Feature; Suncare 2012
John Woodruff

When the use of UV absorbers in everyday skin care products is taken into account protection against solar radiation continues to be the most active area of cosmetic formulation. The American Cancer Society predicted that melanoma skin cancer would be diagnosed in about 70,230 persons resulting in 8,790 deaths in 2011. However the death rate in the USA from melanoma has been decreasing by 3% per year in men younger than 50 and by 2.2% per year in women. This decrease may be attributed to a better understanding of the risks involved when exposed to the sun and the increased level of care taken by the general population, including the use of sunscreens. It is thought that the use of sun beds is responsible for the slower rate of decrease in young women.

Trends in sunscreen formulation make interesting reading; Thirty years ago sunburn preventative agents were defined as sunscreens which absorbed 95% or more of UV radiation within wavelengths 290nm – 320nm. Suntanning agents absorbed at least 85% radiation between 290nm – 320nm but transmitted UV above 320nm to produce a light transient tan. Apparently some erythema was to be expected but without pain! [Ref 1]

When that book was written PABA derivatives and benzophenone-3 were the most popular sunscreens, SPF10 was considered high protection and SPF15 was termed ultra protection. Titanium dioxide and zinc oxide were used in their pigment forms and were not popular. Ten years later micronised oxides were making a substantial impact, methods for determining SPF were being standardised and an in-vitro method for determining UVA was being developed [Ref 2]. It was at this time that the harmful effects of UVA were being fully understood and Boots the Chemist introduced its star rating system to indicate the level of UVA protection given as a proportion to the UVB rating or SPF of the composition.

1995 saw the launch of the UVA Conference in London [Ref 3], which has been repeated every two years and, as its title suggests, UVA was the overriding theme. It was at about this time that the problem of UV absorber instability was being realised and this continues to be of concern. Also receiving attention at this conference was the emergence of microfine titanium dioxide as a sunscreen and this technology was the main topic at the UVA Sunfilters Conference in 1998 [Ref 4].

Another aspect receiving much attention in the 1990's was that of water-resistance, its measurement and the claims for it on products. Ethyl methoxycinnamate was the UVB organic filter of choice but a mixture of regulations, patents and instability problems was inhibiting UVA protection. These problems are still real when formulating sun protection products and various suggestions for overcoming them is a principal theme of this feature.

Currently there are only eight organic UVB filters and two UVA filters with world-wide acceptance. Of the two microfine inorganic oxide filters available only titanium dioxide is accepted in all markets while zinc oxide is excluded from Europe. This exclusion only applies to nano-sized particulates, i.e. those under 100nm in diameter, and various suppliers offer grades of treated zinc oxide above this size that are claimed to be transparent.

No longer is SPF15 considered ultra protection: in the EU high protection refers to SPF > 30 and very high protection is SPF >50. The EU authorities also recommend that the UVA protection factor measured at 370nm should be at least 1/3rd of the declared SPF, see Table 1.

Table 1: European and Australia Recommendations			
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 SPF 2 to 15			

To prepare photostable sun protection products with high SPF values that meet expected levels of proportionate UVA protection and water resistance while keeping within world-wide legal requirements and not contravening existing patents is, to put it mildly, a challenge! Fortunately suppliers of the principal UV absorbers have been working to give formulators guidance on how to meet these challenges. The tools to work with are shown in Table 2.

Table 2: UV absorbers accepted world-wide

INCI Name	USA Name	Abbreviation	Max %	Solubility	λmax nm
Butyl methoxydibenzoylmethane	Avobenzone	BMDBM	3%	Oils	357
Terephthalylidene dicamphor sulfonic acid	Ecamsule [Note 1]	TDSA	3%	Water	345
Benzophenone-3	Oxybenzone	BP3	5%	Oils	325
Benzophenone-4	Sulisobenzone	BP4	5%	Water	311
Ethylhexyl methoxycinnamate	Octinoxate	EHMC	7.5%	Oils	310
Ethylhexyl salicylate	Octisalate	EHS	5%	Oils	307
Ethylhexyl dimethyl PABA	Padimate O	EHDP	8%	Oils	311
Homomenthyl salicylate	Homosalate	HMS	10%	Oils	306
Octocrylene	Octocrylene	OCR	10%	Oils	296
Phenylbenzimidazol sulfonic acid	Ensulizone	PBSA	3%	Water	306
Titanium dioxide	Titanium Dioxide	TiO2	25%	Insoluble [Note 2]	UVB/UVA range

Note 1 Also known as Mexoryl SX; exclusive to L'Oreal	
Note 2 Titanium dioxide is insoluble in water and oils but different grades are surface treated to render them dispersible in either oils or water.	

