

Suncare 2017

1st published in SPC 2017

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The author of this feature chaired the UV Conference in Paris that saw the launch of the Sunscreen Simulator, hosted by **BASF** [<https://www.sunscreensimulator.basf.com>]. Since then it has been one of the most important tools on my computer as a reference for those filters that are allowed and to what level in all the major markets around the world. It is also the first step in estimating what SPF and UVA protection to expect from various combinations of UV filters.

Referring to the Sunscreen Simulator it is disappointing to see that there are still only three UVA filters with global approval. They are butyl methoxydibenzoylmethane (BMBM) at 3% and known as Avobenzone in the USA; terephthalylidene dicamphor sulfonic acid (TDSA) at 3% and known as Ecamsule in the USA and zinc oxide to 25%. Because of the difficulties of getting new filters approved there have not been any new additions world-wide in the past twelve months but at last zinc oxide has EU approval although not yet (January 2017) listed in Annex VI of the European Cosmetic Regulation.

Approval of zinc oxide as a sun filter by the EU has stimulated interest by suppliers that are looking at ways to improve its clarity and sensual feel on skin. Zinc oxide has consumer appeal because of its long history in skincare products such as calamine lotion and diaper rash creams and it gains approval by dermatologists for patients with skin disorders, or those suffering sensitisation or irritation from chemical based sunscreens. It can provide sufficient broad-spectrum protection to be the sole UV filter in a product or can be used with an additional UVB filter to give sufficient UVA protection in high SPF compositions.

Under its ZinClear trade name **Antaria** provides a 50% zinc oxide dispersion in C12-C15 alkyl benzoate and caprylic/capric triglyceride and in Simmondsia chinensis (jojoba) seed oil for natural claims. It is also available at 55% in neopentyl glycol diheptanoate for a lighter, drier feel and at 65% in coco-caprylate/caprate. Antaria claims that the zinc oxide particles in its ZinClear dispersions 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. It claims this technology allows ZinClear to offer transparencies exceeding those of first-generation nanomaterial inorganic products.

Grant Industries offers zinc oxide dispersed in water, caprylic/capric triglyceride and in cyclopentasiloxane and dimethicone and in mixtures of these with C12-15 alkyl benzoate. The zinc oxide dispersed in cyclopentasiloxane or dimethicone is treated with PEG-10 dimethicone and Grant claims this offers enhanced compatibility with silicone-based systems including elastomer gels, emulsifiers, and oils. Grant also supplies Granpowder Z-35, which is a solid dispersion of ultrafine zinc oxide in polymethylsilsesquioxane and Granpowder T-35, titanium dioxide dispersed in polymethylsilsesquioxane. The particles are adsorbed onto the surface of the polymer through a dehydration mechanism and avoids the typical unpleasant sensorial properties of metal oxide sun filters. Suggested applications include colour cosmetic formulations such as foundations, pressed powders, lipsticks, and anhydrous make up.

Although dispersions simplify processing metallic oxides in powder form are still popular and **Kobo Products** claims that its UV Balance Powder 100 [INCI: titanium dioxide, alumina, hydrogen dimethicone] is attenuation grade TiO₂ (nano) that can provide UV balanced protection with 1 unit of UVA protection for every 3 units of UVB protection. This material is also available with a jojoba surface treatment as well as in a silicone dispersion, enabling easy UV balanced formulating. Sunjin T-80, **Sunjin Beauty Products**, consists of a non-nano TiO₂ that enables formulators to use just one UV filter to develop broad spectrum sun care products. Sunjin claims that T-80 can provide UVB

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protection comparable to that of 15nm TiO₂ and UVA protection better than that of 35nm ZnO. The T-80 series exhibits good photo-stability and is alumina free. This material is available with a range of surface treatments and in a variety of dispersions.

