Thomas G. O'Lenick, PhD - SurfaTech Corporation, US

Improving sunscreen performance

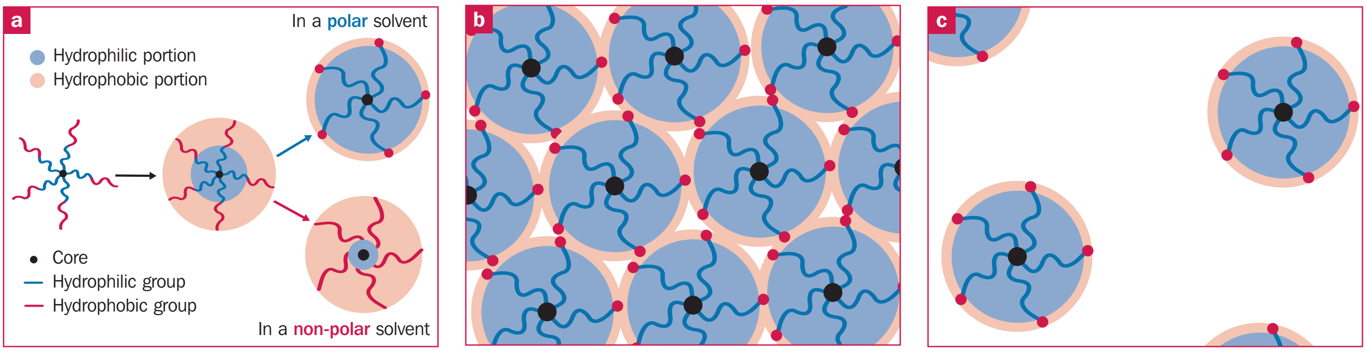

Figure 1: a) *Behaviour of sorbeth hexaoleate in different solvents, with* **b)** *above critical concentration of entanglement (c*), and* **c)** *below c*.*

Recently, there has been growing interest in sunscreen performance. This interest includes not only making more efficient formulations but also more effective formulations. There are many factors that need to be considered when determining the efficiency of sunscreen formulations, including: desired SPF[1] UVA/UVB coverage,[2] wavelength shift, and photostablity,[3] just to name a few.

The quest for complete protection from the sun has led to numerous research efforts are aimed not only effective sunscreens, but also products that efficiently used sunscreens, minimising the concentration of filters. A product that protects over a wide variety of ultraviolet (UV) spectrum and is effective has become a priority. This quest has led to a new series of amphiphilic polymers that have been developed to help improve the efficiency of sunscreens. These amphiphilic polymers have a polar core surrounded by a fatty oil soluble group. This series of polymers can provide not only a shift in wavelength, but also boost the SPF of the sunscreen formulation. These new polymers have been coined 'Spider Esters'.

Spider esters

Spider esters were specifically designed[4–8] to have a hydrophilic core surrounded by a hydrophobic periphery. This produces an amphilphilic polymer. The term, amphiphilic polymer, means that the polymer contains two distinct regions that have different polarities covalently bonded together. This amphiphilic nature makes spider esters very attractive because of their unique solubilites. Amphiphilic polymers are covalently bonded together and do not have the same inherent stability issues that emulsions suffer from. Oil-in-water emulsions have pockets of hydrophobic oil contained in the core of micelles surrounded by an aqueous environment. When hydrophobic organic sunscreens are added into the emulsion, they migrate into the hydrophobic micelle cores and remain suspended in a unified matrix. When the spider ester is introduced into a polar solvent, the hydrophobic periphery will collapse upon itself to minimise its contact with the solvent environment (see Fig. 1).

Figure 1 allows for a simple breakdown of how these spider esters behave in solvent. Please note that this is not an actual representation, just a simple way to

Table 1: Formulations 1 and 2.