It is virtually impossible to provide high levels of broad spectrum protection without using a combination of UVB and UVA absorbers. However with only two true UVA absorbers available and one of those exclusive to L'Oreal only BMDBM is left. This is very effective in the UVA region but there are problems of photostability and it proved particularly unstable in the presence of EHMC, which was the most popular UVB screen before protection against UVA became a serious issue. There are various ways to keep the BMDBM/EHMC combination and work by Craig Bonda of **Hallstar Laboratories** [recently bought out by ?] into the reasons why UV absorbers should be unstable and into finding methods of stabilising them was the subject of a paper given by Bonda at the IFSCC Conference 20009.

When exposed to UV radiation the sunscreen molecule absorbs energy, which causes the molecule to reach an excited singlet 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 EHMC, which reduces the ability of both compounds to absorb solar radiation in the UV region. Bonda proposed using materials that quench the singlet molecule, returning it to its original configuration and said that ethylhexyl methoxycrylene is very effective in this regard.

Some mixtures are less reactive than the BMDBM/EHMC combination and this has resulted in the popularity of octocrylene which can give stable broad spectrum protection with BMDBM. Octocrylene also improves the solubility of BMDBM and of benzophene-3. **DSM** suggests that when formulating with BMDBM it is essential to use enough solvents to maintain the product in solution. It is also necessary to heat the oil phase containing BMDBM to 80 - 85°C to get a clear solution and it recommends that chelating agents be incorporated in the oil phase to avoid coloured complexes with ions of transition metals. It is also necessary to avoid PABA and PABA derivatives and formaldehyde and formaldehyde donors in the preservative system.

Table 3:Solubility of BMDBM

INCI Name	Solubility	INCI Name	Solubility
Dimethicone	0%	Isostearyl benzoate	10%
Cyclomethicone	0%	Hexyl laurate	11%
Mineral oil	1%	PEG-7 Glyceryl cocoate	12%
Isostearyl isostearate	3%	Isoamyl laurate	14%
PG/Dicaprate/dicaprylate	5%	C12-C15 Alkyl benzoate	14%

Octyldodecyl benzoate	10%	Caprylic/capric triglyceride	14%
Isopropyl myristate	10%	Diisopropyl adipate	19%
Isopropyl palmitate	10%	EHMC	25%

Merck produces the Eusolex products including a number of UV absorbers encapsulated in silica, which enables the formulator to include BMDBM with EHMC in the same compositions. An example is Eusolex UV-pearls OB comprising a 40% dispersion of encapsulated BMDBM stabilised with OCR in the ratio 1 part BMDBM to 3.5 parts OCR. The octocrylene acts as a solubiliser and photo stabiliser of the BMDBM and encapsulation prevents it crystallising.

Sunjin offers BMDBM encapsulated in PMMA beads, which also protects it from photodegradation in the presence of other actives and gets over the solubility problem as the beads are finely dispersed throughout the product. The beads are less than 7 microns in diameter and have a pleasant sensorial feel. As well as encapsulated BMDBM and EHT **Sunjin** also supplies encapsulated mixtures of UV filters under its Hybrid trade name and these include BMDBM with OCR and BMDBM with EHS. The company also encapsulates sun filters in porous methyl methacrylate beads and suggests that EHMC, when encapsulated this way, is ideal for makeup applications. It can also be added to gels in association with its Hybrid BMDBM/OCR beads to provide translucent, oil and emulsifier-free compositions.

