

Sun Care 2005

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Once worshipped as the bringer of life the sun now gets blamed for all human ills, from grey hair to dry skin, facial lines, wrinkles and skin cancer. However it is still appreciated for its warmth and the sense of well being that it brings, especially to Northern Europeans. In order for us to enjoy its benefits without deleterious side effects a multi-million pound industry has arisen with the emphasis on filtering out harmful UV-A and UV-B radiation from the total solar spectrum reaching earth.

Unfortunately sun filters, as opposed to physical sunshades, are active chemicals and they, or the products of their degradation can themselves be irritants or allergens and their use and concentrations are restricted by legislation, which varies from country to country. Therefore to maximise product benefits formulators use two approaches; the use of microfine inorganic oxides either as the sole provider of protection or in combination with traditional organic filters, and various means of enhancing SPF values by careful formulation techniques.

The problem with early attempts to use microfine oxides was the white or blue sheen imparted to skin. However better micronising and dispersion techniques have substantially reduced this problem and materials such as the Clarius range from **Uniqema Solaveil** can give high levels of protection from elegant formulations that are virtually transparent on the skin.

Enhancing SPF values applies to all types of sun protection products and generally relies on promoting good dispersion of the active in an unbroken film on the skin. This is achieved by the solvent properties of the carrier in the case of organic actives and by dispersing aids with insoluble oxides. Frequently both types of material exist in the same product, which further complicates formulation. The rheology of the product is also of great importance; once applied the material should remain where required in a film of reasonable thickness. Products for spray application present difficulties in this respect and to make formulation even more interesting, most sun protection products are required to be water-resistant.

Various silicone compounds are particularly useful in sun care formulations as they can solubilise actives, improve surface films, increase water-resistance and provide enhanced SPF. The alkyl methyl silicone (AMS), stearyl dimethicone, was first proposed for improving sun protection products at the IFSCC Congress, Sydney, 1996. Cetyl dimethicone is a translucent, white AMS fluid that imparts a substantive and occlusive film on the skin; it retains the soft, emollient and non-tacky aesthetics of silicones, and provides controlled moisturising. It also increases the effectiveness of sunscreens and, more specifically, physical sunscreens. In published details an o/w emulsion with 7.5% TiO₂ showed an increase in *in-vitro* SPF from 9.1 to 22.4 when cetyl dimethicone was introduced into the formulation. For formulating ease, cetyl dimethicone is compatible with a wide range of organic cosmetic ingredients and is easy to incorporate in the oil phase. In most formulations it can be used to partially or completely replace mineral oil or petrolatum.

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A more recent example of silicone technology is demonstrated by Dow Corning 9040 silicone elastomer blend, which contains silicone elastomer swollen with cyclopentasiloxane. This product is useful as a rheology modifier for various types of personal care formulations where it can improve stability, suspend active ingredients, and modify the aesthetics of the formula. A study published by **Dow Corning** illustrates a dramatic increase in SPF obtained from a composition comprising 4.0% ethylhexyl methoxycinnamate (EHMC) with 1.5% butyl methoxydibenzoylmethane in an o/w emulsion. Replacing 4% cyclomethicone with the elastomer blend increased *in-vivo* SPF from 5.7 to 18 and conferred significant water-resistance to the formulation. Not all silicone compounds are compatible with organic sunscreens; Dow Corning publishes an invaluable chart showing compatibilities; whereas cyclomethicones are compatible with EHMC the dimethicones with viscosity above 1.5cs are not.

For optimum SPF results when using microfine oxides it is important not only to obtain a good dispersion but also to avoid subsequent agglomeration of the particles. The dispersing aid is critical in this respect and the use of pre-dispersed material such as the Tioveil and Solaveil products from Uniqema is recommended. Once the material is incorporated into the composition product rheology is an important factor. Carbomers and xanthan gum give poor results in *in-vitro* determinations and clay-type rheology modifiers are favoured as suspending aids.