Part	Ingredient	% w/w	
		Formulation 1	Formulation 2
A	Water	74.20	67.20
	Acrylates/C10-30 Alkyl Acrylate Crosspolymer	0.25	0.25
	DiSodium EDTA	0.05	0.05
B	Triethanolamine	1.00	1.00
C	Octocrylene	3.00	3.00
	Octisalate	3.00	3.00
	Oxybenzone	2.00	2.00
	Avobenzone	1.00	1.00
	Stearic Acid	2.00	2.00
	Glyceryl Monostearate SE	3.00	3.00
	Benzyl Alcohol	1.00	1.00
	Dimethicone	0.50	0.50
	C12-15 Alcohols Benzoate	8.00	8.00
	Sorbeth 2 Hexaoleate (Spider Ester ESO)	–	5.00
	Octyldodecyl Citrate Crosspolymer	–	2.00
	Octocrylene	3.00	3.00
D	Parabens/Phenoxyethanol	1.00	1.00

A typical preparation procedure:
Disperse part A. Add part B while heating to 80˚C stir until clear. Add part C to combined part AB while mixing. Cool with stirring to 50˚C and add part D. Continue cooling, QS and mix.

illustrate how the esters behave in a perfect world. As shown in Figure 1b, when the new polymers are above the critical concentration of entanglement (c*),[9] they organise into structures to maximise the overlap of the periphery. Hydrophobic materials can be loaded into the regions of fatty groups surrounding the hydrophobic core (the red overlapping regions on the cartoon).

The dual polarities of the new polymers make them soluble and effective when added into polar oil based sun care formulations as well as non-polar oil-based sunscreen formulations. The major benefit of these spider esters is that they are capable of 'encapsulating' sunscreen filters in the core and 'shielding' them from the surrounding environment. This allows the filters to be placed into a wide variety of solvents, while also this 'shielding' of the filters can drastically improve their performance. The hydrophilic core will respond to the polar solvent in the opposite manner, and the solvent will cause the core to swell and maximise its contact with the polar solvent. This phenomenon is the basis for the 'loading' or encapsulation of small molecules into the core of the spider ester. We have coined this phenomenon the 'Spider Effect'. To better illustrate the spider effect, a simple experiment was conducted. Spider ester was heated at a constant heating rate of 5.0˚C/min in the presence of avobenzone, a commonly used organic sunscreen. The temperature of the ester was monitored and recorded.

As seen in the Figure 2, in the temperature range of 20˚C to 50˚C, the temperature of the spider ester increased in a linear fashion and the avobenzone remained in powder form. Once the temperature reaches 50˚C, the temperature of the spider ester solution remained constant over a 2.5 minute period. During this period, the energy being introduced into the solution is being used to drastically change the ester's structure and not increase temperature. The core of the spider ester expands and starts to interact with the hydrophobic periphery. This temperature range (50˚C to 60˚C) represents the 'loading' region of this ester. Small molecules can be loaded into the core of the spider ester during this temperature range. This loading zone allows for the solubilisation of the avobenzone and a clear solution is observed. After the ester's core is expanded, a linear response in temperature is restored. When the solution is cooled to ambient temperature, the avobenzone remains in the core of the spider ester and a clear solution is maintained. The release of the entrapped avobenzone is controlled by the diffusion through the hydrophobic periphery and can be controlled by introducing the loaded spider into different solvents.