There are only two water-soluble filters accepted world-wide: phenylbenzimidazol sulfonic acid [PBSA] and benzophenone-4 [BP4]. PBSA has to be neutralised in-situ to a pH >7 using a weak base otherwise crystallisation will occur. **DSM** advises that it then acts as a salt so salt sensitive thickening agents such as carbomers are best avoided. The advantages of a water-soluble filter are two-fold: it can be used to prepare clear hydro/alcoholic gels and also, when used in the aqueous phase, it reduces the loading in the oil phase, giving a lighter and less greasy feel to the composition.

The two salicylates; ethylhexyl salicylate and homosalate both form reasonably stable combinations with BMDBM and aid its solubility in oils. Even though they are not as effective as EHMC on a weight for weight basis these properties make them worth consideration when formulating for world-wide acceptance.

If not restricted to adhering to the limited range of filters with world-wide approval formulating high SPF products that also provide acceptable UVA protection becomes much easier. Table 4 shows the additional filters allowed in Europe.

Table 4: Additional filters allowed in Europe

INCI Name	USA Name	Abbreviation	Max %	Solubility	λmax nm
Bis-ethylhexyloxyphenol methoxyphenyl triazine	Bemotrizanol*	BEMT	10%	Oil/Water [Note 1]	UVA

Diethylamino hydroxybenzoyl hexyl benzoate	-	DHHB	10%	Oil	354
Disodium phenyl dibenzimidazole tetrasulfonate	Bisdisulizole disodium	DPDT	10%	Water	UVA
Drometrizole trisiloxane	-	DTS	15%	Oil	330/344
Methylene bis-benzotriazolyl tetramethylbutylphenol	Bisoctrizole	MBBT	10%	Insoluble	Broad UV
4-methylbenzylidene camphor	Enzacamene*	MBC	4%	Oil	300
Diethylhexyl butamido triazone	Isocotrizinol	DBT	10%	Oil	311
Isoamyl p-methoxycinnamate	Amiloxate*	IMC	10%	Oil	UVB
Ethylhexyl triazone	Octyltriazone*	EHT	5%	Oil	314
Polysilicone-15	-	PS15	10%	Insoluble	310

Note 1: BEMT is supplied as Tinosorb S (oil soluble) and Tinosorb S Aqua (Water soluble) by BASF.

* UV Filters currently being assessed for acceptance in the USA under the Time and Extent Application (TEA).

There are four UVA filters, two of which can be distributed in the aqueous phase, thus reducing the oil content of the finished composition and improving its sensorial properties. By adding combinations of UV filters to both the oil phase and aqueous phase there are improvements in application and SPF and UVA results. In addition to the above filters the European Commission (EC) published a positive opinion of the Scientific Committee on Consumer Safety (SCCS) for the use of a new organic UV-absorber in sunscreens, consisting of the active tris biphenyl triazine (TBT). This new UV filter for sunscreen protection covers the UVB and UVA range and could provide more formulation flexibility when creating products for use in Europe.

There are many suggestions from suppliers aimed at improving the efficacy of sun filters and skin feel on application. **DSM** recommends that water-soluble filters such as phenylbenzimidazole sufonic acid are added to the aqueous phase to avoid oil overload. It also suggests using UV filters with different solubility's to optimise distribution of sunscreens on the skin and maximise SPF. **DSM** is the supplier of polysilicone-15 and this polymeric sun filter based on a silicone backbone imparts a pleasant skin feel and can be used in association with BMDBM to provide broad spectrum protection and improve the photostability of BMDBM.

Not registered as UV filters but accepted as cosmetic ingredients are the Sylvar Clear polyamide polymers from **Arizona Chemical**. They are film forming polymers that repel water, bind actives and improve skin hydration. They have a demonstrated SPF enhancing effect and the polyamide structure provides uniform dispersion and suspension of inorganic filters. Their gel structure may be used to control rheology ranging from spray to stick and by reducing or eliminating the need for emulsifiers they reduce wash-off and improve water resistance. Depending on the grade they may be used to gel low to medium polarity organic liquids such as mineral oils, hydrocarbons, esters and emollients or high polarity materials like ethers, surfactants, glycols and glycol water blends.