Three commercially available types are in common use: Laponite from **Rockwood Additives Ltd.** is a synthetic material; Veegum from **R.T.Vanderbilt** is mined volcanic smectite clay and Polargel is montmorillonite clay from **Amcol Inc.** Laponite produces very thixotropic dispersions. Water-clear gels may be obtained that can be used in spray applicators. Veegum is available in various grades and also produces thixotropic dispersions but with a much lower viscosity, making them suitable for lotions. Polargel UV1116 is montmorillonite with titanium dioxide and Picea excelsa (spruce) extract in an aqueous dispersion and published data shows that it is capable of virtually doubling SPF results when added to o/w formulations at 7.5%.

Arch Personal Care Products recently launched a high-molecular weight polymeric ester trade named Liquiwax PolyEFA, which is octyldodecyl/PPG-3 myristyl ether dimer dilinoleate. It has high wetting characteristics that improve the dispersion of physical sunscreens and make the lotions easier to apply. High solids loading can be achieved with minimal increase in viscosity and it also imparts high emolliency and moisturising to the skin. SMEC Sun is another interesting material from Arch. It uses liposome preparation technology to prepare a sub-micron emulsion concentrate that contains 15% EHMC with 6% ethylhexyl salicylate and 1% Benzophenone-3. Tests show that a 25% dilution of this concentrate returns SPF 10 in *in-vitro* testing.

Various solvents improve organic sunscreen solubility and inorganic sunscreen dispersion. C12-16 alkyl benzoate is well known for this function and **Finetex** produce a proprietary blend of this material in association with dipropylene glycol dibenzoate, which adds an occlusive property, and PPG- 15 stearyl ether

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benzoate, which helps in coupling the three esters. This unique blend produces a moisturiser with superior tactile and performance properties and is an excellent solvent for benzophenone-3 and butyl methoxydibenzoylmethane. Also from Finetex is phenylethyl benzoate, trade named Finsolv Sun, which has even better solvent properties for organic actives.

Other solvents that are particularly suitable for improving sun screen products include butylphthalimide isopropylphthalimide, available as Pelemol BIP from **Phoenix Chemical Inc.** and Pecosil PS-100, INCI: dimethicone PEG-7 phosphate. Pelemol BIP is a eutectic mixture of N-butylphthalimide and N-isopropylphthalimide that has excellent solubilising properties and Pecosil PS-100 is an effective solubiliser for organic sunscreens and a dispersing aid that prevents agglomeration of inorganic oxides.

Degussa has launched a high solids dispersion of micro fine hydrophobically modified titanium dioxide in diethylhexyl carbonate. The primary particle size is approximately 20 nm and it provides a high SPF response and one star rating UV-A protection. Trade named TEGO Sun TDEC 45, it is claimed that sunscreen products containing it show no whitening and are transparent on skin after rub-in. Diethyl carbonate is a good solvent for many organic sunscreens so combining inorganic and organic actives in one product is helped significantly.

UV-filter Solubility in %	Solubility in % ^{w/w}
Benzophenone-3	4.5
4-Methylbenzylidene Camphor	10
Butyl Methoxydibenzoylmethane	5
Ethylhexyl Triazone	3
Diethylhexyl Butamido Triazone	6
Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine	1.5

Also from Degussa is TEGO Sun Z 800, a hydrophobically coated zinc oxide particle that can be readily dispersed into any common cosmetic oil with high shear mixing. Its strong hydrophobic character keeps it stable within the oil phase and it has no significant influence on the pH value of the emulsion. Its small particle size allows the formulator to use up to 15 % in products with a transparent appearance and a pleasant skin feel.

A favoured and highly effective dispersant for ultrafine titanium dioxide and zinc oxide microfine pigments is polyhydroxystearic acid. This may be obtained as Octacare DSP-OL100 from **Associated Ocel Co. Ltd.** It can significantly increase UV absorption of sunscreens containing pigments, in addition to reducing

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whitening when applied to skin and it dramatically decreases viscosity of dispersions, allowing higher concentrations of pigment to be used.

