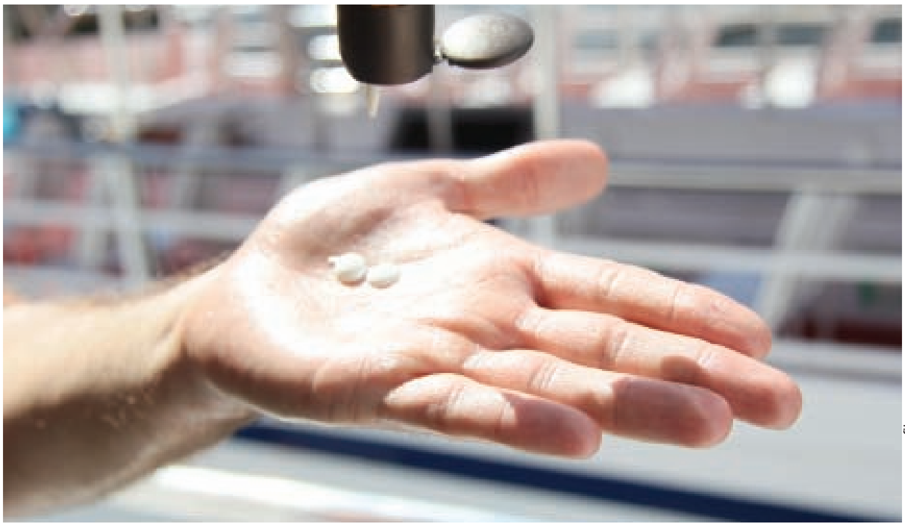
Sensoriality and targeting regular sunscreen usage

Substantial progress has been made in the protection of skin from the sun since the first commercial sunscreen products were introduced in the 1930s.[1] Erythema, primarily from UVB light (290 nm-320 nm), is the first negative consequence experienced as a result of excessive sun exposure. So it is no surprise that early sunscreens focused on extending the period of time that one could spend in the sun without burning and, in time, the concept of the sun protection factor (SPF) was developed. A sunscreen's SPF is determined by exposing human subjects to a light source meant to mimic noontime sun. The amount of light that first induces redness in sunscreen-protected skin, divided by the amount of light that first induces redness in unprotected skin, is the SPF. This concept was incorporated in the regulation of sunscreens in the 1970s by the European Union,[2] the United States[3] and other countries.

In time, the longer term detrimental effects of UVA (320 nm-400 nm) light exposure – increased skin cancer risk and premature ageing and photosensitisation disorders of the skin[4] – became known. As a result, the concept of the UVA-protection factor (UVA-PF) was developed. In Japan, this value is determined in a manner analogous to SPF by assessing persistent pigment darkening (PPD) as a result of exposure of human skin to UVA light.[5] In the EU[6] and many other areas, the UVA-PF has been determined indirectly using an in vitro method based on a reduction in UVA light passing through a sunscreen film, analogous to that developed by Colipa.[7] In the US, labelable protection from the effects of UVA light from sunscreens requires only a critical wavelength (the wavelength at which 90% of the area under the extinction curve from 290 nm upwards to 400 nm occurs) of at least 370 nm.[8]

Concurrent with the development of methodologies for the determination of SPF and UVA-PF it became increasingly evident that not all sunscreens were photostable.[9] Indeed, some of the seemingly most cost-effective UV filters (e.g., butyl methoxydibenzoylmethane, a UVA filter, and



www.morguefile.com

ethylhexyl methoxycinnamate, a UVB filter) were not only photolabile, but became even more unstable when combined.[10] A quest for photostabilisation led from:

- Solvent polarity optimisation using sunscreen solvents of higher polarity, such as dimethyl capramide and diisobutyl adipate, to
- Triplet state quenchers such as polyester-8 and undecylcrylene dimethicone, to
- Much more rapid and efficient single state quenchers such as polyester-25, octyldodecyl methoxycrylene and ethylhexyl methoxycrylene.[11]

An additional factor related to sunscreen performance, water resistance, has also been addressed, albeit on an 'as needed' basis. So called 'daily wear' sunscreens (for example, those incorporated in body lotions) are intended for use under environmental conditions in which the product is unlikely to be removed from the skin during use. For such products, water resistance may be optional. But for beach or active wear sunscreens (e.g., those used while swimming or playing tennis), resistance to removal by water or sweat is a necessity. Consequently, film-forming water resistance-enhancing polymers are typically employed in these products. Commonly utilised polymers include VP/eicosene copolymer for oil-in-water emulsions and acrylates/octylacrylamide copolymer for anhydrous alcoholic sprays.