Another material that is not a UV absorber but which provides protection is Liposhield HEV Melanin from **Lipo.** Melanin occurs naturally in the human body where it is released from melanocytes into the skin as a first line of defence against exposure to certain damaging light waves. Liposhield HEV Melanin is thought to be the first cosmetic ingredient designed to protect the skin from damaging high energy blue/violet visible light that occurs at wavelengths between 400 and 500nm. It won the Innovations Award at In-Cosmetics Milan 2011.

Polyurethane dispersions [INCI PPG-17/IPDI/DMPA copolymer] such as **Bayer's** Baycusan RC1000 can be an effective SPF booster in sun care formulations that contain combinations of octocrylene and other UV filters. The SPF boosting effect of Baycusan RC1000 is because it forms a highly flexible, breathable film that mimics the movement of skin. This film creates a naturally soft feel on the skin without any tightening sensation.

Although **FMC Biopolymer**'s Avicel microcrystalline cellulose particles do not in themselves act as UV protectors, they improve efficacy by turning water-thin sunscreen sprays into rich 'non-drip' UV shielding layers on the skin. **Koda Corporation** markets an extensive range of silica spheres, hydrogels and emollient esters. A material of interest when formulating with inorganic oxides is NuNu Gel; a galactoarabinan acrylate/glycerin copolymer. Inorganic pigments and sunscreens in combination with NuNu Gel exhibit faster particle dispersion, better suspension, and greater loading capacity.

Arguably the single biggest event in sunscreen actives in recent years was the introduction of micronised oxides as the screening materials. Initially there were difficulties in reducing whiteness and improving spreading properties but soon dispersions in various oils or water became available. Achieving good SPF and UVA protection was possible and micronised titanium dioxide soon gained world-wide acceptance. Unfortunately European legislation has yet to approve nano-sized zinc oxide and from 2013 all products containing materials that have a diameter less than 100nm will have to include the word “nano” after the offending material on the ingredient list.

Both titanium dioxide and zinc oxide are available from numerous suppliers in many different grades. The emphasis has been on improving dispersion properties and on narrowing the particle size distribution. Improving dispersions and resisting the formation of agglomerates has resulted in various coatings being devised. UV protection from metallic oxides is very much dependent on particle size with particles of diameter more than 100nm blocking light above 400nm, thus becoming visible. On the other hand particles that are too small will not block UVA or UVB radiation. Narrowing particle size distribution enables more precise reduction of solar radiation in the dangerous wavelengths.

The importance of particle size is emphasised by the Creasperse UV-products from **Creations Couleurs.** These are compositions of TiO_2. ZnO and iron oxide (Fe_2O_3)

dispersed in photostable lipids and are available in different crystal sizes for different kinds of applications. The standard grades of Creasperse UV-dispersions are coated with hydroxystearic acid and dispersed in hydrogenated polydecene or vegetable squalane. Dispersions with 14nm TiO_2 crystals provide high SPF with low UVA-protection and very transparent application. Dispersions with 22nm TiO_2 crystals offer high SPF and medium UVA-protection with a slight whitening effect and dispersions with 35nm TiO_2 crystals provide excellent UVA-protection, but only moderate SPF with fairly opaque application.

Another example of a dispersion with a carefully controlled particle size is UV Cut TiO_2 from **Grant Industries.** It is a 40% dispersion of surface-treated titanium dioxide having a primary particle size of 16 nm in cyclopentasiloxane. It is compatible with silicone elastomer gels and imparts a very light, smooth feel. It gives protection against UVB and UVA; is transparent on application and has water-resistant properties. Other dispersions of both TiO_2 and ZnO are available from the same supplier.

OY Granular provides the GranLux range of TiO_2 and ZnO dispersions, which are available in a variety of forms and in many cases include sufficient emulsifier to formulate stable w/o and o/w emulsions. Granular will also build bespoke mixtures for the larger user. As previously mentioned, nano-size ZnO is not permitted as a sunfilter in the EU but is allowed in most countries of the world. **Umicore** provides coated zinc oxide powders as Zano 10, Zano 10 Plus and dispersions of these in various oils under its Xperse trade name. ZinClear by **Antaria** is a range of micron-sized zinc oxide dispersions with hydrophobic coatings, which give both UVA and UVB protection. Data shows that ZinClear can protect skin and hair follicles from sun damage and prevent colour-treated hair from fading.

