Sun Care
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With changes in legislation and improvements in sun protection sun care remains one of the more active areas of cosmetic formulation. The main concerns when formulating sun protection products are consumer safety; compliance with legislation and EU recommendations; photo-degradation of the filters and meeting water resistance claims. Further difficulties are encountered in finding combinations of filters that are permitted in different world markets without contravening the many patents that also restrict product development.

The recast of European legislation has been published as Regulation (EC) No 1223/2009 of the European Parliament and of the Council. Article 14 states that cosmetic products shall not contain prohibited substances listed in Annex II or restricted substances which are not used in accordance with the restrictions laid down in Annex III. On the subject of UV filters it states that cosmetic products shall not contain UV-filters other than those listed in Annex VI and UV-filters which are listed there but not used in accordance with the conditions laid down in that Annex. It also prohibits the use of substances listed in Annex VI but which are not intended to be used as UV-filters and which are not used in accordance with the conditions laid down in that Annex. Annex VI lists permitted UV filters and their maximum concentrations; unfortunately it does not allow any new filters and does not accept nano-sized zinc oxide.

As well as legislation the EU Commission publishes guidelines, which do not require compliance in law but producers are expected to comply. EU Commission guidelines suggest that sunscreen products should be sufficiently effective against UVB and UVA radiation and that the UVA protection factor must be at least 1/3rd of the claimed SPF at a critical wavelength of not less than 370nm [Ref 1]. This figure for UVA protection becomes increasingly hard to achieve when formulating for higher SPF values and it also means that one star and two star ratings under the Boots system are no longer valid. There are compatibility problems between UVA and UVB absorbers; the high levels of oil-soluble UV absorbers required can lead to a sticky feeling on application and there are safety concerns about the effects of the actives on skin.

The importance of protection against UVA-induced skin damage and the difficulties of measuring UVA protection factors were the subject of many papers and much debate at the Sun Protection Conference in London 2009 organised by Summit events. For a review of this see SPC XXXX.

Perhaps one of the better advances in sun filter legislation is the banding of numerous SPF values into practical bands.

European and Australia Recommendation			
SPF 4 to <15	Low Protection	UVA Low	*
SPF 15 to <30	Medium Protection	UVA Medium	**
SPF 30 to <50	High Protection	UVA High	***
SPF 50+	Very High Protection	UVA Highest	****
USA recommendation is very similar but low protection is from SPF2 to 15			

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Organic UVA filters provide good efficacy but photostable ones are expensive and there are safety concerns with some organic filters, especially for products for children or people with sensitive skin. Formulations based on inorganic sunscreens can meet EU, Japanese and Australian requirements, but most fail to achieve the higher ratings on the Boots system or the proposed FDA system. Combination systems are usually the most cost-effective way of achieving the highest UVA ratings [Ref 2]. Titanium dioxide provides a broad spectrum base on which to build UVA/UVB ratio but its efficacy depends on particle size and degree of dispersion. However synergy with organics can be exploited to achieve maximum efficacy and TiO_2 boosts in vivo SPF of combinations of BMDM and OCR and manganese-modified TiO_2 improves the photostability of EHMC and BMDM.

One method of minimising compatibility problems between UVA and UVB absorbers is encapsulation of the active. A poster presentation at the IFSCC Conference described maximising the UV protection ability of UV absorbers using an active interfacial modifier that had peptide, silicone, and alkyl moieties in its structure. Water-soluble and hydrophobic materials could be encapsulated separately and introduced into a suitable composition for topical application. The UV-absorption spectra of a sun care formula containing the microcapsules confirmed that EHMC:DHHB (64:36) and OCR:BMDBM (75:25) mixtures showed a balanced UV-absorption profile. Skin permeation studies were also undertaken and it was found that the microcapsules remained on the surface of the stratum corneum. [Ref 3]

A different approach to encapsulation is that of **Exsymol** that has incorporated EHMC in its Emulzome system. Emulzomes are oil-in-water nano-dispersions containing 50% aqueous phase and 50% oily phase prepared using a high pressure manufacturing process and stable without surfactants. When the protection factors of a composition containing 10% EHMC and 2.5% BMDBM in Emulzome form were determined by an *in-vitro* method they showed a significant improvement in SPF and UVAPF compared to a similar composition containing the same actives without Emulzome protection.

Eusolex pearls from **Merck** also comprise encapsulated UV filters; in this case they are surrounded by a film of silica giving a particle size of approximately 1micron with a 40% loading of the active. In this way BMDBM and EHMC can be encapsulated separately and be incorporated within the same product without a risk of photodegradation. Esolex BO is a new version whereby BMDBM and octocrylene are entrapped within the same capsule. The octocrylene ensures the stability of the BMDBM and provides balanced UVB/UVA protection.