Several new emulsifiers are of interest to the formulators of sunscreen products; Sensanov WR, **Seppic**, is C20-22 alkyl phosphate with C20-22 alcohols. It is an anionic emulsifier that requires neutralisation to reach maximum performance. Said to impart a unique velvety skin feel it may be used at low concentrations and 3% will provide an o/w emulsion capable of holding 15% pigments in suspension. **Symrise** introduced Emulsiphos at Formulate 2004. This is also an anionic emulsifier and is a mixture of potassium cetyl phosphate with hydrogenated palm glycerides. It is used at levels from 1% to 3% to prepare o/w emulsions and is neutralised in-situ to pH 4 – 9 but preferably to a slightly acid pH. It is electrolyte tolerant and may be used with water-soluble actives.

Cognis have recently launched an anionic emulsifier, Eumulgin SG, INCI: sodium stearyl glutamate, an emulsifier that is electrolyte tolerant and capable of emulsifying polar and non-polar oils. It is used at low concentrations and is particularly recommended for sunscreen products containing water-soluble actives. For formulators who prefer cationic emulsifiers **Degussa** proposes the use of Varisoft TA100, INCI:

distearyldimonium chloride, a cationic o/w emulsifier based on renewable raw materials with excellent emulsifying properties. It is said to provide extremely light emulsions that adsorb quickly to form a matte finish on the skin surface and to give a cooling sensation in creams and lotions without a whitening effect.

Protecting hair and hair colour from solar radiation may not be as medically important as protecting the skin but it is a rapidly growing marketing niche. (The author believes that he was first to formulate such products in 1979!) Solar radiation induces local production of photo-induced free radicals which destroy natural and artificial hair colour; they rupture cysteine bonds thus reducing hair strength, and generally result in hair looking dull and lifeless. Although the same actives may be used as for skin there are problems of substantivity and a number of alternative materials are now available.

One of the first materials to be launched specifically to protect the hair against photodegradation was Escalol HP-610 from **International Specialty Products** (ISP). It is a mixture of dimethylpabamidopropyl lauryldimonium tosylate with propylene glycol stearate, which is substantive to hair and it minimises tryptophan degradation and disulphide bond cleavage. More recently ISP has launched Escalol HP; INCI: dimethylpabamidopropyl laurdimonium tosylate, as a 100% active powder and ISP has published extensive test protocols and results that show it reduces disulphide bond cleavage by nearly 50%, tryptophan degradation by up to 25%, resistance to combing by about 50% and that it is substantive to hair, even when used in rinse-off products.

Parsol SLX from **DSM Nutritional Products**, INCI: polysilicone-15, is also backed by extensive test data that show 5% in a leave-on product significantly protects semi-permanent dyed colour from fading and reduces chromatic changes after UV irradiation, and only 1% is required to significantly protect colour fade in natural hair and hair coloured with permanent dyes. Tests also show a 50% reduction in tryptophan and

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cysteine degradation and improved combing when a conditioner containing 3% Parsol SLX is used.

Substantivity to hair can be dramatically improved by incorporating guar hydroxypropyltrimonium chloride or polyquaternium-10 into the formulation, enabling a reduction in the Parsol SLX concentration.

The third material developed specifically to protect hair from UV radiation is Crodasorb UV-HPP from **Croda**. It is a 65% active solution of polyquaternium-59 in butylene glycol and is water-soluble and can be cold-processed. Extensive efficacy data show that when used at 3% in hair products it affords significant levels of protection against UVB damage. **Grant Industries** suggest the use of CRT-W, a silicone/polyacrylate resin, at 3-5% to retain hair colour and it may be combined with sun protection actives to enhance longevity of effect.

Hair damage on exposure of the hair to sunlight is caused by photo-induced superoxide anions and hydroxyl radicals and these effects are cumulative. **Sederma** has taken a natural approach by providing Heliogenol, which comprises concentrated actives from *Helianthus annuus* (Sunflower) seed extract in butylene glycol. According to Sederma this plant was chosen because the flower follows the movement of the sun during the day and therefore deliberately exposes itself to more radiation than other species. The petals, but also the seeds contained in the centre of the flower, must contain a particularly effective solar protection system, especially as the seeds must ensure the very future of the species, without any harmful mutations, and without degradation of the genome or biochemical mechanisms.