Solashield products from **TRI-K Industries** are dispersions of microfine titanium dioxide in cosmetic esters. They were designed by **New Paradigm Technologies'**, a division of TRI-K, to offer enhanced performance and better esthetics and ease of use in sunscreen products and in daily use cosmetics with SPF claims. Solashield dispersions are manufactured by applying recent advances in emulsion technology to sunscreen dispersion formulations, claims TRI-K. They achieve higher SPF values per unit TiO_2 and greater efficiency in the use of TiO_2 particles, which also produces better finished product esthetics.

There are many other suppliers of TiO_2 and ZnO sunscreens, including companies like **BASF** that promotes ZCote zinc oxide screens and **Croda**, which added the Uniqema range of dispersions to its own collection of inorganic sunscreens. As a result of acquiring this technology Croda has now launched Solaveil SpeXtra dispersions of titanium dioxide. Croda claims that they provide both UVB and UVA protection and that with just one material it is possible to formulate sun protection products that comply with European guidelines for UVA protection.

Solaveil XT-100 comprises 55% solids in C12-15 alkyl benzoate; XT-300 is dispersed in caprylic/capric triglyceride and XT-40W is in emulsion form; [INCI: Titanium dioxide, aqua, polyglyceryl-2 caprate, sucrose stearate, Simmondsia chinensis seed oil, stearic acid, alumina, glyceryl caprylate and squalane]. The Croda brochure on

Spextra dispersions is particularly informative about sunscreens and European legislation.

Improving sunscreen efficacy is achieved in various ways; one being finding synergy between two actives. Adding materials such as the polyamides already mentioned can give substantial enhancement and so can stabilising the active against photo or chemical degradation. Solvents can have a big influence as improving the solubility of the active; improving its spreading properties and improving waster-resistance can all be a function of the solvent.

Work by Thomas O'Lenick of **SurfTech Corporation** has studied the effects that different solvents have on SPF results and he found that polar solvents can significantly affect results. O'Lenick reported that while UV absorbance by BMDBM was improved if it was applied in an alcohol solution ethylhexyl dimethyl-PABA was rendered unable to conjugate and therefore unable to absorb UV radiation. He found that sorbeth-2 hexaoleate esters were effective in improving UV absorbance by organic sunscreens. Such materials are called spider esters and are characterised by having hydrophilic arms covalently bonded to a hydrophobic end group. These macromolecules act in the same way as micelles in emulsions and if organic sunscreens are added they are enclosed within the arms of the molecule, preventing aggregation of the actives and greatly improving application as an unbroken film on the skin.

Many inorganic oxide dispersions are in silicone oils and volatile silicones; offered as an alternative is Vegelight TiO_2-60, a 60% dispersion of TiO_2 in coconut alkanes from **Biosynthis.** Coconut alkanes are non-polar and emollient and promote a pleasant skin feel, in a similar manner to D5 volatile cyclomethicone. They have exceptional spreading power and improve the distribution of UV filters when combined in emulsions or milk preparations.

Laracare 200 from **Lonza** is a natural polysaccharide, galactoarabinan, with sugar units consisting of galactose and arabinose. It is extracted from the N. American larch and this natural, mild, non-irritating and water-dispersible polymer provides SPF enhancement. LaraCare A200 has the ability to aid reduction of oil droplet size and to improve particle dispersion and homogeneity and it is the uniform distribution of sunscreen on the skin surface in a water-resistant film that contributes to improved SPF results.

Providing water resistance is an important part of sun care formulation and incorporating the sunscreen actives in gels or oils that aid the solubility or dispersion of the actives and which form unbroken films on the skin boosts SPF results and can provide water-resistance. Adding 2 – 3% dimethicone will help but for better results various polymers are available. Of interest are Creagel Crystals from **Creations Couleurs**, which is a range of transparent gelled lipids based on synthetic and natural oils and thickened by a polymerisation process. The standard products are based on photostable oils and are completely hydrophobic. The polymer structure stabilises emulsions and helps the product to be applied evenly and then it dries to leave a water-resistant film.