The problems of stabilising UV absorbers have been extensively studied by Craig Bonda who delivered a paper on the subject at the IFSCC Conference [Ref 4]. Bonda explained that organic molecules consist of a positively charged nuclear framework surrounded by a negatively charged electron cloud. Most UV filters in sunscreens are organic molecules that absorb solar UV radiation and the energy absorbed initially causes the molecule to reach a singlet excited state, after which it may dissipate the absorbed energy as fluorescence and return to its original ground state or rapidly decay to a less energetic triplet excited state. The bi-radical character of the triplet excited molecule makes it vulnerable to a number of chemical reactions that may destroy its ability to absorb another photon. In this way, BMDBM is particularly vulnerable to destructive chemical reactions and it reacts chemically with OMC, which reduces the ability of both compounds to absorb UVR.

Some compounds such as octocrylene (OC) have the ability to limit or "quench" BMDBM's triplet excited state, returning it to the ground state and thus reducing or eliminating destructive chemical reactions. Octocrylene and a few other compounds are effective at high concentrations, but less effective at low concentrations or when BMDBM and OMC are combined in the same formulation.

Investigations at **Hallstar Laboratories** into ways of improving photostability of BMDBM led to the synthesis of a molecule it named methoxycrylene; obtained by adding a methoxy group to one of the phenyls of cyanydiphenyl propenoic acid, and the ethylhexyl ester was then formed. It was found that at equal weight concentrations ethylhexyl methoxycrylene is more effective than octocrylene at preserving UVA/UVB absorbance of BMDM in the absence of OMC and that ethylhexyl methoxycrylene is greatly superior to octocrylene at preserving the UVA/UVB absorbance of BMDM in the presence of OMC and it was possible to create compositions with high UVA protection factors using this system.

Several decades ago the author suffered his only product recall when a sunscreen containing PABA started growing crystals that felt like broken glass. Ever since he has been very aware of the problems of dissolving organic sun filters. Also, by using the optimum solvent significant improvements in protection factors may be obtained. **ISP** markets phenethyl benzoate under the trade name X-Tend 226. Literature from ISP shows that not only is it an excellent solubiliser for BMDBM, BEMT and benzophenone-3, it is an effective stabiliser of BMDBM when exposed to UVR. Dermofeel Ssensolv from **Dr Straetmans** is isoamyl laurate, which is also a good solvent for organic sunscreens and its low viscosity and surface tension improves the dispersion of inorganic ones.

Formulating sunscreen sprays with moderate to high SPF values is not easy. Work being done at **Alfa Chemicals** shows that Sucragel CF, a mixture of capric/caprylic triglycerides, glycerine, water and sucrose laurate, is capable of gelling many different organic sunscreens. The gels self-emulsify on dilution with water and the mix is stabilised with gellan gum to give spray compositions. By selecting optimum mixes and levels of sunscreens products up to SPF50 can be attained that give good spray patterns. This is ongoing work but early stability results show the products remain stable at 45°C for 3 months.

Attaining water resistance is another problem facing formulators. Even if not claimed, consumers expect reasonable longevity of their sunscreen under normal conditions of use. **AkzoNobel** is promoting the qualities of an acrylates copolymer marketed as Dermacryl AQF that when added at 4.4% to an oil-in-water sunscreen emulsion not only confers good water-resistance, enabling it to pass the FDA 80 minute immersion test, but it is also shown to have good moisturising properties. Baycusan C is the name of a range of polyurethane powders and dispersions that are available from **Bayer,** which improve the product film on skin after application, enhance SPF values and impart significant water resistance.

Also claimed to improve water resistance **ISP** offers a number of polymers under its Ganex/Antaron trade name. V-216 is VP/hexadecane copolymer; V-220 is VP/eicosene copolymer and WP-660 is triacontanyl PVP and each is shown to improve water and abrasion resistance and to boost SPF values. Other polymers from ISP include Advantage S, INCI: Vinyl caprolactam/VP/dimethylaminoethyl methacrylate copolymer, which is suitable for adding water resistance to spray formulations and Aquaflex, INCI: VP/vinyl caprolactam/DMAPA acrylates copolymer, which boosts SPF values. ISP also proposes the use of an acrylic acid/VP polymer marketed as Ultrathix P-100 as a rheology modifier for adding viscosity to sun protection products and to prevent agglomeration of zinc oxide nanoparticles.

Another polymer designed specifically to increase the efficacy of UV absorbers is Syntran PC 5227 from **Interpolymer Corporation** . When an emulsion is topically applied the waxes within the oil phase tend to migrate to the film surface. This mixture of Polyacrylate-15 and Polyacrylate-17 is incorporated into the oil phase to slow the migration of waxes to the film surface so that they are more evenly distributed throughout the film, resulting in a more uniform distribution of actives and optimising their efficiency. Carbopol Aqua CC from **Lubrizol Advanced Materials** is polyacrylate-1 crosspolymer that also provides film forming properties, enhanced SPF results and improved water resistance.