When titanium dioxide was first introduced as a possible UV filter formulators were faced with the difficulties of achieving dispersions without agglomeration of particles and of providing UVB protection with non-whitening on the skin. It was about the same time that the importance of UVA protection and the problems of photo-instability in sun care products became generally known and this gave impetus to the use of microfine metallic oxides. Producers made improvements in surface treatments and controlled particle size distribution and dispersions in a wide variety of carrier liquids became available.

The Innovation Company offers nano~ zinc oxide dispersed in hydrogenated polydecene and zinc oxide rendered non-nano by encapsulating the particles in silica spheres. It names this its Eospoly system and claims Eospoly UV composites provide UVA and UVB protection and an instant optical illusion of smoothness and luminosity. By varying the particle size, it is able to offer three grades of Eospoly zinc oxide giving different ratios of UVB/UVA protection. The silica spheres provide a soft-focus effect and **The Innovation Company** uses the same silica encapsulation technology to offer non-nano titanium dioxide dispersions, again with differing ratios of UVB/UVA protection. The Innovation Company also produces Creasperse CC dispersions, which are a range of ready-to-use colour shade dispersions that offer UV protection in anhydrous systems such as BB and CC creams.

It is well known that BMBM is unstable when exposed to UV radiation, particularly in the presence of other sunscreens like ethylhexyl methoxycinnamate. This led to the development of stabilising solvents and the same solvents have proven useful in providing photostability to TiO₂ and ZnO dispersions. **Hallbrite** has two TiO₂ dispersions and is launching a ZnO one at In-Cosmetics. A silica coating protects the oxide particles, which are dispersed in SolStay S [Ethylhexyl methoxycrylene] and Hallbrite BHB [Butyloctyl salicylate]. SolaStay S1 interacts with both the singlet and triplet states and acts to return UV filters to their ground states without absorbing sunlight. HallBrite BHB is highly polar with a low viscosity and improves formulation aesthetics while imparting an elegant moisturising feel to the skin. Both these solvents are available from Hallbrite to formulators facing problems of photo-instability and they have the added benefits of being good solvents for organic sunscreens and of providing a pleasant skin feel.

Stearine Dubois/Seppic supplies DUB Optima [INCI: Diisopropyl adipate, diisopropyl sebacate, propylene glycol dicaprylate/dicaprate, C12-15 alkyl benzoate] described as an optimised mixture of esters to facilitate the solubilisation of sunscreens, boost the formula's SPF, improve its photostability and achieve unique sensory qualities. Dermofeel BGC [C12-15 alkyl benzoates] from **Dr Straetmans** is a polar oil that is a good solvent for organic UV filters and a dispersing aid for inorganic oxides. The sensorial profile delivered to the finished product gives a light and non-greasy skin feel and supports good spreadability on the skin. Dr Straetmans makes similar claims for its Dermofeel Sensolv [Isoamyl laurate] and Dermofeel TC-7 [Triheptanoin]

Suppliers offer dispersions of TiO₂ in a variety of solvents and many make mention of being photostable. **The Innovation Company** disperses oxides in its Alphaflow [Hydrogenated polydecene] and Dedraflow [Hydrogenated polyisobutene] carriers. Alphaflow is a pure emollient with inert and photostable characteristics while Dedraflow is a very soft emollient often used to replace cyclomethicone. C12-15 alkyl benzoate or caprylic/capric triglyceride are the carriers of choice for **Croda Clarus** inorganic sun filters and polyhydroxystearic acid with isostearic acid is used as the

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preferred surface treatment. Croda claims that its ZnO dispersions are highly stable offering UVA protection, true transparency on application and conferring a light and elegant skin feel.

Croda also markets Solaveil SpeXtra dispersions of coated TiO₂ with a mean particle size of 179nm dispersed in a choice of carrier media. Each dispersion contains 55% solids and the TiO₂ content is specifically designed to deliver an optimal balance of UVA and UVB attenuation and to act as a physical shield to reduce UV and near-UV induced free radicals within the skin. The newest addition to the SpeXtra range, Solaveil XT-40W, uses an aqueous base, giving the freedom to formulate light and spreadable O/W emulsions and can also be easily combined with organic sunscreens in the oil phase to give exceptional synergy for high SPF performance, states Croda.

