

Ingredients designed to afford sun protection are subject to world-wide legislation, which unfortunately, is not helpful for progress towards new ultraviolet absorbers. In North America eight OTC sunscreen ingredients have been submitted to the FDA through the time and extant (TEA) process for review and approval but none of these reviews have yet been completed (January 21st 2013). It is not only the FDA that is delaying improved sunscreens; European manufacturers are still waiting approval for nano zinc oxide.

With no new UV absorbers to play with formulators and their ingredient suppliers continue to look at ways of enhancing the efficacy of those that are allowed and at means of mitigating the deleterious effects of sunlight to human skin and that, plus sunless tanning, is the focus of this article.

One material that does have (almost) worldwide approval for use at up to 25% by weight of the total composition is nano-sized titanium dioxide (TiO₂). Approval in the EU is still not confirmed despite Opinion SCCS/1516/13, which declared Nano-TiO₂ applied topically as UV-Filter is safe at a maximum use concentration of 25% in cosmetics, provided the material is 99.5% pure TiO₂, that it is predominantly in its rutile form with a maximum content of 15% anatase TiO₂ and that it is photostable in formulations and has low photo-catalytic activity.

Parsol TX from **DSM** claims greater than 99.5% purity in the rutile form and therefore meets all the criteria required in the above listing and it is easy to disperse in the oil phase of emulsions due to its highly hydrophobic surface treatment. This coating of silica and dimethicone also ensures that it does not react with sensitive ingredients and polyacrylate thickeners so gel formulations are possible.

According to the **Innovation Company**, when the Creasperse range of UV-dispersions was developed, the most important criteria was the photostability of the UV pigments and carrier oils. This resulted in the range containing only rutile type TiO₂-crystals and photostable lipids, such as hydrogenated polyisobutenes, hydrogenated polydecenes and silicones. The range includes titanium dioxide, zinc oxide and ferric oxide and materials may be offered in more than one particle size, enabling controlled compromises between transparency and UVB and UVA protection.

Kobo offers a new patent pending product; Composite ACT-50, which contains attenuation grade TiO₂ entrapped within a micron size acrylates copolymer matrix. This moves the particle size outside the nano range. Kobo's process reduces the agglomeration of TiO₂ aggregates, which enables the creation of a product that can offer high SPF efficacy, low whitening effect and better tactile properties. Other non-nano versions from Kobo are found in its T-80 range, which comprises titanium dioxide in a variety of coatings. It is claimed they enable formulators to use just one physical TiO₂ UV filter to develop broad spectrum sun care products providing UVB protection comparable to that of 15nm TiO₂ and UVA protection better than that of 35nm TiO₂. TX-80 from Kobo is nano-TiO₂ that has been coated in silica and then dimethicone. It is alumina-free so it can be combined with butyl methoxydibenzoylmethane (BMBM).

Despite SCCS Opinion SCCS/1518/13 that the use of nano-zinc oxide (ZnO) as a filter up to a concentration of 25% is safe for non-spray products approval has yet to be given [January 31st 2014] for its use

within the EU. However formulators are no doubt planning ahead and **Umicore** has a range of zinc products including Zano 10 Plus, which is nano-ZnO coated with triethoxycaprylylsilane. It is claimed to provide maximum levels of UV protection, while maintaining a high level of transparency when applied onto the skin. Zano 10 Plus provides UVA protection and it can be used with TiO₂/Xperse, also from **Umicore**, to give full broadband UVA-UVB protection with exceptional transparency and aesthetics in a finished formulation.

Solar radiation or free radical generation by TiO₂ and ZnO can lead to the instability of BMBM but a mixture of colourless carotenoids from **IBR** is claimed to prevent this. The material is trade named IBR-Phyto(flu)ene and comprises two carotenoids, phytoene and phytofluene that are colourless in visible light but absorb in the UV range. They are present in most carotenogenic organisms including microorganisms, algae, fungi and plants and they inhibit melanin synthesis and the generation of free radicals while providing measurable UVB and UVA protection. The same carotenoids appear in Phytofloral from **IBR**, which is marketed as a dietary supplement to protect the skin from UV damage. As with Phyto(flu)ene, it reduces inflammation, inhibits collagenase expression and protects DNA from oxidative damage.

Northern Europeans do not like to look pasty white and believe that their appearance is enhanced by a tan; hence the popularity of tanning booths and tanning sprays. Tanning lotions have been available for at least 40 years yet the most effective active ingredient remains dihydroxyacetone or DHA, and it is the only sunless tanning active to be approved by the FDA. It is a colorless 3-carbon sugar that when applied to the skin causes a chemical reaction with amino acids in the surface cells, thus producing a darkening effect. It does not damage skin as it only affects the stratum corneum. A colour change is usually apparent within an hour of application but maximal darkening may take 8-24 hours to develop and should last until the dead skin cells rub off, usually 5-7 days with a single application.

