Changes in sun care: UV protection and beyond

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Modern consumers lead busy lives and are becoming increasingly demanding of the products that they purchase. Although most consumers are aware that excessive sun exposure can be dangerous, everyday use of sunscreen products is often neglected. Manufacturers are therefore motivated to constantly improve sun care products to make them more aesthetically pleasing, as well as effective. High efficiency, multi-functionality, and easy application are crucial to the modern sun care product.

The importance of product aesthetics and correct application

In general, sunscreen products are perceived as difficult to apply and likely to leave greasy, white marks on clothes and digital devices, which are factors leading to their improper use. Consumers usually apply insufficient amounts of sun protection products to the skin, and as a result, obtain 20-50% lower protection than desired.[1] A key challenge of formulators is therefore to improve the sensory properties and spreadability of the product. Consumers are also lax in subsequent reapplications, so it is important to extend the durability of the cream by increasing its resistance to water and other factors such as chlorine, temperature, sweat, and transfer.

Product form

Emulsions

The form of the product undoubtedly influences its sensory properties and ease of application onto the skin. Oil-in-water (O/W) emulsions are usually lighter and feel more pleasant, but water-in-oil (W/O) systems are characterised by greater water resistance, which is a significant advantage for sunscreen products.

To counter the heavier feel of W/O systems, silicones are often used in the continuous phase of the emulsion as they provide a silky feel. They also improve the even distribution of the cream on the surface of the skin, contributing to a higher SPF value. Thanks to a new emulsifying system based on a blend of *polyglyceryl-4 isostearate, coco-caprylate/caprate*, and *disteardimonium hectorite*, it is possible to obtain natural W/O emulsions with extremely light textures, similar to that of water-in-silicone emulsions.[2] The emulsifier achieves this by promoting the formation of large droplets in the internal aqueous phase, giving a lighter, fresher feel than traditional W/O emulsifiers.

Sticks

Emulsions are the most common form of sun care products, but less common formats include oils, two-phase mists, and most recently sticks. The recent trend for sticks came to Europe from South Korea where they are very popular because of their convenience and clean, 'hands-free' application.

A popular sub sector of sun sticks are transparent sticks, which leave no colour residue upon application and are perceived as more suitable for sensitive skin. Hydroxystearic acid is a structuring agent that can gel hydrocarbons, esters and even some silicones whilst retaining clarity, giving formulators an easy-to-use tool for making this product format.[3] Novel silicone elastomers such as PEG-10 dimethicone/vinyl dimethicone crosspolymer also allows the use of water-soluble components in a stick structure, greatly increasing the range of actives that can be included in otherwise anhydrous formulations.[4]

The stick format is also often used for soothing and cooling applications in after sun products. Menthol is often used for a cooling effect upon application. Menthol can be irritating to the skin so it is recommended to use it in the form of menthyl PCA in combination with octyldodecyl PCA, giving a milder cooling effect without skin irritation, while also stimulating the synthesis of epidermal lipids.[5] Calamine is another material that is often incorporated into after sun sticks for its skin calming properties.

Convenience, ease of use, and multi-functionality are becoming ever more important for consumers. For these reasons the range of available sunscreen products is constantly expanding and now also includes more controversial formats such as wet wipes, shower bars and sun care products with 'wash on' technology.[6,7]

UV filters: Avoiding issues and obtaining ideal performance

Formulating with UV filters is not easy and there are numerous factors to consider when using them. There are two main types of UV filters; organic filters, also known as 'chemical' filters, and inorganic or 'physical' filters. Recently, there has been a slight move away from the use of organic filters, which absorb UV radiation, as they can degrade and can cause allergic reactions. Inorganic filters such as nano titanium

dioxide and nano zinc oxide, which reflect UV radiation, are more stable and therefore are becoming more widely used.

