

Sun care remains a very active area for new ingredients, improved product formulations and patent activity. Ongoing discussions between COLIPA and the European Commission, with the aim of harmonising the testing and labelling of sun protection products have focussed attention once more on UVA protection. One proposal being discussed is a requirement that all sun protection products should have a UVA protection factor that is at least one-third of the labelled SPF. A limited number of materials are available for providing UVA protection and existing patents further complicate formulation.

Butyl Methoxydibenzoylmethane (BMDBM) is the only organic UVA filter permitted for use throughout the world. Unfortunately it is not photostable and may lose 60% or more of its activity at 360nm when exposed to solar radiation. L'Oreal was quick to notice this problem and make it a marketing plus by taking out patent, EP 0 514 491 B1, to protect ways of improving its photostability using other sun filters and in particular, Octocrylene (OC). Roche also protected combinations of BMDBM and OC by patent EP 780 119 A1. The combinations claimed were:-

BMDBM	1.00%	1.50%	2.0%	2.50%	3.00%
OC L'Oreal	≥0.95%	≥1.43%	≥1.90%	≥2.38%	≥2.85%
OC Roche	≤0.90%	≤1.35%	≤1.80%	≤2.25%	≤2.70%

The L'Oreal patent was revoked in November 2004 but variations of it are still in force in the USA, Australia and Japan and the Roche patent is still in force in Europe and abroad. Other patents also claim various combinations of sun filters with BMDBM so the patent situation needs careful study before formulating with this material.

Improved photostability can also be achieved by careful formulation of the oil phase. Craig Bonda *et al* [Ref 1] found a relationship between the rate of photo decay of BMDBM and the dielectric constant of the oil phase. As the dielectric constant was increased BMDBM became progressively more stable until it reached maximum stability at about 8.8, after which its rate of decay increased again. A composition based on the same actives had SPF 17 when the oil phase dielectric constant was 5.48 and SPF 25 at 8.71.

Oxynex ST, **Merck**, is diethylhexyl syringylidene malonate with caprylic/capric triglyceride suggested as a stabiliser for BMDBM and laboratory tests indicate that it is comparable to Octocrylene. Also it acts as an antioxidant and inhibits lipid peroxidation and is an excellent additive to prevent colour fade in water-soluble cosmetic colorants.

Another way to improve UVA performance is by the use of Neo Heliopan AP, **Symrise**. This

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material, INCI: Disodium phenyl dibenzimidazole tetrasulfonate, was described in detail by Bill Johncock [Ref 2] at In-Cosmetics 2003. It is an insoluble material that becomes water-soluble when neutralised and has its maximum absorbance at 338nm. It is photostable and when used with BMDDBM it improves the stability of that material.

Arguably the greatest advance in cosmetic sun protection products in the last 25 years was the introduction of micronised oxides as UV filters. Initially there were problems of agglomeration of the particles, instability of the material and whitening on the skin. However with the introduction of dispersions by Tioxide, now Uniqema, many of these drawbacks were overcome and now products containing these materials may be as cosmetically elegant as those based solely on organic screens. The concentration of UV filters which need to be used in a sunscreen formulation in order to achieve the desired SPF is primarily dependent on the efficacy of the UV filters and secondarily on the composition of the formulation in which they are to be used. The sunscreen activity of micronised titanium dioxide (TiO₂) works by scattering, reflecting and absorbing solar radiation. Its efficacy is a function of particle size and in preventing agglomeration of the particles [Ref 3]. Preventing agglomeration is the reason for various surface treatments by the suppliers of the oxides.

Surface treatment with polymers creates a barrier that protects the micro-pigment against strong aggregation by steric hindrance. **Kemira Pigments** uses PVP for surface treatment. It has a strong affinity for the TiO₂ particles and is not displaced from the surface when the material is dispersed in the formulation. As well as preventing particle aggregation it is said to also reduce the chemical and photo-activity of the TiO₂. **DSM** is well known for its range of Parsol organic filters and it has now added a micro-fine titanium dioxide with a hydrophobic coating of silica and dimethicone to the range under the trade name Parsol TX. This coating ensures the photo stability of the UV-B filter, which has good compatibility with BMDDBM and it improves its photostability.

LCW Sensient has Covascreen WTI, an aqueous dispersion of alumina-coated microfine titanium dioxide. It is a rutile crystal coated with alumina and supplied as an aqueous-glycolic dispersion. The coating protects the metallic oxide from photo reactivity. It also improves dispersion and compatibility in non-polar media and it confers an electrostatic charge at the surface of the particles, which should ensure an efficient repulsion between them, thus avoiding agglomeration of particles over time.