However adding DHA to an existing moisturising lotion or sun protection product is likely to create problems. It is prone to instability, manifesting as colour changes in the product and the development of a distinctly unpleasant odour. It highlights skin imperfections such as lesions and scarring and can also colour it an exciting shade of orange. The first problem to overcome is that of creating a stable formula. Avoiding prolonged heating above 40C, avoiding the presence of amino acids, peptides and proteins and buffering the composition to pH 3.5 – 4.5 using citric acid is recommended. Using citric acid for pH adjustment has the added advantage that it improves the stability of the composition through its antioxidant and chelating properties.

The DHA fake tan reaction is Maillard Browning taking place at body temperature. Because the Maillard Browning reaction requires an amino group and a reducing sugar (DHA), formulators are advised to remove all sources of reactive nitrogen when making stable pure white formulas. The rate limiting stage in Maillard Browning/DHA tanning is the formation of a Schiff's base between the reactive nitrogen in skin and DHA, paradoxically there are merits in including low levels of amino acids such as tyrosine in formulas. To achieve instant skin colouring preparations may incorporate cosmetically approved soluble dyes

but iron oxides are to be avoided unless surface treated. Patent USP 7,875,264 describes using DHA with inorganic pigments made hydrophobic with octyltriethoxysilane in order to provide an instant tan appearance combined with a prolonged tanning effect. USP 8,206,731 describes the inclusion of iron oxide pigments encapsulated within Unispheres [INCI: Mannitol, cellulose, hydroxypropyl methyl cellulose] from **Induchem** in a composition containing DHA and erythrose.

Other recommendations include incorporating ethoxydiglycol, ethylene glycol, glycerin or sorbitol at quite high levels in the formulation [USP 623,187] and using cetearyl glucoside with cetearyl alcohol or polyglyceryl-2 dipolyhydroxystearate with lauryl glucoside as preferred emulsifier systems, [USP 6,348,202]. USP 8,182,794 claims the addition of methylsulfonyl methane to DHA compositions greatly improves the tanning process and that the addition of glycerin results in a poor tanning response. The addition of butylene glycol or pentylene glycol was found to impart the most natural looking tan from a solution containing 5% DHA and 5% methylsulfonyl methane at a pH of 3 – 3.5.

The addition of metabisulfite salts is also said to improve stability. Products containing DHA are susceptible to microbial attack and a preferred preservative system is benzyl alcohol with methyl paraben. Hydantoin derivatives, imidazolidinyl urea, diazolidinyl urea, quaternary ammonium compounds and cationic polymers, are to be avoided. **Global Seven** suggest using Hest G-18-0 [INCI: Glycereth-18 ethylhexanoate, glycereth-18] as a water-soluble emollient with antimicrobial properties. Thickening low pH solutions can present a problem but Pure-Gel B994 from **Grain Processing** is a modified starch [INCI: Sodium hydroxypropyl starch phosphate] that adds viscosity and a nice skin feel, even at pH 3.5.

A method of stabilizing DHA by encapsulating it is the science behind CC DHA 50% from **IRA**. It comprises DHA solution encapsulated in cyclodextrins obtained from starch to provide a time release system and tests showed that the colour was more intense, lasted longer and was more even than from DHA alone. Additionally, unlike the free form of DHA, CC DHA was found to not stain fabric, making it a more desirable option for cosmetic application.

Erythrose also undergoes Maillard Browning and tans skin in much the same way as DHA does but not as intensely so it is not as effective. However combining erythrose with DHA with is a common way of providing a better shade and more even skin tone and of prolonging the tanning effect. **Spec-Chem Industry** markets Tanbest TM 8810 as a mixture of erythrose and DHA, which also contains Poria cocos extract that has antioxidant and anti-inflammatory properties and an aloe extract with moisturizing properties. USP 8,263,045 describes a composition containing DHA with an amphoglycinate such as sodium oliveamphoacetate to provide fast development of a uniform, more intense, longer-lasting and a more natural looking tan with more predictable colour characteristics than with DHA alone.

Soliance in France make DHA by fermentation of local agricultural waste, which is fed into sophisticated fermenters to produce 60% DHA solution, which can be used by manufacturers who prefer using solutions. Pure DHA (Vegetan) powder is prepared by precipitating the fermented DHA using natural alcohol. Odour can be a problem with DHA so **Soliance** worked with **CPL Aromas** to produce a masked blend of DHA

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trade named Vegetan FL Creation [INCI: Dihydroxyacetone, aqua, parfum, polysorbate 20, caprylyl/capryl wheat bran/straw glycosides] that has none of the characteristic smell of DHA lotions.