Avobenzone (butyl methoxydibenzoyl methane) is the most commonly used organic UVA filter, but has low stability and is susceptible to crystallisation. UVB-absorbing filters such as octocrylene and oxybenzone, or even some antioxidants, such as quercetin, can help to stabilize avobenzone. However other UVB filters contribute to its degradation. Ethylhexyl methoxycinnamate (OMC) is a widely used UVB organic filter as it provides good protection, has a light skin-feel, and is low in colour and odour. While OMC has its positives, it also destabilises avobenzone and so it is not recommended to use these together, as it can result in formulations that are not photostable. This stabilising/destabilising action comes from the fact that when avobenzone absorbs a photon of UV light, it is excited to a triplet energy state. While stabilising substances such as octocrylene help quench avobenzone to return it to its ground energy state, ethylhexyl methoxycinnamate reacts with high energy avobenzone to form products that do not function as UV filters.[8]

It has also been shown that avobenzone degrades when used with untreated titanium dioxide and zinc oxide. The FDA has banned the use of these inorganic filters with avobenzone for precisely this reason.[9]

Encapsulating avobenzone can be beneficial, as it separates the filter from the environment and the skin, minimising the risk of degradation and irritation. Encapsulation in polymer microspheres effectively protects avobenzone, minimising interaction with materials such as ethylhexyl methoxycinnamate, improving photostability while also improving the skin-feel.[10-13]

Formulators of natural products tend to prefer using solely inorganic filters for sun protection, and non-nano filters where possible, due to concerns surrounding the potential effects of nano materials on human and environmental safety. Non-nano filters generally provide poorer sun protection and cause more whitening than nano filters as the larger particle size means the spectrum of light they reflect is shifted away from the UVB region.

Environmental considerations are also becoming more important in consumers' choice of sun care products. The bleaching of the Great Barrier Reef has led to research on the impact of UV filters on coral. As a result, Hawaii has banned the common UVB organic filters, oxybenzone and ethylhexyl methoxycinnamate, and a 'reef-safe' claim has propagated in the sector, although this claim is poorly defined. The issue of reef safety has so far been focused on organic UV filters but there is evidence to show that untreated titanium dioxide and zinc oxide also bleach coral.[14]

Many of the drawbacks of inorganic sunscreens can be countered to a degree through surface modifications. Surface treatments help to prevent agglomeration, and so reduce whitening and improve skin-feel. They also reduce interactions between the inorganic filters and other materials, improving compatibility with avobenzone and reducing the impact on coral bleaching.

Beyond UV filters, the choice of emollients in the formulation is also critical to performance. It is essential that organic UV filters remain fully solubilised as crystallisation or separation will lead to a reduction in protection. Esters are a fantastic option as they tend to be good solubilisers of organic UV filters and also have a lighter skin-feel than traditional oils. UV filters tend to have a greasy or heavy skin-feel, but this can be improved through the use of dry, light esters such as octyldodecyl neopentanoate, methylheptyl isostearate, or shea butter ethyl esters. As previously discussed, silicones are often used to formulate light W/O creams to counter the unpleasant feel of UV filters. However they tend to have poor compatibility with organic UV filters, which limits their use in some formulations. When using silicones, diphenylsiloxy phenyl trimethicone can be used to improve compatibility between silicones and organic filters due to their phenyl groups.

High SPF products

Several brands are competing in the development of creams with ever-increasing SPF, and we can see products on the market with SPF 70, 90, and even 100! Many wonder whether such high protection is necessary, and if it could even be detrimental. Properly applied sunscreen with SPF 50 should block 98% of UVB rays, and when doubling the SPF to 100, the protection from UVB rays only raises to 99%.10 UVB radiation is the main cause of sunburn, but UVA penetrates deeper into the dermis and is more difficult to block. Exposure to both UVA and UVB causes the formation of harmful free radicals in the skin and is associated with a greater risk of developing cancer. It is therefore not only important to look for products with a high SPF, but also to look at the degree of UVA protection a product provides. In the EU, products must have a UVA / UVB protection ratio of at least 1/3. Most sun care products emphasise the importance of frequent application, but 'once-a-day' products have become very popular and are the source of some controversy. Anti-cancer organizations are concerned that such products can give a false sense of security that puts consumers at greater risk of sunburn. The submission of such declarations on the label is prohibited in Australia, a country with some of the strictest regulations regarding sun protection.[15, 16]

Protection beyond UV light

As in many of the personal care sectors, consumers are expecting multifunctionality from their sun care products, as a time and cost saver. Beyond mass market, sun care products are expected to contain not only UV filters, but also active ingredients, antioxidants, vitamins, and more.