The inorganic oxides commonly used for sun protection are either titanium dioxide or zinc oxide; either may be used in association with aluminium oxide or iron oxide. A recent introduction by **Granula** is cerium dioxide, which is claimed to be more transparent and more photostable than

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titanium dioxide. It is supplied coated with silica and aluminium hydroxide and may be used in conjunction with TiO₂ for broad band protection. A material produced by **Oxonica** in association with **Croda** is Optisol. It consists of crystals of TiO₂ that incorporate manganese within their core. The manganese ions are said to have enhanced free radical scavenging properties, which significantly reduces photo-degradation of other UV absorbers such as BMDDBM, thus improving sunscreen performance over time. Also from Croda is Crodasperse, a dispersing agent for inorganic sunscreen actives and for colour pigments. It provides drier feel on the skin, more stable formulations and greater formulation flexibility.

Uniqema are launching two new dispersions at In-Cosmetics in Barcelona 2006; they are Solaveil CZ-100 and Solaveil CZ-300. These dispersions contain a new grade of zinc oxide (ZnO) with a narrower particle size distribution than previous grades. This, together with a novel dispersant system, results in a dispersion providing high UVA protection and ease of use and is completely transparent on skin. Both dispersions contain 60% solids; the carrier fluid in Solaveil CZ-100 is C12-15 alkyl benzoate, while in Solaveil CZ-300 the carrier is caprylic/capric triglyceride. By combining one of these new dispersions with Uniqema's transparent Solaveil titanium dioxide dispersions formulators can develop high SPF formulations using only inorganic sunscreens. Also Solaveil TiO₂ or ZnO dispersions can be combined with organic sunscreens; the well-documented synergistic effects that often occur with such combinations mean that very cost-effective formulations can be developed for high SPF and broad spectrum protection.

Sunjin Chemical Co. produces a wide range of inorganic filters including TiO₂ with a particle size of 20nm that is then coated with silica and alkyl silane to produce a product that is said to have a pleasant skin feel without whitening. It is compatible with BMDDBM and SPF results are comparable to other micronised oxides. Even smaller particle size are used to produce Sunsil T40; TiO₂ particles 12nm in diameter are encapsulated in silica beads to produce spherical particles with good skin feel, minimal whitening and a synergistic boost in SPF results. An interesting composite suggested for incorporation in pressed powder make-up is Sunsil TZin50AS. TiO₂ is encapsulated in silica, which is then surrounded with a coating of ZnO and treated with a hydrophobic coating of alkyl silane. Sunjin also supply TiO₂ dispersed in cyclomethicone, a hydrophobic dispersion in water and ZnO treated with alkyl silane.

Also combining TiO₂ with ZnO are SunCap encapsulated spherical UVA & UVB filters from **Whisper Chemicals**. Offering excellent sun protection and tactile performance each compound is designed to be dispersed and formulated with ease in both water and oil based compositions including pressed powders.

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Improving the efficacy of UVA/UVB filters enables the formulator to use significantly less active to deliver the same level of SPF. As a result, potential irritation caused by the actives is reduced, and the formulator is able to create more aesthetically pleasing products.

SunSpheres SPF Booster is a styrene/acrylates copolymer from **Rohm & Haas**. The material is supplied as a dry free-flowing powder the particles of which are hollow spheres approximately 325nm in diameter. The air in the void has a refractive index of 1.0. The refractive index of the polymer shell is approximately 1.6. In a sunscreen formulation, the refractive index of the dried film is typically 1.4 to 1.5. As radiation passes through material of one refractive index into a material of another refractive index, it is bent, or scattered. The presence of a large number of SunSpheres polymers in a formulation will therefore cause increased scattering of radiation. When incorporated in a sunscreen they raise the UV protection over the whole UVA/UVB spectrum and work equally well with organic and inorganic sunscreen actives.

A mixture of polyacrylates 15 and 17 is supplied by **Interpolymer Corp.** as Syntran PC5227. Designed specifically to increase the efficacy of UV absorbers *in vivo* tests performed on ten volunteers demonstrated a 70% increase in SPF in a SPF20 control formulation and *in-vitro* tests on an SPF15 control formulation demonstrated a boost of nearly 300% when 3% Syntran PC5227 was added to the compositions. It is thought that the increases are due to an affinity between the polymers and UV absorbers, such as ethyl hexyl methoxycinnamate, benzophenone and ethyl hexyl salicylate. This affinity leads to more ordered structures and therefore better exposes the UV segments to photo-excitation. Also the polymer contains a significant number of polar groups which assist in the formation of the dipoles necessary to change the spectral position of the UV absorbers.