With all of these factors – UVB and UVA protection, sunscreen photostability and water resistance – taken into account in product development, formulators who are new to the industry may consider their work done. But this is rarely the case because customers have another factor in mind: aesthetics. No matter how stable, water resistant and effective the sunscreen, if it does not look, feel, smell and, for lip care, taste, 'right' – going on, during dry-down and until re-application – repurchase intent will be adversely affected. Complicating the task of the formulator are the various skin types of target consumers: lighter or darker coloration; dry, oily or combination skin; skin that is youthful or aged (prematurely or not), and with or without good dermal integrity; and perhaps troubled by Sensory Processing Disorder, such that feel of the product at any point in the application or wear process may be critically important to its acceptance.[12] So as with so much of the personal care marketplace, superior sensoriality must be a consideration in sun care product development. It is of sufficient import that trained evaluators and/or consumer use testing may be employed to ensure suitability.

In the remainder of this article, challenges and solutions related to sunscreen sensoriality will be explored towards the design and development of sunscreens that not only perform, but delight the senses.

Sensorial design

Regardless of where one markets sunscreens, there is a limited number of UV filters which may be used in their development.[13] The higher the desired level of sun protection, the greater the likelihood that the UV filters themselves will contribute to undesirable sensory properties.

With respect to appearance, if only inorganic (mineral) UV filters are used (i.e., titanium dioxide, with or without zinc oxide, should the latter be added to Annex VI[14]), the higher the use level, the greater the whitening effect on the skin, both during and after application. The most effective way to counter this whitening effect is through the use of nano versions of these oxides in formulation bases that ensure the absence of agglomeration and aggregation during storage and use. If the oxides are used with organic UV filters, and especially if butyl methoxydibenzoylmethane is used, then the pretreatment of the oxides with 2-cyano-3-(4-methoxyphenyl)-3-phenyl-2-propenoic acid (methoxycrylene) esters will markedly diminish their photoreactivity towards susceptible organic materials.[15] Another effective approach for eliminating whiteness, when the marketing platform allows, is the conversion of the sunscreen to a decorative (colour) cosmetic. Lesser coverage BB or CC creams may be suitable for lower oxide levels, while a high coverage foundation or makeup may be required for higher oxide levels.

When only liquid and oil-soluble solid UV filters are used, it is skin feel and gloss that are most likely to prove unacceptable, especially at higher sun protection levels (e.g., SPF 50 and 50+). This is due to the oiliness of the liquid UV filters, exacerbated by the additional solvents needed to adequately solubilise the solid UV filters. A first step towards limiting oiliness and shine is the use of light, dry solvents with high solvency for the solid UV filters. This produces less oil phase and may also reduce the oiliness of the liquid UV filters in the formulation. Such solvents include dimethyl capramide (with greater than 35% wt/wt solvency for six commonly utilised solid UV filters) and diisobutyl adipate (see Table 1). Another way to reduce the oil phase is the use of water-soluble UV filters as part of emulsion-based sunscreen formulations. A further step that can be taken to reduce oiliness in oil-in-water (O/W) emulsion systems is the incorporation of feel additives including organosilicone elastomers delivered in cyclopentasiloxane, such as C30-45 alkyl cetearyl dimethicone crosspolymer, and/or spherical microbeads, such as 12 µm silica or aluminum starch octenylsuccinate.

Table 1: Viscosities and solvencies of various liquids for solid oil soluble UV filters.

