Formulating Water-Resistant Sunscreen Emulsions

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The sunscreen market has been ever-changing and has become more segmented since the publication of the proposed sunscreen monograph more than 20 years ago. To those of us who formulated sunscreen products in the good old days (actually I didn't get into the sunscreen business until 1983), it was indeed a simpler time. The maximum SPF (Sun Protection Factor) ever targeted was 15, and most products were not required to be waterproof. Note that today we aren't permitted to use the term "waterproof" since the FDA believes that this term implies an absolute–it never washes off–and feels that consumers might be inclined not to reapply sunscreen after swimming or perspiring. So, we must now use the term "very water resistant" in its place.

It is now quite commonplace to see marketed products that claim an SPF of 45 or even greater. I've been told that there are products with claimed SPFs of 100+. I would estimate that a product that provides an SPF of 100+ should be used by fair-skinned people sunbathing at noon on the planet Mercury on a cloudless day, assuming they have cloudless days on Mercury! One could argue whether there is a consumer need/benefit for these very high SPFs, but that is a topic for another column.

Minimizing Hydrophilic Emulsifiers

The most popular sunscreen products used today fall into the category of SPF 15-45 and are designed for beach use. These products are also designed to be very resistant to water. A cosmetic formulator has several strategies to develop sunscreen products that are very water resistant. We will explore a few of these here. Probably the single most important factor to consider rests with the choice of sunscreen vehicle.

We must first understand the mechanism by which sunscreen products "wash off." If we place a drop of water (very polar) on our skin, the drop doesn't spread; it remains a drop. If we perform the same "experiment" using a drop of mineral oil or IPM (isopropyl myristate), the drop spreads out. We see them spread out. Because most sunscreen actives are lipophilic (esters) in nature they inherently have an affinity for skin (which is also lipophilic). They don't want to wash off. Something in formulations encourages their wash off. This "something" is a hydrophilic emulsifier. Typical of these types of emulsifiers are soaps (TEA stearate) and nonionic ethoxylates (PEG-100 stearate). Probably the single most important factor to be considered in the design of these products relates this. In order to develop very water-resistant products, you *must minimize* the level of hydrophilic emulsifier.

W/O Emulsions

While emulsions are by far the most popular sunscreen vehicle, they can be very difficult to formulate and can present stability and performance problems.

Without doubt, W/O (water-in-oil) emulsions are more efficient sunscreen vehicles than their O/W (oil-in-water) counterparts. This is due to several factors. Oil-soluble sunscreens are soluble in the external (continuous) phase of W/O emulsions where they are uniformly distributed. We will not consider solubility parameter mismatches here that might result in agglomeration on the micro level. When the emulsion is applied, the sunscreen spreads quickly and uniformly on the lipophilic skin. Thus we can achieve a uniform sunscreen film and an inherently higher SPF.

These products, such as Formula 1, contain hydrophobic emulsifiers (alkyldimethicone copolyols, dimethicone copolyols, polyglyceryl esters, ethoxylated di-fatty esters, and other) that promote the formation of W/O emulsions. Typically they do not contain any hydrophilic emulsifiers and therefore are inherently very water resistant. In fact, it would be most difficult to formulate a W/O emulsion that did wash off.

It is not necessary to incorporate a film former in these systems to achieve water resistancy. However, you often see

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film formers utilized to thicken the film on the skin and thus boost the SPF. This SPF boost is caused by increasing the optical path length. The photons (with an energy corresponding to the UVA/UVB wavelengths 290-400 nm) travel a greater distance before reaching the skin, where they do their dastardly deed, and thus have a greater likelihood of bumping into a molecule (sunscreen) that can absorb heir energy.

O/W Emulsions

Minimize hydrophilic emulsifiers: Formulating O/W emulsions that are very water resistant is a much more difficult task. In order to prepare classical emulsions, significant levels of hydrophilic emulsifiers are required. These emulsifiers will remain behind on the skin after the water and other volatiles have gone, and will emulsify the sunscreen when water is added (swimming or perspiring). This product will not be very water resistant. Often the formulator will then add film formers to try to overcome this effect. It is, however, an effort that is doomed to fail.

If hydrophilic emulsifiers must be used, their concentration should be kept as low as possible. Titrate them down, very carefully balancing stability with emulsifier concentration. Water-phase thickeners (such as carbomer, acrylates/steareth-20 methacrylate copolymer, xanthan gum) can assist in this process. Some companies have found that adding a small amount of lipophilic emulsifer further inhibits the re-emulsification of the sunscreen on the skin. This technique can be quite successful.

Form liquid crystal structures: Another approach for formulating O/W emulsions uses emulsifiers that stabilize emulsions via the formation of liquid crystal structures. Most often, the development of a lamellar gel network thickens the external (water) phase and stabilizes the emulsion.