Despite constant publicity about the dangers of too much exposure to solar radiation people still sunbathe and damage their skin. UVA induces the formation of reactive oxygen species (ROS) and free radicals that react with membrane lipids and amino acids, causing the peroxidation of fatty acids and generating inflammatory reactions. They also polymerise proteins in the dermis leading to complex brittle structures, which lead to slack wrinkled skin.

To diminish the destructive effects of UV-induced oxygen radicals, anti-oxidants are recommended in addition to sunscreens. Vitamins A, E and C are popular but there are problems of solubility and photostability and they lose their efficacy as they become saturated. Often they only protect the sunscreens from oxidation and have no significant effect on the skin. **Atrium Biotechnologies** launched a new material, EUK-134, that has auto-regenerating anti-oxidant properties giving protection to lipids and proteins. EUK-134 displays the potential to operate in a

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way similar to the two anti-oxidant enzymes superoxide dismutase and catalase, and is able to provide MMP inhibiting activity and assure the protection and repair of DNA. Atrium has also recently introduced Abyssine PF, which protects Langerhans cells and Aldavine, a material claimed to protect the skin's micro-capillary network from UV damage.

As previously mentioned, vitamins can exhibit stability problems. To overcome this **Greentech** have encapsulated natural vitamin C obtained from the fruit of a cherry tree originating in the West Indies. Trade named Aceromine the *Malpighia punicifolia* (acerola) fruit extract is spray dried with maltodextrin and encapsulated in a liposome. An extract of the acerola, *Malpighia punicifolia* is an optional active ingredient in US patent UP 6,989,150, which claims the use of a bark extract of quebracho blanco, a silkworm extract which contains the peptide cecropine, amino acids and a vitamin mixture, a hydro-gel, phospholipids, a yeast disintegration product and cyclodextrins.

Phytosan, **CLR**, is a plant derived active made from soybeans that contains proteins, glycoproteins and polysaccharides that is designed to counteract biological and UV-induced premature aging of the skin by stimulating synthesis of extracellular matrix constituents and providing comprehensive photoprotection. Phytosan was tested *in vivo* on humans and *in vitro* on cultured human skin cells and this series of tests show that it is able to counteract stress-induced premature skin aging and that it activates regenerative cell functions and improves condition and appearance of mature skin.

Studying plants that have developed survival mechanisms under stress has led to many new cosmetic active ingredients. **Laboratoires-Serobiologiques** provides various plant-derived actives including an extract of the senna plant, *Senna alata*. Trade named DN-Age it is said to protect nuclear DNA against UVB radiation, mitochondrial DNA against UVA radiation and to support the natural repair process of skin cells.

Also plant-derived, Reasun, **CEP-Solabia**, is derived from *Curcuma longa*, a plant native to French Polynesia. It is a food colouring agent used to colour saffron rice and traditionally the indigenous population marinate curcuma rhizomes in monoi oil for the relief of sunburn and to soothe mosquito bites. Studies showed the presence of curcuminoids similar to polyphenols, which have notable soothing properties. These and the essential oils also associated with the plant are extracted by a hydro-glycolic mixture to produce Reasun, which is recommended for the relief of sunburn. It has anti-free radical properties, it protects Langerhans cells and, because of its UV absorption properties, it enhances SPF values of sun screen preparations.

Solarine II, **Greentech**, is a mixture of fatty acids, carotenoids and tocopherols obtained from Sea buckthorn oil, wild rose hip seed oil and Voacanga oil extract. Rose hip seeds have a high content of linoleic, linolenic and oleic acid, and these are able to inhibit lipid oxidation and regulate

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inflammation. Sea buckthorn is traditionally used in Tibetan medicine to treat cutaneous burns, skin complaints and wounds and it is effective in protecting skin from UV damage. Voacanga seed oil is rich in essential fatty acids, mainly oleic, palmitic and linoleic, and all three oils contain carotenoids and tocopherols and have anti-oxidant properties. Carotenoids inhibit inflammation linked to sunburn and reduce free radical formation generated by UV radiation. Tocopherols limit lipid peroxidation and decrease inflammation by reducing IL 6 interleukin production.

Finally for those people for which the answer to life's problems is chocolate, **Active Concepts** provide ACB Cocoa Bioferment; rich in xanthine alkaloids, flavonols and related oligomers it is claimed to inhibit lipid peroxidation and excess ornithine decarboxylase activity and to reduce the number of sunburn cells resulting from UV radiation.

Ref. 1: Bonda, Crais: Solvent Polarity and Sunscreen Photostability; European Sun Filters Conference, 2003.

Ref. 2: Johncock, W. Optimising UVA Protection; In-Cosmetics 2003

Ref. 3: Aro H, Dahms G, Compatibility of Microfine Titanium Dioxide with Organic Filters, Cosmetics & Toiletries Manufacture Worldwide