Lubrizol suggests the use of Pemulen TR-2 INCI: Acrylates/C10-30 alkyl acrylate crosspolymer] for the emulsification of emollients and humectants in low viscosity spray systems such as after sun and screens. Whilst the system exhibits low viscosity, the Pemulen TR-2 generates high relative yield values and can be used to stabilise systems containing up to 50% oil without using a secondary emulsifier. **Lubrizol** also supplies Avalure AC120 [INCI: Acrylates copolymer] as a low viscosity emulsion which blends well into most cosmetic preparations and it readily forms a water resistant film on the skin.

Other materials that have been recommended are NuLastic Silk [INCI: C 4-24 Alkyl dimethicone/divinyldimethicone crosspolymer, isononyl isononanoate] and Polyderm PPI-PE [INCI: Polydiethylene glycol adipate / IPDI copolymer], both from **Alzo International.** Fluorosil LF is perfluoronyl dimethicone from **Biosil Basics**, which is a good pigment dispersing aid and it adds water-resistance to the product. Melactiva from **Lucas Meyer** is a natural active from Kapi Kacchu seeds that is able to improve a natural tan in reduced UV conditions. For example, when added to an SPF sun cream it allows natural levels of tanning, with skin protection from UV damage.

There is no such thing as a UV absorber of natural origin with sufficient activity to provide adequate sun protection but some materials can improve the skin feel, product dispersion and application and enhance SPF values. Shea butter appears to work well in this regard and a material from **ICSC** marketed as Rejuvenated Exolipid SPF is an oil blend with sun-protective properties.

Rejuvenated Exolipid SPF is obtained by fractionation and recombination technologies to yield highly active polar lipids which are claimed to provide exceptional healing, anti-microbial, anti-oxidative, anti-inflammatory and natural sun-protective properties. It is a mixture of fatty acids with a high content of natural antioxidants and unsaponifiable matter from Sesamum indicum, Oryza and Elais guineensis oil, which contribute to its unique properties.

Avenacare offers Oat Beta Glucan as a material that prevents UV-induced irradiation and various other materials are available that mitigate the effects of solar UV damage. These are not UV absorbers and will be discussed in a separate feature as skin care actives.

It appears that ferulic acid is one molecule found in nature that can add a little UV protection to formulas. The seeds of many botanicals, such as coffee, apple and orange as well as in both the seeds and cell walls of rice, wheat, oats and pineapple contain ferulic acid and rice bran with its ferulic acid content may be used to make a small increase in UV protection and to help sooth sunburn. **Active Concepts** markets cationic hydroxypropyltrimonium rice protein standardised to contain 10% ferulic acid that may be used as an effective photoprotectant, especially for hair.

Kalichem proposes the use of Apalite either in combination with or as a replacement for titanium dioxide. Apalite is calcium hydroxyapatite, which is naturally present in bones and skin. It is claimed to be comparable with TiO_2 in its sun screening efficacy, to be non-whitening and to form an unbroken film on application to skin.. Once on the skin it is slowly dissolved by the acid mantle and it is claimed that calcium ions are absorbed into the skin, where they improve its moisture levels and structure.

It should be noted that many of these materials are supplied with Ecocert approval and that those interested should contact the supplier for full details.

Ref 1 Harry's Cosmeticology 7th Edition, 1982, Longman Scientific & technical, page 231

Ref 2 Poucher's Perfumes, Cosmetics and Soaps, 10th Edition 1993, Kluwer Academic Publishers, 467 – 503

Ref 3 UVA Skin Response, Protection and the Consumer; March 1995 London, Summit Events

Ref 4 European UV Sunfilters, November 1998, Paris, Step Exhibitions.

Ref 5 Taking the next step in sunscreen photostabilization; Craig Bonda *et al.* IFSCC Congress 2009.

John Woodruff
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