

Sun Care & Protection

1st Published in SPC - 2015

John Woodruff

When looking at sunscreen formulation the starting point has to be the list of permitted UV absorbers for the target region. The good news is that an additional material, tris-biphenyl triazine, was admitted to the European list in August 2014 and it is available as Tinosorb A2B, a 50% glycolic dispersion, from **BASF**. It may be used at up to 10% active by weight in the final composition and it protects the skin against UV wavelengths ranging from 290 to 340 nanometres. It is described as a water-dispersible and efficient UVB/UVA II filter that offers more flexibility for the formulator making it easy to achieve the required UVA criteria using only Tinosorb A2B and metallic oxides.

A second material commonly called HAA299 that received a favourable opinion [Ref 1] by the Scientific Committee on Consumer Safety (SCCS) is that the use of non-nano HAA299 at a concentration up to 10% as a UV-filter in cosmetic products, does not pose a risk of systemic toxicity in humans. HAA299 is also known as FAT 75'808 and has the CAS No 919803-06-8.

It may just be possible that in 2016 this feature will report that new sunscreens are permitted for use in the USA as President Obama has signed into law S.2141, the Sunscreen Innovation Act, which modifies the process for the review and approval of over-the-counter sunscreen ingredients by the Food and Drug Administration. Currently besides ecamsule, (terephthalylidene dicamphor sulfonic acid), which is exclusive to L'Oreal, the only UVA filter permitted in both the USA and Europe is avobenzene (Butyl methoxydibenzoylmethane = BMDBM). It is now expected that within the year the UVB filter ethylhexyl triazone (Uvinul T150 from **BASF**) and the two UVA filters, bemotrizinol (Tinosorb S from **BASF**) and bisoctrizole (Tinosorb M from **BASF** and Milestab 360 from **MPI Chemie**) will gain FDA approval.

Inorganic Oxides

Micronised oxides continue to gain in popularity as the problems of whitening on the skin and dragging skin-feel are overcome. There is also confirmation that Ecocert would approve TiO₂ and ZnO irrespective of particle size as long as they meet the criteria outlined in the recent SCCS Opinion [Ref. 2], and this represents another positive development for nano grades of TiO₂ and ZnO. This led to the announcement by **Croda** that it has Ecocert approval for two transparent dispersions of mineral UV filters from the Solaveil Clarus range; Solaveil CT-300 (TiO₂) and Solaveil CZ-300 (ZnO).

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Parsol TX is microfine titanium dioxide with purity greater than 99.5% in the rutile form from **DSM**, which because of its highly hydrophobic surface treatment, is easy to disperse in the oil phase of emulsions. This same surface treatment also inhibits reactions with other “sensitive” components of the formulation such as BMDBM, which can commonly occur with some aluminium treated titanium dioxides, resulting in crystal formation and reduction in UV-A performance. It also allows compatibility with polyacrylate thickeners such as acrylates/C10-30 alkyl acrylate crosspolymer to allow production of gel formulations. A 50% dispersion in C12-C15 alkyl benzoate under the trade name Parsol TX50 AB is also available.

A material from the **Innovation Co.** is Creasperse UV DUO. It combines two different sizes of TiO₂ crystals and when compared to single TiO₂ crystals it doubles the UVA protection due to an internal synergy. Also from the **Innovation Co.** Eospoly UV products comprise nanofine rutile TiO₂ encapsulated into silica or polymer spheres that provide UVA and UVB protection and an instant optical illusion of smoothness and luminosity. Eospoly UV-composites are photostable and available with hydrophobic or hydrophilic properties or in combination with boron nitride as BNPoly to provide a luxurious skin feel.

Inorganic UV filters are preferred over chemical sun filters by many formulators because of their physical and chemical stability and non-irritating properties. In order to be transparent on the skin and effective against UV light, nano-sized particles of TiO₂ and ZnO are required. However, responding to controversy over the use of nano particles in cosmetics, **Kobo** offers a range of TiO₂ and ZnO where attenuation grade oxides are entrapped within a micron size acrylates copolymer matrix. Kobo's process reduces the agglomeration of aggregates, which enables formulators to create a product that can offer high SPF efficacy, low whitening effect and better tactile properties. The particles are coated with either organic or inorganic surface treatments and dispersed in various vehicles for easier use in formulation.

There is a growing trend towards supplying ingredient mixtures from the raw material supplier to the product manufacturer. It enables the supplier to be the only source of unique combinations and the manufacturer can reduce its material inventory, avoid multiple MOQs and very often, use cold temperature processing.

One such combination is Uvinul Easy introduced at In-Cosmetics 2014 by **BASF**.