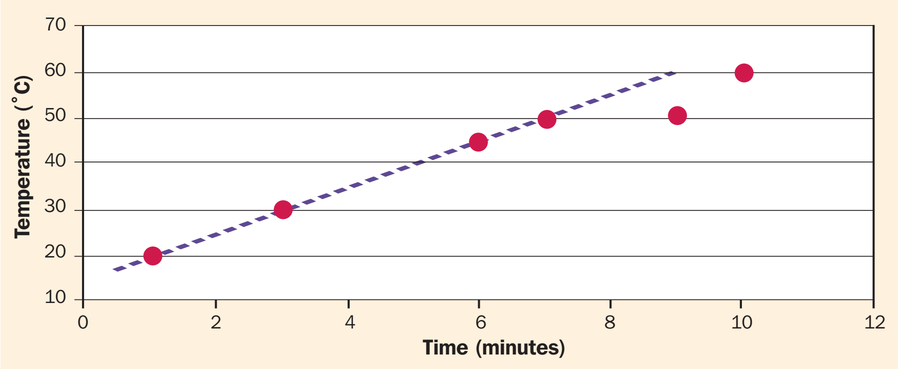

Figure 2: *The spider effect.*

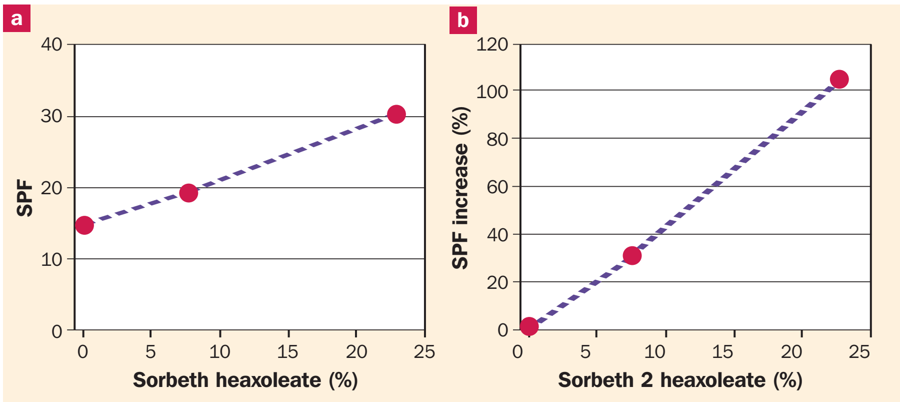

Figure 3: a) *SPF versus concentration of sorbeth 2 hexaoleate, and* **b)** *%SPF increase by by the addition of sorbeth 2 hexaoleate.*

Table 2: Formulations 3, 4 and 5.

Ingredient	% w/w		
	Formulation 3	Formulation 4	Formulation 5
Sorbeth 2 Hexaoleate (Spider Ester ESO)	0.00	7.58	22.75
Octyldodecyl Citrate Crosspolymer	0.00	1.16	3.50
Octocrylene	2.90	2.90	2.90
Octisalate	2.90	2.90	2.90
Oxybenzone	1.94	1.94	1.94
Avobenzone	0.98	0.98	0.98
C12-15 Alcohols Benzoate	45.66	44.26	34.97
Caprylic/Capric Triglyceride	45.66	44.26	34.97

Boost in SPF

Spider esters have been the subject of multiple studies in sunscreen formulations and articles.[10] The use of spider esters in improving the SPF of sunscreen formulations is focused on making the sunscreen formulations more efficient. SPF sunscreen products work based on the ability of the sunscreen actives to absorb photons in the UVA and UVB range. The absorbance of these actives follows Beer's law,[11] which shows that the concentration of filters is directly proportional to the absorbance. Beer's law is the principle behind one of the most common ways to increase SPF, which is increasing the amount of filters in the finished formulation. From the published absorbance of sunscreen actives approved for use in the US it can readily be deduced that many sunscreens utilised actives at levels many times greater than that should be necessary to obtain the desired SPF. This can be attributed to several factors but certainly one that is extremely important is the sunscreen active solvent system used in the formulations.

Until recently, there have been three major types of sunscreen formulations:[12,13] water-in-oil emulsions, oil-in-water emulsions, and alcohol-based formulations. All have their respective advantages and disadvantages. Spider esters used with these major types of sunscreens can drastically improve the SPF.

Materials and methods

The sunscreen formulations were prepared by Lott Research Incorporated of Ormond Beach Florida and tested by Florida Suncare Testing Incorporated of Ormond Beach Florida.[14] Sunscreen formulations were tested for SPF using a single port Solar Light Model 15S Xenon Arc. Solar Simulator Lamp. Which has a continuous light spectrum in the UVA and UVB spectrum (290 nm to 400 nm). The spectral output of the solar simulator is filtered so that it meets the spectral output requirements for testing Sunscreen Drug Products for over-the-counter human use.[15,16]

Results and discussion

To test the SPF increase of sunscreen formulations with the addition of Spider Ester ESO (sorbeth 2 hexaoleate), a series of formulations (Tables 2 and 3) were prepared and the sets of formulas were SPF tested on the same subjects.

Formulations 1 and 2 were prepared in the US by a research consultant and tested in an independent test laboratory. Formulations 3-5 (Table 2) were prepared by SurfaTech Corporation and tested by an independent test laboratory. Table 3 shows the results of Formulations 1-5.

Sorbeth 2 hexaoleate provides dramatic effect upon the SPF when used in different types of formulations. Formulations having the same concentration of actives but varying concentrations of sorbeth 2 hexaoleate, have drastically different SPF values. The organic filters, when loaded into the core of sorbeth 2 hexaoleate, come into intimate contact which leads to more efficient absorbing of photons thus leading to a higher SPF value. This intimate contact will also provide better transfer of excited state electrons, thus providing better photostability.