Instabronze from **Alban Muller** is a combination of DHA with N-acetyl tyrosine. The amine function of N-acetyl tyrosine is blocked by the acetyl group, which prevents a reaction within the mixture. When spread on the skin, the acetylated amino acid is hydrolysed by the enzymes of the epidermis and can then combine with DHA. Evenly massaged on the skin, it compensates for the differences in protein composition between skin areas and provides a more regular and longer lasting colour.

The tan is lost through natural cell desquamation so an interesting way to prolong it has been suggested by **IBR Ltd.** the suppliers of IBR-Dormin. This ingredient is an extract of Narcissus tazetta bulb and is said to prolong the tan by slowing down cell proliferation. It maintains younger healthier skin and provides the means for better skin protection and prevention of hyper proliferative cell disorders.

Floraesters K-20W Jojoba from Floratech are hydrolyzed jojoba esters in aqueous solution. They are emollient with high substantivity to skin and clinical trials show that sunscreen actives in combination with K-20W are retained on the skin after water immersion. Further trials showed that adding 1% K-20W or a combination of 0.5% K-20W and 1% erythrose to a lotion containing 5% DHA produced the greatest percent increase and retention of skin colour. Test subjects preferred the formulations that contained K-20W for evenness and longevity of tan, moisturising effect and odour.

Biomimetic technology has produced several actives that mimic natural MSH in skin and so can trigger natural tanning. For example Heliostatin [INCI: Pisum sativum extract] from **Vincienc** stimulates melanocytes in a dose-time dependent manner to produce increasing levels of melanin. Ronacare Bronzyl [INCI: Palmitoyl dihydroxymethylchromone] from **Merck** is said to increase the melanin content of the basal layer of skin by 43% when applied over a period of 10 days. This increase is not triggered by sunlight but by stimulating the elongation of dendrites of melanocytes and to their connectivity with keratinocytes.

For those seeking a tan with minimal sun exposure the use of tanning accelerators could be of interest.

From **Alban Muller** we have Actibronze, a mixture of hydrolyzed wheat protein, acetyl tyrosine and copper gluconate in powder form. It is said to accelerate sun tanning by bringing an extra source of tyrosine to the epidermis. L-tyrosine is the precursor of melanin and needs the enzyme tyrosinase during the initial steps of melanogenesis to be oxidised into melanin. The production of melanin is stimulated by exposure to UV rays and by increasing the availability of tyrosine in the skin less sun exposure is required to form a tan.

Acetyl tyrosine is also the principal active in MelanoBronze, which also contains an extract of Monks pepper [Vitex agnus-castus] from **Mibelle Biochemistry**. Monk's pepper contains beta-endorphin-like compounds that actively stimulate the melanin production in melanocytes and the combination of acetyl tyrosine and extract of Monk's pepper accelerates and enhances skin pigmentation independent of exposure

to the sun. Patent USP 8,414,869 suggests the use of acetyl tyrosine with curcumin and phenyl isothiocyanate to maximize sun tanning with minimal sun exposure.

A similar effect is claimed for Phototan LS 2261E from **BASF Beauty Creations**. It is a mixture of arginine, ornithine and tyrosine with sorbitol and silica and is said to stimulate the enzymatic activity of dopa oxidase within the melanosomes, resulting in an acceleration of the biosynthesis process of epidermal melanin pigments. Zymo Tan Complex PF from **I.R.A** increases the melanogenesis process by providing its substrate tyrosine and its specific enzyme tyrosinase. Tanositol [INCI: Inositol] from **Provital** is a material derived from *Ceratonia siliqua* (Carob) fruits that is claimed to increase the melanin content of the melanocytes, to stimulate collagen synthesis and to provide a deep and prolonged tan.

The exact opposite is the function claimed for Origa'light from **Berkam**; obtained from oregano leaves this material has anti-tyrosinase properties so inhibits skin darkening. It is also rich in polyphenols from the hydroxycinnamic acid family and is able to absorb UV radiation and contribute to protecting the epidermis. Also claimed to inhibit erythema and pigment darkening is a combination of AA-2G and Alpha Glucosyl Hesperidin from **Hayashibara Biochemical Laboratories Inc.** Activoil Spotless from **Innovacos** is a combination of *Ribes nigrum* (black currant) seed oil with extracts of *Paeonia suffruticosa* root, *Rosmarinus officinalis* (rosemary) leaf and *Solidago virgaurea* (goldenrod), specifically targeted at reducing age spot pigmentation and colour.

Concerns about sun exposure are because of the damage that it is now known it to cause to both the epidermis and dermis, particularly through the generation of free radicals within the skin. It is claimed that UV radiation is responsible for 80% of skin aging and it especially affects the extracellular matrix (ECM) proteins, which form the skin's connective tissue and the degradation of which accelerates due to the increasing level of matrix metalloproteinases (MMPs). Mitigating this damage is claimed for various ingredients, usually by providing natural antioxidants and free radical scavengers and also by inhibiting the release of MMPs.