		Solubilities (wt/wt)					
Sunscreen solvent	**Viscosity (cSt, 25˚C)**	**% AVO**	**% BTZ**	**% DHHB**	**% EHT**	**% MBC**	**% OBZ**
Spectrasolv DMDA (Dimethyl Capramide)	5	40	39	45	40	36	38
HallTress DIBA Special (Diisobutyl Adipate)	5	16.5	4.9	30	11	25	28.5
HallBrite BHB (Butyloctyl Salicylate)	17	12.7	8.7	9.1	1.8	18	16
C12-15 Alkyl Benzoate	13	12	9.3	8.2	1.8	20.4	17.5
Caprylic/Capric Triglyceride	25	12	4.2	14	4.0	20	13.5
Dicaprylyl Carbonate	7	11.7	11.8	17.6	3.0	25.1	14.1
Butylene Glycol Dicaprylate/Dicaprate	15	11.6	5.7	–	3.4	–	16.2
Butylene Glycol Cocoate	28	11	12	–	7	18	8

AVO: Avobenzone (Butyl Methoxydibenzoylmethane)
BTZ: Bemotrizinol (Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine)
DHHB: Diethylamino Hydroxybenzoyl Hexyl Benzoate
EHT: Ethylhexyl Triazone
MBC: 4-Methylbenzylidene Camphor
OBZ: Oxybenzone (Benzophenone-3)

Whether intended for body or face, sunscreens are most commonly emulsion-based products. O/W emulsions are typically encountered, although water-in-oil (W/O) emulsions are often preferred in some countries including Korea and Japan. The emulsifiers that are utilised exert varying sensorial influences on the sunscreens. Generally, the lower the quantity of emulsifier, the lesser the effect on product aesthetics.

The least amount of emulsifier for O/W emulsions is required when utilising polymeric emulsifiers such as acrylates/C10-30 alkyl acrylate crosspolymer in conjunction with a small amount of traditional emulsifier. The latter is used to assist with particle size reduction of the oil phase in the water phase. Total emulsifier content of less than 1% to under 3% minimises its effect on aesthetics while concurrently enhancing water resistance. This allows the film-forming water-insoluble polymer level required to retard UV filter wash-off to be reduced or even eliminated, along with the long rub-in times and heavy and/or tacky skin feel associated with them.

Also valuable in the preparation of O/W emulsion-based sunscreens are liquid crystal-forming emulsifying systems. These compositions, such as that of INCI name Cetearyl Olivate (and) Sorbitan Olivate, mimic the lipid bilayers of skin cells and so provide a barrier function. Such self-bodying compositions strengthen the interface between the oil droplets and the water phase and form a gel network structure that extends into the water phase, enhancing sunscreen shelf stability. Properly formulated, the ordering that results is adequate to increase product viscosity and keep oil droplets apart, but not strong enough to prevent bulk product flow, and delivers a favorable sensoriality in use. As compared to polymeric emulsifier systems, somewhat more emulsifier is needed. Also, hot processing is required so liquid crystals are formed and retained in formulations.

W/O emulsion-based sunscreens present the formulator with a different set of benefits and challenges. On the positive side they are inherently protective, forming a water-resistant barrier on the skin. On the negative side, total ingredient cost is typically greater, there are fewer ingredients and mechanisms available for ensuring emulsion stability, and their oily or greasy occlusive skin feel must be overcome.

While O/W emulsions have aqueous continuous phases, W/O emulsions typically utilise cyclopentasiloxane. Although of relatively low viscosity (3.8 cSt) and volatile (vapor pressure 0.015 kPa at 25˚C), cyclopentasiloxane is still a half an order of magnitude more viscous than water and more than two orders of magnitude less volatile. This can lead to markedly increased dry-down times for W/O emulsions as compared to O/W emulsions. One way to address this, at least in part, is through the incorporation of alcohol (denat.).

Given the high silicone content of W/O sunscreens, it is no surprise that a diverse array of organosilicone emulsifiers are utilised in their preparation. Especially when inorganic UV filters are used, non-silicone emulsifiers such as sorbitan olivate can also be of benefit. As with O/W emulsion systems, polymeric emulsifiers such as PEG-30 dipolyhydroxystearate are useful for W/O emulsion stabilisation. Multifunctional nonemulsifying polymerics such as dimethicone/vinyl dimethicone crosspolymer may be used to further stabilise the emulsions while also contributing to a smoother, silkier feel and exerting a mattifying effect. And, as for O/W emulsion systems, spherical microbeads can be incorporated to enhance the lubricity and spreadability of W/O sunscreens, further contributing to a softer, smoother and less oily or greasy skin feel. Spherical polymethylsilsesquioxanes of up to 11 µm particle size are particularly beneficial in this respect.