The uniformity of the SPF values developed on formulations made and tested by two different labs, one in North America and the other in Europe, is both unexpected and very important. It is well known in the industry that different testing laboratories can obtain significantly different results on the same formula. With this in mind, it is important to note that the SPF results from each separate test 1, 2, and 3 were obtained from the same subjects. For example, the same five subjects tested by the same clinicians obtained an average SPF of 19 on Formulaion 1 and an average SPF of 32 on Formulation 2.

Figure 3b certainly suggests a linear relationship between increasing the sorbeth 2 hexaoleate concentration and increasing SPF. If a slope is calculated, it could be projected that the SPF might keep increasing to an astronomical number if the sorbeth 2 hexaoleate is increased to a high level. As shown in Figure 3b, the SPF value for an oil-based sunscreen formulation increased by 104.1%.

To test the wavelength shift of sunscreen actives in formulations with the addition of a series of spider esters were tested including: Spider Ester ESO (Sorbeth 2 hexaoleate), Spider Ester AB-1 (glycereth 9 monococoate), and Spider Ester ABN (sorbeth 2 monoleate sorbeth 2 pentaoleate cross polymer [proposed INCI Name]). A series of four sunscreen formulations were prepared with altering solvents to test the wavelength shift.

Table 3: Results of Formulations 1-5.

Formulation	% ESO	SPF	Formula type
1	0.0	19	OW emulsion
2	5.0	32	OW emulsion
3	0.0	14.8	Oil
4	7.6	19.3	Oil
5	22.8	30.2	Oil

Table 4: SPF increase with the increase in sorbeth 2 hexaoleate.

Ingredient	Formulation 3	Formulation 4	Formulation 5
Sorbeth 2 hexaoleate (%)	0.0	7.6	22.8
SPF	14.8	19.3	30.2
Increase of SPF (%)	–	30.4	104.1

These formulations were tested for absorbance in the UVA and UVB range. This study is based on the improvement of the UVA region of the spectrum. Figure 4 shows the absorbances of the four formulations in the high UVA range (370 nm to 400 nm).

Several factors were compared including critical wavelength, UVA/UVB ratio, and increase in UVA (370 nm to 400 nm). The results are summarised in Table 5.

Formulations 6-9 show a shift of absorbance closer to 400 nm. The UVA to UVB ratio increased from 0.86 to 1.09. This ratio can be a little misleading because spider esters also boost the UVB portion of the spectrum. In order to determine the increase in UVA spectrum, the absorbance from 370 nm to 400 nm was compared. Mineral oil (Formulation 6) was used as a standard. The absorbance of the spider ester formulations from 370 nm to 400 nm was divided by the absorbance of the mineral oil. The spider ester formulations showed an increase the absorbance between 370 nm to 400 nm by 66.93%.

Table 5: Formulations 6-9.

Ingredient	% w/w			
	Formulation 6	Formulation 7	Formulation 8	Formulation 9
Mineral Oil	89	–	–	–
Spider Ester ESO	–	89	–	–
Spider Ester AB-1	–	–	89	–
Spider Ester ABN	–	–	–	89
Octocrylene	3	3	3	3
Octisalate	5	5	5	5
Avobenzone	3	3	3	3

Table 6: Results of Formulations 6-9.

Formulation	Critical Wavelength (λ)	UVA/UVB	Increase in $\lambda_{370-400}$ (%)
6	373.4	0.86	–
7	377.3	1.00	47.12
8	379.5	1.09	60.82
9	377.2	1.06	66.93

Conclusion

Spider esters are amphiphilic polymers that can be used to encapsulate small molecules into the core. The actives or small molecules inside the core are held in intimate contact with the polymer, this provides: a boost in SPF, the actives can stabilise into more polar forms which can shift the wavelength (λ), and the encapsulation of the actives can shield any taste, colour or odour associated with the actives.