Comprising dibutyl adipate, diethylamino hydroxybenzoyl hexyl benzoate, ethylhexyl methoxycinnamate, laureth-7 citrate, polyglyceryl-2 dipolyhydroxystearate, ethylhexyl

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triazone, bis-ethylhexyloxyphenol methoxyphenyl triazine, lauryl glucoside and triethanolamine to create a sun protection lotion it can simply be diluted with water and preservatives, a perfume and a rheology modifier added. For each 1% Uvinul Easy added to a formulation it results in 1 unit of SPF and also provides balanced UVA protection.

Merck KGaA also uses the word “Easy” in the trade name Eusolex T-Easy for a sunscreen material based on TiO₂ suitable for multi-functional skin products. It comprises nano~ TiO₂ coated with silica and cetyl phosphate and is compatible with BMDBM, ascorbyl palmitate and dihydroxyacetone.

Boosting Protection

Whether it is by finding better solubilisers for organic sunscreens or inhibiting their photo-degradation or by improving dispersions of particulate sunscreens increasing sun filter efficacy is a constant goal of formulators. Also important is the spreading characteristics of the composition. It must be easy to apply and the screen needs to stay on the skin surface in an even and unbroken film. Introduced at Formulate 2014 by **Suretech** in association with **Surfchem** new multi-domain polymers can boost SPF, produce waterproof films and enable emulsions to be applied to wet skin without the emulsion breaking.

The CosmoSurf CE series from **Suretech** are citrate polymers ranging from an alcohol-soluble liquid (octyldodecyl citrate crosspolymer) to oil-soluble solids (stearyl/octyldodecyl citrate crosspolymer). They can be used to improve deposition of an even sunscreen film from alcohol or oil-based sun protection products. The CosmoSurf PG series are polyglycerol esters that aid dispersion and prevent agglomeration of metallic oxide filters, particularly ZnO.

Unimer U-1946 is a VP/Hexadecene copolymer in octyldodecanol from **Induchem** that aids particulate dispersion and improves spreading properties. Because of its amphiphilic form it is able to rearrange itself and capture the particulates, providing long lasting stability and wash-off resistance. Performa MAV 6112 Polymer [INCI: C28-52 olefin/undecylenic acid copolymer] from **New Phase Technologies** is described as an innovative polyalphaolefin that offers a unique combination of both acid functionality and hyper-branched morphology to provide numerous benefits to personal care formulations. It can be neutralised in-situ to aid emulsification of actives, boost SPF and improve UVA protection and provide superior water resistance for sunscreens.

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Croda offers a number of SPF boosting materials: its OleoCraft polyamide structuring polymers can be incorporated into a wide range of sun care formulations, from emulsions to clear oil sprays. Their high molecular weight enables the polymers to stay on the surface of the skin, forming a cohesive water-resistant film. The polymers can also be used for rheology modification of the oil phase within the formulation and they can be incorporated into the oil, aqueous or ethanol phase of formulations.

SolPerForm 100 from **Croda** is a crosspolymer derived from PVP and wheat protein [INCI: Hydrolyzed wheat protein/PVP crosspolymer], which optimises the film forming properties of sunscreen emulsions and hence enhances the efficacy of the active ingredients. SPF can be boosted by as much as 70%, claims **Croda**.

Crodafos MCK is potassium cetyl phosphate and this emulsifier can effectively disperse the titanium dioxide in the formula and significantly increase its effectiveness, leading to a boost of SPF of the formulation. Finally Syncrowax ORM [INCI: Sorbitol/sebacic acid copolymer behenate] and Syncrowax OSM [INCI: Tribehenin, sorbitol/sebacic acid copolymer behenate] from **Croda** give structure to the oil phase and by laying down an even film on the skin, they effectively boost SPF by over 40%.

SunBoost ATB from **Kobo** is a proprietary mixture of antioxidants, anti-irritant and anti-inflammatory agents that when used in sunscreens in combination with organic or inorganic UV filters, provides an increase in SPF and PFA scores by more than 30%. An all-natural version, SunBoost ATB Natural, [INCI: Argania spinosa kernel oil, tocopheryl acetate, bisabolol], is also offered. SunBoost ATB is also available coupled with a TiO₂ dispersion that can provide up to 4.5 SPF units for each percent of TiO₂ in sunscreen formulas while delivering all the benefits of the antioxidants contained in SunBoost ATB.

When 5% Solarine III from **Greentech** is added to a solution of ethylhexyl methoxycinnamate it is claimed to increase SPF results by 70%. It is a mixture of dicaprylyl carbonate, cocos nucifera (coconut) oil, hippophae rhamnoides fruit oil, rosa canina fruit extract and voacanga africana seed extract and it also has anti-free radical and soothing properties.