Sunscreen aerosol and pump sprays in the marketplace include both anhydrous solution and emulsion-based products. The anhydrous products are typically alcohol-based and are inherently water resistant. When an alcohol-free claim is required, cyclopentasiloxane may prove a viable alternative volatile carrier. Despite their anhydrous nature, the addition of a small amount of lower HLB emulsifier such as PEG-8 dilaurate can prove beneficial. While not imparting enough hydrophilicity to adversely affect water resistance, the emulsifier can assist with the removal of the sunscreen from both skin and clothing when exposed to cleansing compositions such as soaps, body washes and laundry detergents. As earlier noted, liquids such as dimethyl capramide and diisobutyl adipate, which are of low viscosity and have high solvency for the oil-soluble solid UV filters in these anhydrous formulations, can contribute positively to the sensorial properties of the sunscreen by imparting a lighter feel.

Sunscreen lotion sprays are typically O/W emulsions and require different emulsification systems than those used for standard lotions and creams. The emulsion must be less cohesive, such that the force imparted to the sunscreen as it passes through the nozzle is sufficient to disperse the emulsion into a uniform pattern of tiny droplets. So emulsifiers that are not liquid crystal formers, such as ceteareth-6 olivate, are needed to produce the hyperfluid emulsions desired. Synthetic (e.g., acrylates/C10-30 alkyl acrylate crosspolymer) or natural (e.g., xanthan gum) polymers are recommended to enhance emulsion stability in the absence of liquid crystalline structures.

Conclusion

Although not harmonised on a global basis, the performance requirements for sunscreens with respect to sun protection and water resistance have been well defined. Yet even if a product's sun protection is superb, if its aesthetics are lacking, both continued use and repurchase intent will be at risk. Sensoriality must be addressed during sunscreen product development. Each product form and delivery system presents its own unique challenges, for which a variety of sensory solutions exist. PC

References

1 http://inventors.about.com/od/sstartinventions/a/sunscreen.htm (accessed 15 Sep 2014).

2 Council Directive 76/768/EEC of 27 July 1976 on the approximation of the laws of the Member States relating to cosmetic products. *Official Journal* L 262 (27.09.1976): 0169-0200.

3 Sunscreen Drug Products for Over-the-Counter Human Use, Proposed Rule. *Federal Register* 43 (25 August 1978): 38206-69.

4 https://www.cosmeticseurope.eu/safety-and-science-cosmetics-europe/products-and-ingredients/uv-filters-.html (accessed 16 Sep 2014).

5 http://www.jcia.org/n/all_pdf/gul/SPF-jcia-h240620.pdf (accessed 16 Sep 2014).

6 Commission Recommendation of 22 September 2006 on the efficacy of sunscreen products and the claims made relating thereto. *Official Journal* L 265 (26.09.2006): 39-43.

7 COLIPA method for the *in vitro* determination of UVA protection provided by sunscreen products (2007). The European Cosmetics Toiletry and Perfumery Association – COLIPA (now 'Cosmetics Europe – The Personal Care Association'), Rue de la Loi 223/2, B-1040 Bruxelles.

8 Labeling and effectiveness testing: sunscreen drug products for over-the-counter human use – final rule. *Federal Register* 76 (17 June 2011): 35620-65.

9 Maier H, Schauberger G, Brunnhofer K, Hönigsmann H. Change of ultraviolet absorbance of sunscreens by exposure to solar-simulated radiation. *J Invest Dermatol* 2001; **117**: 256-62.

10 Bonda C. Sunscreen photostability 101. *Happi* 2009; **46** (10): 72-5.

11 Bonda C *et al*. Method of quenching electronic excitation of chromophore-containing organic molecules in photoactive compositions. US Patent 7,588,702 (issued 15 Sept 2009).

12 http://www.webmd.com/parenting/sensory-processing-disorder (accessed 16 Sept 2014).

13 Neudahl G. The current state of UV filters. *Personal Care Europe* 2013; **6** (5): 27-34.

14 Regulation (EC) No 1223/2009 of the European Parliament and of the Council of 30 November 2009 on cosmetic products. *Official Journal* L 342 (22.12.2009): 59-209.

15 Hu R, Zhang J, Neudahl G, Bonda C. Photoprotection of TiO_2 using propenoic acid esters. *Cosmetics & Toiletries* 2014; **129** (7): 54-9.