apr 25, 2002)
3. K Klein, Sun products: background, delivery and formulation, a presentation at the Advanced Technology Conference in Milan, Italy
4. US Food and Drug Administration, *Code of Federal Regulations*, Title 21, Vol 5, part 352: Sunscreen products for over-the-counter human use, (Revised Apr 1, 2003)
5. G Dahms, Efficacy of sunscreen emulsions on skin, a presentation at the 2001 SCC Florida Chapter Sunscreen Symposium (Apr 25, 2002)

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Formula 3. Water resistant sport lotion (SPF 30)

A.	Polyethylene (PERFORMALENE 400 Polyethylene, New Phase Technologies)	2.50% w/w
	C20-40 pareth-40 (PERFORMATHOX 480 Ethoxylate, New Phase Technologies)	0.25
	Stearic acid	1.30
	Cetearyl alcohol (Crodacol CS-50, Croda)	2.00
	Diisodecyl adipate (DIDA, Trivent)	8.50
	Triethanolamine, 99%	0.25
B.	Benzophenone-3	6.00
C.	Octocrylene	10.00
D.	Ethylhexyl methoxycinnamate	7.50
E.	Water (*aqua*)	qs
	Carbomer, 2% (Carbopol 940, Noveon)	7.50
	Acrylates C10-30 alkyl acrylate crosspolymer, 2% (Pemulen TR-1, Noveon)	7.50
	Propylene glycol	1.00
F.	Phenoxyethanol (and) methylparaben (and) propylparaben and butylparaben (Phenonip, Clariant)	1.00
	Fragrance (*parfum*)	qs

Procedure: Heat A to 85-90°C while propeller mixing. When ingredients are fully dispersed, reduce heat to 80-85°C. Add B, C and D in order, dispersing each phase before adding next. Combine ingredients of E and heat to 80-85°C while propeller mixing. Emulsify, adding first mixture to E with high speed mixing. Continue mixing for 10-15 min. Remove from heat and continue propeller mixing until cooled to 70-75°C. Change to sweep mix and allow mixture to cool to 25-30°C. Add F with mixing.

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