Hair is also affected by sunlight and UV radiation is known to cause hair bleaching and sun damage by degrading keratin and releasing carbonyl groups. It is possible to quantify the carbonyl groups in order to measure the degree of protection offered by applying suitable UV absorbers. Whereas sun protection products are applied as a film to be left on the skin it is more difficult to deposit a substantive film on hair, not least because of the difficulties of solubilising the actives. A poster at the IFSCC Conference, Melbourne 2009, described the solubilisation of BEMT using phytosterol surfactants and the measurement of its protection compared to unprotected controls in in-vitro experiments. It was found that a solution of 0.1% BEMT resulted in significant reduction of hair damage [Ref 5]

Inextricably linked to sun protection is the wish for a “healthy looking” tan and self-tanning products are a booming market. The two most popular ingredients to impart the tan are erythrulose and dihydroxyacetone (DHA). Although DHA has been used in this context for the last 40 years it still presents formulation problems, particularly when trying to ensure long-term stability. **Rona** are now marketing two mixtures containing DHA. DHA Plus is stabilised with sodium metabisulphite and magnesium stearate, which is claimed to have an extended shelf life. The other material is named DHA Rapid that is said to generate quick tanning and to impart a smooth and even skin tone when used in skin care formulations. It is a mixture of DHA with troxerutin; this latter material is an effective anti-inflammatory agent and is used in cosmetics for its anti-oxidant effects, its iron chelating ability and its ability to protect the skin cells from singlet oxygen damage. Rona suggest the use of this product at 3% in daily use skin care to gently tan the skin and to maintain an even tone as well as to utilise its anti-ageing properties.

Erythrulose is a natural keto-sugar that reacts with free primary or secondary amino groups on the skin leading to the formation of brownish polymers. Erythrulose is said to overcome the problems of irregular and streaking tans sometimes seen when DHA has been the main ingredient. It also has moisturising properties and combinations of it with DHA are said to give superior results compared to DHA alone. Whichever material or combination is used a gentle exfoliating step prior to application will improve the tan. Lexorez TL8 from **Inolex** is a polyester polymer that promotes partitioning of alpha-hydroxy acids and beta-hydroxy acids into the stratum corneum. By concentrating hydroxy acids in the stratum corneum, it enhances the rate of desquamation associated with hydroxy acids and contributes a sustained delivery effect while mitigating the potential for hydroxy acids to cause skin irritation or stinging. If used with DHA it improves its delivery into the stratum corneum, resulting in an improved and longer lasting tan.

Recent studies by **BASF** show that the number of free radicals generated in skin increases dramatically if the skin is exposed to natural daylight shortly after the application of self-tanning products. The addition of 5% UVA filter Uvinul A Plus (DHHB) to a self-tanning product not only completely suppresses the free radical boost triggered by the self-tanning reaction but also reduces the level of free radicals below that of the untreated skin, providing protection against skin damage resulting from free radicals.

Uvinul A Plus is photostable and soluble in a wide range of cosmetic oils and in alcohol and BASF also offer combinations of DHHB with EHMC as Uvinul A Plus B as a ready mixed broad band filter system. Other sunscreens from BASF include ethylhexyl triazone as an oil-soluble UVB filter and PEG-25 PABA as a water-soluble UV filter suitable for preparing clear gels and especially suitable for product protection. In addition it offers zinc oxide and titanium dioxide in powder form and with hydrophobic surface treatments and as dispersions in a variety of carrier oils.

Despite its long history of use in inorganic sunscreens to deliver effective UVA protection with excellent photostability in countries such as Australia the use of nano-sized particles of zinc oxide in products for the EU is still unresolved and currently is banned. **Antaria** offers a number of zinc oxide dispersions where the particle size is greater then 1nm including dispersions in caprylic/ capric triglyceride with glyceryl isostearate; in C12-15 alkyl benzoate, in Simmondsia chinensis (Jojoba) seed oil and in neo-pentyl glycol diheptanoate. Despite their larger particle size the Antaria products are said to offer excellent transparency due to its patented Index Match Technology whereby the zinc oxide particles have a unique porous structure that provides a closer match between the refractive index of the particle and the refractive index of the emollient, thus achieving a very high level of transparency.