Without making any claim to be natural a low molecular weight branched polyethylene wax from **Honeywell International** named Asensa PR 200 was found to improve sunscreen performance by approximately 12% when determined by in-vivo SPF measurement. Because of its film-forming properties it also adds water resistance to the composition.

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An excellent presentation at Formulate 2014 on behalf of **Stearinerie Dubois** is available through **Paroxite-Lehvoss**. It gives much background information about UV filters and contains many formulations illustrating high SPF results obtained by using a mixture of up to five different esters for maximum effect. **Dr. Straetmans** also offers many esters that improve application and increase SPF results including Dermofeel Sensolv [INCI: Isoamyl laurate]. It is a polar oil that exhibits excellent solvating power for commonly used UV-filters and is a good pigment dispersant.

Ashland supplies most of the commonly used UV filters plus its Antaron polymers. Differing hydrophobic/hydrophilic characteristics of the series provide a wide range of solubility and functionality. All have film-forming and pigment dispersing and suspending properties and are substantive to skin, which helps boost UV protection and provide water-resistance.

Advantage Plus polymer [INCI: VA/butyl maleate/isobornyl acrylate copolymer] from **Ashland** helps boost formula SPF and improves water resistance, while providing a low-shine finish on the skin. This polymer is recommended for anhydrous spray formulations.

Avoiding Photo-instability

Synoxyl HSS [INCI: Trimethoxybenzylidene pentanedione] from **Sytheon** is a photo-stabiliser and SPF booster when used with broad-spectrum sunscreens. It is said to be comparable to octocrylene in stabilising BMDBM and remains effective even at high UV exposure. It does not contribute to SPF at recommended use level but provides up to 50% in-vivo SPF boosting to both organic and inorganic sunscreens. It also acts as a skin protectant by reducing oxidative stress and is a stabiliser for retinol, natural vitamin E, vanillin and water-soluble organic dyes.

Encapsulating BMDBM in Hybrid PMMA beads improves its photo-stability and enables it to be used with other UV filters. The **Sunjin Chemical Co.** provides the beads, which contain 30% BMDBM, and they provide a means of incorporating BMDBM into silicon-based formulations and in the water phase of o/w emulsions. Hybrid PMMA is a physically tough solid and the physical shape of PMMA hybrid beads is maintained during high shear stress test or by topical pressure during application. Hybrid PMMA beads sit on top of the skin, forming an invisible physical barrier against UV rays and can be used on sensitive skin because the hybrid system eliminates penetration of organic filter into the stratum corneum.

Sunless Tanning

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Developing a tan is the skin's way of providing natural protection from solar radiation however the process of sun tanning results in the very damage that the tan is supposed to prevent. There was a presentation on behalf of **Gova** at Formulate 2014 at which Tosolin [INCI: Aqua, mannose, glucose, beta-glucan, sodium hyaluronate] was described as a means of speeding up the tanning process to provide natural protection with minimal skin damage. It was said that Tosolin optimises the activity of the melanocytes, which results in a deeper, faster and more prolonged tan for increased natural sun protection. It also regulates the Langerhans cells, reduces UV-induced redness, protects against DNA-damage and protects the collagen.

A similar claim is made for SymBronze 1659 from **Symrise**. It is a natural ingredient from the microalgae *Isochrysis galbana* and is a pigmentation enhancer with a proven efficacy to induce and accelerate sunless self-tanning. In after sun products it prolongs the tan and in 2005 it received the BSB Innovation Award as 'Most Innovative Raw Material - Cosmetics Functionals' 2nd place.

Another material to gain an innovation award [Ref 3] is Liposhield HEV Melanin from **Lipo Chemicals Inc.** 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 a fractionated vegetable derived melanin designed to be used topically as an additional defence. It shields the skin from high energy blue/violet visible light (HEV) that may induce premature ageing according to recent scientific studies.

Also claiming to offer protection against HEV is Solaveil ST-100 from **Croda**. Tightly controlled particle size distribution offers excellent UV protection and provides true transparency on skin. Solaveil ST-100 is very easy to use and suitable for all skin types. Its innovative silane coating enhances aesthetic appeal and Croda claims that it enables the formulation of light and luxurious UV protection products.

Melitane from **Lucas Meyer Cosmetics** contains acetyl hexapeptide-1 as a natural photoprotector and inflammation modulator. Melitane stimulates pigmentation and melanin under UV-inducing condition and represents an ideal complement to the skin's own level of natural melanin. It strengthens the skin's own defence mechanism and makes the skin less sensitive to UV-induced erythema.