Finding synergy between sunscreens, between sunscreen and solvent or between sunscreen and additional ingredients is an important step in achieving high SPF without an overload of UV absorbers. Patent USP 9265715 describes compositions comprising an organic sunscreen in combination with silica particles and barium sulphate particles and nylon-6 particles surface treated with hydrogen dimethicone that provides a minimum 10% improvement in SPF. The patent also lists virtually every material that could also be added to block or diffuse sunlight. One of those listed as a possible additive is apatite and **Kalichem** supply hydroxyapatite in powder form as Apalight 100 and Apalight PF as an aqueous dispersion. When used in sunscreen formulations they show comparable sunscreen efficacy to micronised titanium dioxide with significantly less whitening. Hydroxyapatite is listed as a UV filter so it should always be used in combination with classified UV filters.

For those that prefer using ready-mixed bases Olisun from **Kalichem** is a carefully formulated mixture of ethylhexyl methoxycinnamate, aqua, butyl methoxydibenzoylmethane, octocrylene, C12-15 alkyl benzoate, glycerin, bis-ethylhexyloxyphenol methoxyphenyl triazine, sodium cocoyl hydrolyzed wheat protein and alkyl polyglucosides. It is described as a semi-finished sunscreen base that when added at 20% gives SPF 15 and 36% gives SPF30. Kalichem claims that its composition overcomes solubility problems with the organic UV filters, that it is stable and complies with EU restrictions on UV filters, including the requirement to provide a ratio of 1/3 UV-A/UV-B.

Providing water resistance is an essential claim for most sunscreen products. This can be achieved by the addition of suitable film-forming polymers and Covestro offer two polyurethane polymers; Baycusan C1000 [Polyurethane-34] is for high SPF emulsion products and Baycusan C2000 [Polyurethane-64] is for high SPF aerosol, dry oil spray and clear gels. They provide water resistance and can be applied to wet skin. **AkzoNobel** supply three polymers that provide water and abrasion resistance: Demacryl 79 polymer is a hydrophobic, high molecular weight acrylates/octylacrylamide copolymer suitable for spray application. Dermacryl E is a styrene/acrylates copolymer suitable for adding water resistance to emulsion products and Dermacryl AQF is an acrylates copolymer that may be used in emulsions and for spray applications.

Holding actives to the site of application is also a claim made for Volarest FL from **Croda**. It is a 30% active solution of acrylates/beheneth-25 methacrylate copolymer optimised to create high viscosity systems with pseudoplastic shear-thinning properties and immediate recovery of structure. It creates targeted sprays with an even dispersion of fine droplets and excellent viscosity build-up at low concentrations. It can suspend particulates and can be used to hold active ingredients on the site of application by imparting resistance to abrasion or rub-off.

Croda also supplies OleoCraft high molecular weight polyamide polymers that stay on the surface of the skin, forming a cohesive non-water-soluble film. When incorporated into sun care formulations they provide SPF boosting and aid water resistance and can be used for rheology modification of the

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oil phase within the formulation. Also, from Croda and claiming to improve SPF efficacy is SolPerForm 100, a hydrolyzed wheat protein/PVO crosspolymer derived from PVP and natural wheat protein. It optimises the film forming properties of sunscreen emulsions and hence enhances the efficacy of the active ingredients, boosting SPF by as much as 70%. SolPerForm 100 works with both organic and inorganic UV filters, and enhances UVA efficacy as well as SPF.

Bentone clay-based rheological modifiers from **Elementis** are recommended to improve application characteristics of sun care products and have an SPF boosting effect. Bentone hydrophilic clays offer a shear thinning viscosity to water-based formulations while organoclay powders and Bentone gel dispersions impart a unique rheological performance to anhydrous oil systems and to the oil phase of w/o emulsions. Bentone gels are offered in a wide variety of solvents including silicones, hydrocarbons and natural oils and they improve the sensorial feel and physical stability of oil-based products and emulsions. They maintain an even layer on skin so if used in sun care the UV absorbers are evenly applied and do not slump between the ridges on skin. In-vitro testing shows an improvement in water-resistance and a small but nevertheless significant boosting in SPF in a wide variety of sun care formulations.