Another company trying to avoid the controversy over nano particles is **Kobo** which has a range of titanium dioxide and zinc oxide grades where the particles are greater than 100nm when measured by image analysis and light scattering sizing. These non-nano materials are available coated with either organic or inorganic surface treatments and dispersed in various vehicles for easier use in formulation compositions. ISDMP50TEL is a 50% dispersion of surface treated TiO_2 in dimethicone and MTMX80MZCM is an 80% dispersion of ZnO with methyl trimethicone, dimethicone, PEG/PPG-18/18 dimethicone and hydrogen dimethicone. There are also dispersions in caprylic/capric triglyceride or Simmondsia chinensis (Jojoba) seed oil and in volatile silicone mixtures that avoid cyclomethicones.

Grant Industries offers its UV-Cut series as ultra fine dispersions of TiO_2 and ZnO in a silicone matrix, providing a unique, soft, luxurious skin feel. Various grades are available including dispersions in PEG-10 dimethicone with either cyclopentasiloxane or low molecular weight dimethicone; in C12-15 alkyl benzoate and also in caprylic/capric triglycerides. Combinations of organic filters are also available; that of Gransil UVG-7 being a blend of EHMC and BMDBM encapsulated in an elastomer gel of polysilicone-11, which may be used for preparing anhydrous sun protection products.

Croda launch Solaveil SpeXtra at In-Cosmetics 2010; this new grade of TiO_2 provides high attenuation across both UVA and UVB ranges, significantly improving the UVA protection offered by existing grades without compromising SPF efficacy. The Solaveil SpeXtra range initially comprises two dispersions. Solaveil XT-100 is based on C12-15 alkyl benzoate as the carrier fluid while Solaveil XT-300 uses caprylic/capric triglyceride. Both dispersions contain 55% solids and enable the formulator to make globally-approved, high SPF sunscreen products that conform to EU guidelines for UVA protection using a single ingredient. An example W/O emulsion containing 18% Solaveil XT-100 (10% solids) gave an *in-vivo* SPF of 30, with a UVAPF measured according to the COLIPA protocol of 10.

Eusolex T-PRO from **RONA** is a microfine titanium dioxide that provides broad spectrum UV filter performance with high transparency and it is readily dispersed in cosmetic oils. It has a special manganese dioxide coating that enables the product to exhibit an outstanding degree of activity against free radicals. **Croda** also offers titanium dioxide grades stabilised with manganese in its Optisol products.

As well as its well-known organic absorbers **DSM** also offers TiO_2 as a UV filter under the trade name Parsol TX. It comprises rutile crystals of TiO_2 with an inner coating of silica and an outer one of dimethicone resulting in a hydrophobic particle with an average size of 20nm. There is also a 50% dispersion in C12-15 alkyl benzoate available as Parsol TX AB and both materials are fully described in a very informative brochure. This describes checking the colour stability of BMDBM when mixed with TiO_2 with various coatings, the majority of which discoloured within one hour. Similar tests were run using ascorbic acid or ascorbyl palmitate to check the coating integrity and again, the majority rapidly discoloured. Tests to prove photostability and compatibility with polyacrylates are also described and the brochure is a handy guide to all the problems that may be encountered when working with TiO_2.

Since the author first started creating sun protection products using microfine TiO_2 some 20 years ago there have been enormous technological improvements in the material as we gained a better understanding of its properties and the problems that it could cause and now stable materials conferring a high degree of broad band protection with minimal whitening on the skin are widely available. There have also been significant advances are in the ways of minimising UVA damage and repairing cells already exposed to it and this will be covered in the (June) issue of SPC.

Abbreviations used in the text. Names used in USA are in brackets.	
BEMT	Bis-ethylhexyloxyphenol methoxy-phenyltriazine
BMDBM	Butyl methoxydibenzoylmethane (Avobenzone)
DHHB	Diethylamino hydoroxybenzoyl hexyl benzoate
DPDT	Disodium phenyl dibenzimidazole tetrasulfonate
EHMC	Ethylhexyl methoxycinnamate
IFSCC	International Federation of Societies of Cosmetic Scientists
MBBT	Methylene Bis-benzotriazolyl tetramethylbutylphenol
MBC	4-methylbenzilidene camphor
OCR	Octocrylene

OMC	Octyl methoxycinnamate (Octinoxate)
UVA	Ultraviolet radiation between 320 and 400nm
UVAPF	Protection Factor in UVA range
UVB	Ultraviolet radiation between 290 and 320nm
TiO2	Titanium dioxide
ZnO	Zinc oxide

Ref 1 2006/647/EC Commission Recommendation of 22 September 2006 on the efficacy of sunscreen products and the claims made relating thereto

Ref 2 Suncare formulating strategies in the changing regulatory environment, Helen Hine, Julian Hewitt

Ref 3 Peptide-silicone based microcapsule suitable to sun care products; Yumiko Iga *et al*

Ref 4 Taking the next step in sunscreen photostabilization; Craig Bonda *et al*

Ref 5 New solubilisation method of ultraviolet absorbers and its application to hair care products; Takashi Teshigawara *et al*.

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