Published tests indicate that Heliogenol has a reparative effect on the hair, and that the anti-oxidant efficacy was related to the concentration of the active agent. An efficacy of 50% was obtained with 0.50% Heliogenol and 100% was obtained when Heliogenol was added to compositions at a concentration of 1.5%. According to Sederma, even after shampooing and rinsing, Heliogenol at a concentration of 0.2%, actively protects hair exposed to the sun, and provides protection which is three times as effective as that produced by Vitamin E.

Inhibiting free radical damage in skin is an essential part of solar protection; *Punica granatum* (Pomegranate) extract available from **Active Concepts** through **Optima Chemicals**, has been shown to reduce oxidative damage and it also appears to boost SPF results. An interesting study [Noah Worcester Dermatological Society, 2004, Dr. Murad] described using the extract in sunscreens for topical application plus taking it as an oral supplement. Results showed that SPF protection of regular sunscreen increased by about 25% and oral pomegranate extract appeared to increase SPF protection of regular sunscreen by an average of 18%.

EUK-134, INCI: ethylbisiminomethylguaiacol manganese chloride from **Atrium Chemicals** is said to mimic the activity of superoxide dismutase (SOD) and catalase with one molecule. SOD occurs naturally in skin and combines singlet oxygen with water to form hydrogen peroxide. However, this is still a harmful chemical and catalase, which is also part of the skin's natural defence mechanism, then converts it to water plus oxygen. EUK-134 achieves this process by reduction and oxidation of the manganese ion and clinical

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trials show it to inhibit DNA damage and reduce inflammation caused by pro-inflammatory cytokines, which are the result of oxidation of lipids and proteins in the skin.

Trade Name	% w/w	Supplier	INCI
Phase A			
Arlamol HD	1.50	Uniqema	Isohexadecane
Finsolve TN	3.00	Finetex	C12-15 Alkyl benzoate
Estol 1540	3.00	Uniqema	Ethylhexyl cocoate
DC 245 Fluid	2.25	Dow Corning	Cyclopentasiloxane
Antaron V220	1.00	ISP	PVP/Eicosene copolymer
Span 60	1.00	Uniqema	Sorbitan stearate
Arlacel 165F	1.50	Uniqema	Glyceryl stearate, PEG-100 stearate
Parsol MCX	8.00	DSM Nutritional Products	Ethylhexyl methoxycinnamate
Tinosorb S	2.00	Ciba	Bis-Ethylhexyloxyphenol methoxyphenyl triazine
Uvinul BMBM	1.00	BASF	Butyl methoxydibenzoylmethane
Titriplex III	0.10	S.Black	Disodium EDTA
Phase B			
Aqua (Water)	54.45		
Veegum Ultra	0.40	R.T.Vanderbilt	Magnesium aluminium silicate
Keltrol RD	0.10	Kelco	Xanthan gum
Arlatone MAP 160K	3.00	Uniqema	Potassium cetyl phosphate
Glycerine	3.00	Various	Glycerin
Phase C			
Solaveil CT-100W	11.30	Uniqema	Aqua, Titanium dioxide, Isodeceth-6, Oleth-10, Aluminum stearate, Alumina, Simethicone
Phase D			
Preservatives	Qs		
Tinosorb M	3.00		Aqua, Decyl glucoside, Propylene glycol, Xanthan gum
Perfume	0.40		

1. Disperse Keltrol RD and Veegum Ultra into cold water, then add other Phase B ingredients and heat to 75-80°C with agitation.
2. In a separate container combine Phase A ingredients and heat to 75-80°C.
3. Add Solaveil CT-10W to phase B with stirring (500rpm) and maintain temperature at 75-80°C.
4. Add phase A to B/C with stirring (500rpm), then homogenise for 2 minutes at high shear.
5. Cool with moderate stirring (300rpm) to RT, add phase D below 45°C.

In-vitro SPF 40.42

In-vivo SPF 36.7