The encapsulation of organic filters in a wide variety of sunscreen formulations provides improvement in SPF and shift the of the absorbance towards 400 nm. Spider ester in a sunscreen formulation, with organic filters, shows a dose dependent response when the concentration of Spider Ester ESO (sorbeth 2 hexaoleate) is altered. As seen in Table 4, the SPF of an oil-based sunscreen formulation was increased from 14.8 to 30.2 (*in vivo*). While the sunscreen formulations were not optimised to achieve maximum SPF, the spider esters provide the ability to increase the SPF of a formulation by 104.1%. Spider Esters ESO provides the ability of sunscreen formulation to decrease the amount of actives and maintain the same SPF value. Also, as seen in Table 6, spider esters can be used to shift the absorbance of typical organic filters. Spider Ester ABN was shown to increase the absorbance from 370 nm to 400 nm by 66.93 %.

Spider esters are very versatile polymers and can be used to improve sunscreen formulations in many different aspects. The wide variety of spider esters provide a way to maximise the performance of sunscreen formulations. The ability of decreasing the amount of small molecule organic filters and adding large polymeric materials will lead to better consumer products. PC

References

1 Lademann J, Rudolph A, Jacobi U *et al*. Influence of nonhomogeneous distribution of topically applied UV filters on sun protection factors. *J Biomed Opt* 2004; **9** (6): 1358-62.

2 Beattie PE, Dawe RS, Ferguson J, Ibbotson SH. Dose-response and time-course characteristics of UV-A1 erythema. *Arch Dermatol* 2005; **141** (12): 1549-55.

3 Bonda C, Steinberg D. *Cosmetics & Toiletries* 2000; **115**: 37-45.

4 US7723456 entitled: *Crosslinked silicone polymers based upon Spider esters.* Issued to O'Lenick *et al.* Assigned to SurfaTech Corporation.

5 US7569607 entitled: *Spider esters in personal care applications.* Issued to O'Lenick *et al.* Assigned to SurfaTech Corporation.

6 US7473707 entitled: *Spider esters in personal care applications.* Issued to O'Lenick *et al.* Assigned to SurfaTech Corporation.

7 US7462729 entitled: *Spider esters in personal care applications.* Issued to O'Lenick *et al.* Assigned to SurfaTech Corporation.

8 US Patent Application 20090253812 entitled: *Spider esters as delivery systems.* Issued to O'Lenick *et al*. Assigned to SurfaTech Corporation.

9 de Gennes PD. *Scaling concepts in polymer physics*. Ithaca, NY: Cornell University Press, 1979.

10 O'Lenick T, Lott D. *Cosmetics & Toiletries* 2010; **6**: 430-6.

11 http://en.wikipedia.org/wiki/Beer%27s_law

12 Shaath N. *J Soc Cosmet Chem* 1987; **82**: 193-207.

13 Agrapidis-Paloympis L, Nash RJ. *Raman Spectrosc* 1987; **38**: 209-21.

14 http://flsuncaretesting.com/

15 *Spectral output requirements for testing sunscreen drug products for over-the-counter human use*. Proposed amendment of final Monograph, CFR Part 352. 70 (b) Light sources, Federal Register 72, 165 (Aug 27, 2007).

16 International sun protection factor (SPF) test method. www.colipa.eu/downloads/86.html

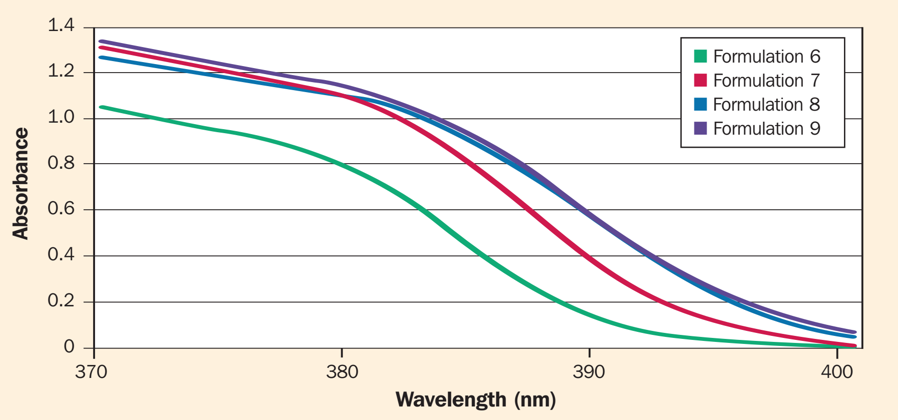

Figure 4: *The absorbance of formulations.*