Because of the lack of new filters development continues to look at ways of maximising the potential of existing filters and of mitigating the deleterious effects of sunlight, which now involves offering protection from near Infra-red (IR) as well as UVA and UVB. Patent USP 9,480,632 appears in the patent abstracts section of this edition of SPC and the full patent presents a case for IR protection. It maintains that IR occupies 80% of sunlight and near-IR causes active oxygen to be generated through mitochondria, leading to a decrease in anti-oxidant content in the skin. Then, expression of matrix metalloproteinase-1 (MMP-1), a collagen-decomposing enzyme, increases, resulting in wrinkle formation.

Claiming broad spectrum protection and particularly effective against the effects of IR radiation is Arabian Cotton PCF [*Gossypium herbaceum* (cotton) callus culture] from **Vytrus Biotech**. This company specialises in the development and production of ingredients from plant stem cells for dermo-cosmetic applications and claims Arabian Cotton PCF is a natural photoprotector. In vitro and in vivo testing shows broad spectrum protection by suppressing the formation of reactive oxygen species (ROS). Vytrus Biotech describes Arabian Cotton PCF as a glycerin based product derived from cultured plant stem cells from *Gossypium herbaceum*. When topically applied, it complements and boosts the skin cells' own defence mechanisms to overcome the photo-damage and photo-aging caused by sun radiation.

Not only is protection now required against IR but also against blue light. According to **Greentech** more than 50% of free radicals are due to IR and blue light exposure and 60% of people spend a minimum 6 hours per day in front of a digital device. Phenylpropanoids are botanical compounds able to protect the skin against UV and to reduce production of free radicals. Discovered by molecular screening, Soliberine [*Buddleja officinalis* flower extract] is exceptionally rich in two phenylpropanoid derivatives and for its powerful activity against the harmful effects of natural and artificial light.

Although TiO₂ and ZnO are acceptable to COSMOS as "natural" sunscreens the search continues for alternatives that are not listed in Annex VI. **Cosmact** is a French supplier of natural oils and claims that its Karanja oil [*Pongamia glabra* seed oil] has a natural SPF averaging 18.7. If added to an emulsion at 10% the SPF is 3.4 but if gelled this increases to 24.2. Grades with added TiO₂ and ZnO are also available.

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A tan is still seen as an improvement to white skin so a suggestion to get more tan from less sun is to apply a tanning accelerator such as Zymo Tan [INCI: Propylene glycol, water, pentylene glycol, tyrosine, tyrosinase] by **I.R.A.** that increases melanin production under the stimulation of solar radiation. Melitane [INCI: Glycerin, Water, Dextran, Acetyl Hexapeptide-1] from **IFF-Lucas Meyer** is a peptide that stimulates pigmentation by synthesis of melanin from the melanocytes under UV-inducing condition and is suggested as a natural photoprotector and inflammation modulator.

If fully protected against sun light a chemically induced tan is required. Despite the problems of formulating to overcome instability and uneven colouration the most commonly used material is dihydroxyacetone (DHA). A way to enhance its effect, improve stability and offer controlled release is to encapsulate it in cyclodextrin and this is available from **I.R.A** as DHA 50% CycloSystem Complex. Tests versus the free form of DHA found the tan to take longer to develop but the colour was more intense, lasted longer and was more even. For artificial tanning the carrier for DHA is very important and **Sytheon** recommends HydraSynol DOI, [Isosorbide dicaprylate], a new molecule with very green chemistry derived from corn. It improves the tanning effect and offers long-term hydration by up-regulating Aquaporine-3 responsible for skin hydration and skin homeostasis.

Solar radiation causes many unwanted effects in skin and hair. Mitigation of these effects is the focus of the next feature, which will be about skin care actives.

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