SunActin from **Mibelle Biochemistry** is an extract of sunflower shoots [INCI: *Helianthus annuus* (Sunflower) sprout extract, tocopherols, glycerin, lecithin] that is claimed to inhibit the production of MMPs responsible for the degradation of major skin components and to boost the protective effect of sunscreens while neutralizing their oxidant effect. It is added to sun protection products at from 2- 5% to prevent the formation of sunburn cells and protect the skin from oxidative stress. Similar claims are made for a cell culture extract of *Vigna radiata* meristematic tissues from **Innovacos**, which forms part of its Plant C-Stem portfolio of active plant stem cell cultures.

Pomegranate is a rich source of polyphenolic compounds with documented antioxidant, anti-inflammatory and anti-carcinogenic activities. Its efficacy at curtailing free radicals promotes anti-inflammatory activity and protects skin from cell death and erythema by sun exposure. Pomegranate constituents have synergistic and complementary actions, with aqueous extracts promoting regeneration of dermis and its seed oil supporting claims for the regeneration of epidermis. **Innovacos**, the suppliers of InnoPOM, claims this

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combination of aqueous extracts and seed oil [INCI: Punica granatum fruit juice, punica granatum extract, maltodextrin, lecithin] is said to prevent and repair UV-induced skin erythema and damage to the barrier function.

Plerasan Equilibria from **Biophil** is a beta-glucan with skin barrier repair properties that moisturises, soothes, calms and refreshes skin suffering from UV exposure. Nio-Glucan from **Naturalis** comprises carboxymethyl beta-glucan, magnolol and honokiol with anti-inflammatory and antioxidant properties encapsulated within niosomal vesicles. Magnolol and honokiol are isomers of the same chemical found naturally in magnolia bark and they are the principal actives in Herbex Magnosoothe from **Crestchem**, which also supplies a synthetic form called Kopnolia.

SunBoost ATB [INCI: Argania spinosa (Argan) kernel oil, tocopheryl acetate, bisabolol] from **Kobo** is a proprietary mixture of antioxidants, anti-irritant and anti-inflammatory agents that is claimed to increase SPF and PFA scores by as much as 30% when used in sunscreens in combination with organic and inorganic UV filters.

Argan oil is enjoying a popularity boom in personal care products but **BASF Beauty Creations** has investigated the properties of argan leaves and isolated, purified and concentrated the flavonoids found therein to produce Arganyl. It is claimed that Arganyl protects collagen against MMP destruction and elastin from glycation and reinforces the cutaneous structure to provide a firm and smooth skin. **Beauty Creations** also markets DN-Age, an extract of Cassia alata leaves that reduces photodamage to DNA at the nuclear and mitochondrial levels by inhibiting the formation of free radicals and active oxygen species. A third material from **Beauty Creations** is Litchiderm [INCI: Butylene glycol, Litchi chinensis pericarp extract], which also has anti-free radical activity and inhibits MMP-1 expression.

The majority of recent introductions of active ingredients for cosmetics have been obtained from plants and seed oils but synthetic chemistry has given formulators peptides with which to make new functional products. **Lipotec** is a foremost supplier of active peptides and suggests three peptides plus one synthetic molecule that together offer complete protection to the skin against UV-induced skin damage. Chromane [INCI: Dimethoxy chromanol] is an oil-soluble synthetic molecule with powerful antioxidant and free radical scavenging properties. It prevents the nitration of tyrosine and protects cellular DNA from oxidation by reactive oxygen species induced by UVA radiation. Preventhelia is diaminopropionoyl tripeptide-33 that prevents damage caused directly or indirectly by UV radiation to DNA and proteins, so inhibiting the appearance of premature skin aging. Hexapeptide-51 amide is the active in Juvefoxo that is said to protect DNA from UVA-induced damage and to activate its natural repair mechanism to extend cell life. Responses to stressful stimuli decrease with age resulting in fragile, tired and dull skin. Thermostressine from **Lipotec** is acetyl terapeptide-22, which increases heat shock protein levels in skin to provide a protective shield that confers a stress tolerance against solar radiation, pollution and metabolic and osmotic stress.

Note: Only the principal ingredients are shown in the majority of INCI lists in this article and those interested are urged to seek further details from the suppliers.

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Further reading

Brockway, B, (2013) Formulating with DHA. Workshop presentation given at Formulate 2013 and available through IMCD.

For more in-depth studies of the subject of sun protection the following articles have appeared in the International Journal of Cosmetic Science (IJCS).

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- Jain, S. K, Jain, N. K. (2010), Multiparticulate carriers for sun-screening agents. IJSC, 32: 89–98
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