These emulsions can thin out significantly at elevated temperatures (45ºC) and exhibit instability; using a water phase thickener that maintains some viscosity at 45ºC (such as xanthan gum or carbomer) is recommended.

Emulsion stabilization can also occur if the liquid crystals form in the immediate vicinity of the oil droplets, structuring themselves into an "onion skin" type layer. This layer acts as a barrier to coalescence and thus improves stability. Most liquid crystal emulsifiers (polyglyceryl esters, alkyl lactylates, cetearyl glucosides, lecithin, phosphate esters, among others) have rather limited water solubility and do not promote wash off of the sunscreen film.

While these emulsions, such as Formula 2, have many advantages over conventional emulsions, including low temperature emulsification and mildness, they can be quite tricky to manufacture. You should avoid high shear after the liquid crystal structures have formed or instability will surely result.

Use polymeric thickeners/emulsifiers: A final approach for developing very water-resistant O/W emulsions rests with the use of hydrophobically modified polymeric "thickeners/emulsifiers." The most popular of this category is C10-30 alkyl acrylate crosspolymer, as shown in Formula 3. One can say that it allows the formulation of "emulsifier-free" products. When neutralized, it forms a mini gel that surrounds the oil/sunscreen droplets and immobilizes

Formula 1. Very Water-Resistant Sunscreen Emulsion W/O (Particulate/Organic) with Expected SPF=30

Cetyl dimethicone copolyol	Emulsifier	5.0%
Octyl palmitate	Emollient	11.0
Cetyl dimethicone	Emollient, SPF booster	2.5
Cyclomethicone	Emollient	7.5
Ceresin wax	Thickener	1.0
Octyl methoxycinnamate	Sunscreen	7.5
Octocrylene	Sunscreen	6.0
Hydrogenated castor oil	Thickener	0.5
Titanium dioxide (microfine)	Sunscreen	5.0
Zinc oxide (microfine)	Sunscreen	5.0
Water (*aqua*), deionized	Bulk-Internal phase	qs
Quaternium-15	Preservative	0.15
Magnesium sulfate	Stabilizer	0.75

Formula 2. Water-Resistant Lotion with Expected SPF=15+

Water (*aqua*), deionized	Diluent	qs
Tetrasodium EDTA	Chelating agent	0.1%
Glycerin, 96%	Humectant	3.0
Carbomer	Thickener	0.25
Laureth-23	Emulsifier	0.25
Sorbitan sesquioleate	Hydrophobic emulsifier	0.5
Glyceryl stearate	Bodying agent/stabilizer	2.0
PEG-100 stearate	Emulsifier	1.0
PVP/Eicosene copolymer	Film former, SPF booster	2.5
Octocrylene	Sunscreen	10.0
Octyl methoxycinnamate	Sunscreen	7.5
Oxybenzone	Sunscreen	4.0
Octyl palmitate	Emollient, sunscreen solubilizer	5.0
Cyclomethicone	Emollient	5.0
Vitamin E acetate	Label copy	0.25
Alpha bisabolol	Anti-irritant	0.25
Triethanolamine, 99%	Neutralizer	0.25
Propylene glycol (and) diazolidinyl urea (and) methylparaben (and) propylparaben	Preservative	1.0

Formula 3. O/W Polymeric ("Emulsifier-Free") Emulsion Sunscreen with Expected SPF=12+

Water (*aqua*), deionized	Diluent	qs
Acrylates/C_{10-30} alkyl acrylates crosspolymer	Polymeric thickener/stabilizer	0.2%
Propylene glycol	Humectant, improves freeze/thaw stability	2.5
Xanthan gum	Improves product application	0.05
Octyl methoxycinnamate	Sunscreen	7.5
Triethanolamine	Neutralizer	0.18
DMDH hydantoin	Preservative	0.2
Trisodium EDTA	Chelating agent, viscosity control	0.05
Oxybenzone	Sunscreen	3.5
Cetearyl alcohol	Thickener, improves product application	0.25
Octyl palmitate	Emollient	7.5

them. Thus the product exhibits good storage stability.

When the product is applied to the skin, the salt from the skin coagulates the polymer and the emulsion breaks, permitting the sunscreen to spread onto the skin. Since there is no hydrophilic emulsifier left behind, the emulsion is inherently very water resistant.

The use of fatty alcohols in this product, along with high shear agitation, will reduce the particle size and improve application qualities. Use of emulsifiers at any significant use levels should be avoided because these emulsifiers will compete for space at the interface and the polymer will not be able to partition itself properly. An unstable product will be the result. This phenomenon is known as flocculation depletion. C&T