The quantity of melanin produced by the body depends on the availability of tyrosine substrate and tyrosinase catalysing enzyme. The skin's pigmentation increases until a balance

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is reached between melanin production and degradation. In order to increase melanin production and speed up or intensify tanning the body needs to be provided with tyrosine and its catalyst, tyrosinase. Zymo Tan Complex [INCI: Propylene glycol, aqua, tyrosine, tyrosinase] from **I.R.A.** increases available tyrosine and tyrosinase and leads to a quicker and longer lasting tan without the necessity for prolonged sun exposure.

Working on the principal that if the level of tyrosine available could be increased melanin synthesis would also increase **Synerga** introduced Tyrostan [INCI: Potassium caproyl tyrosine]. It is a water-soluble liquid for aqueous products; an oil-soluble version is available as Tyrosinol [INCI: Caproyl tyrosinic acid, glyceryl oleate and sorbitan isostearate]. **Synerga** suggests that 5% Tyrostan or Tyrosinol be added to products for sun care before and during exposure and for suntan maintenance after exposure.

Melactiva [INCI: Maltodextrin, Mucuna pruriens seed extract] from **Lucas Meyer** is a natural tan accelerator extracted from Kapi kacchu seeds native to Australia and New Zealand. Its high L-DOPA content (30%) stimulates UV-induced melanin production so the natural tan appears faster, is intensified and lasts longer. It is compatible with dihydroxyacetone (DHA) so an instant tan can be induced.

Sunless or self-tanning preparations based on DHA have been available for at least fifty years. DHA is effective in quickly developing a tanned look, which fades within a few days. DHA preparations can also develop an unpleasant odour, a green colour or a lurid orange skin tone so with increased interest in sunless tanning much effort has been directed at improving the products.

SMEC DHA PF from **Lonza** is a sub-micron emulsion concentrate containing 10% DHA with trimethylolpropane tricaprilate/tricaprate, glycerin, cetearyl alcohol, cetareth-20, glyceryl stearate, PEG-100 stearate, steareth-2, dimethicone, ceteth-24, choleth-24, ethylhexylglycerin and phospholipids for sunless tanning. It may be used to make a milky, sprayable lotion for easy and even application. The special characteristics of SMEC DHA PF allow for increased stability of the DHA with no change in formulation colour or odour over time. Added emollients and moisturisers in this ingredient mix help counteract the drying effect of DHA.

Encapsulating DHA in a cyclodextrin complex to enhance its effect, improve stability and offer controlled release is the science behind CC DHA 50% [INCI: Dihydroxyacetone, cyclodextrin] from **I.R.A.** Tests versus the free form of DHA found the tan from CC DHA to

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take slightly longer to develop but the colour was more intense, lasted longer and was more even. **Salvona Consumer Care** offers DHA encapsulated in Salsperes, which are sub-micron spheres made of ingredients from botanical sources. The release of DHA from the spheres is activated when rubbed into the skin [INCI: Dihydroxyacetone, butyrospermum parki, aqua, hydroxyethyl behenamidopropyl dimonium chloride, polyquaternium-67, phenoxyethanol, ethylhexylglycerin]. **Soliance** (now Givauden) mixes melanin with DHA as Vegetan Premium that is said to provide a more natural, deeper summer tan. **Soliance** also offers pure DHA powder from vegetable sources and as a 50% solution.

The other popular self-tanning active is erythrulose, which although it provides some tanning effect by itself, it is more commonly used in combination with DHA to provide a more homogenous skin tone and a longer lasting tan with less streaking. Erythrulose also has moisturising properties and improves the stability of DHA. A supplier of erythrulose is DSM, which provides an interesting brochure on its properties.

Finally, the use of plant extracts to protect or heal human skin is well known but a recent patent describes sunscreen compositions for application to plants [USP 8,557,293]. It claims a sun protection concentrate containing TiO₂, ZnO and SiO₂, a wetting agent and a dispersant that is designed for spray application to plants and grass to give protection against heat stress, sunburn and ultraviolet radiation damage.

Space does not permit discussion of materials used to alleviate sun damage so these will form part of a feature on skin care later in 2015.

Ref 1 SCCS/1533/14 Revision of 23 September 2014; Opinion on 2-(4-(2-(4-Diethylamino-2-hydroxy-benzoyl)-benzoyl)-piperazine-1-carbonyl)-phenyl)-(4-diethylamino-2-hydroxyphenyl)-methanone (HAA299) as UV filter in sunscreen products.

Ref 2 SCCS/1516/13 Revision of 22 April 2014: Opinion on Titanium Dioxide (nano form) COLIPA n° S75.

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Ref 3 First Place at the Innovation Zone Best Ingredient Award at In-Cosmetics, Milan 2011.

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