These ingredients are used in self-tanning, after sun and specialist daily care products such as lip balms, as lips contain a small number of melanocytes and are extremely susceptible to sunburn. Creams and lipsticks often include vitamins C and E, also known as the 'vitamins of youth'. These vitamins block the processes that take place in the skin after exposure to the sun, helping to neutralise free radicals. These vitamins degrade rapidly in their natural state and so more stable and functional forms are often used instead. Examples include ascorbyl glucoside, a glucose-stabilised ascorbic acid, and raspberry seed oil / tocopherol succinate aminopropanediol esters, a ceramide-like molecule obtained from raspberry seed oil and vitamin E succinate. Using oils with naturally high levels of antioxidants as an emollient is an easy way to improve the efficacy of after sun products. A specific grade of canola oil that combines oxidative stability with high levels of vitamin E and phytosterols has been shown to reduce sunburn cell formation and soothe irritated skin.[17, 18, 5, 31]

Epigallocatechin gallate (EGCG) is a primary component of green tea and a polyphenol with strong antioxidant properties. Green tea is not only a trendy ingredient, but it has the ability to regenerate DNA.[19] Unfortunately, it is unstable and poorly soluble in water, which makes its use difficult, but this can be improved through modern stabilisation technology. Thanks to the use of a multi-stabilising microemulsion, the solubility of EGCG is improved and the stability is significantly enhanced.

Antioxidants reduce redness and can also reduce or even repair damage caused by harmful radiation. Quercetin is a powerful antioxidant and can also stabilise UV filters. *Sophora japonica* flower extract is a natural source of quercetin and its dimer form shows even greater biological activity than the monomer, helping to restore the skin after oxidative stress.[20, 10]

The inclusion of antioxidants and anti-inflammatory ingredients in sun care products is controversial, as despite their benefits, there is an argument that by reducing the erythemal response of the skin, consumers are likely to spend more time in the sun, leading to a risk of long term damage. Delaying skin erythema in this manner also leads to a higher SPF value, which is not a true reflection of the products' ability to protect skin from UV irradiation.

Protection from pollutants

Anti-pollution is popular in cosmetics; increased pollution negatively affects our skin as it can dehydrate, sensitise, and disturb the regulation of sebum. There are several strategies for preventing the damage that pollution can cause. Biosaccharide Gum-4 forms a non-occlusive film on the skin and hair that acts as a protective barrier against a wide range of pollutants including heavy metals, particulate matter, and carbon particles. It also helps the distribution of UV filters on the skin, leading to a more homogeneous application and improving sun protection. This is a good example of the kind of multifunctionality required by the modern consumer.

A different strategy is to limit the cellular response to pollution and in doing so, reduce skin damage. Fucoidans (sulphated polysaccharides) occur naturally in the brown algae *Ascophyllum nodosum*, and protect against external aggressors not through forming a barrier on the skin, but by limiting the activation of the Aryl Hydrocarbon Receptor (AhR) pathway, which is the major biological pathway of the skin's response to pollutants. The prolonged activation of this pathway leads to numerous deleterious effects: lipid peroxidation, DNA damage, breakdown of the skin barrier, redness, and hyperpigmentation. *Ascophyllum nodosum* reduces the interaction of pollutants with AhR receptors, and hence, the damage they can cause.[20, 21, 22]

Blue light and infrared radiation

Inorganic filters such as titanium dioxide and zinc oxide form a physical barrier and protect against UV radiation and also to some extent against pollution, infrared and blue light. Blue light is high energy visible light (HEV), emitted primarily by the sun, but also by electronic devices. It can have a negative effect on vision, circadian rhythm, and skin by interacting with photoreceptors, which while predominantly present in our retinas, are also present in the skin.[23-27] Blue light can induce oxidation and inflammation, and thus accelerate skin ageing. *In vitro* and *in vivo* testing has shown that *Capsicum annum* red pepper extract is rich in capsanthin compounds. These are classes of carotenoids which have the ability to absorb blue light and thereby reduce its harmful effects. This extract works as an even stronger antioxidant than the well-known beta-carotene, helping to prevent changes in DNA and reducing cellular responses to blue light such as pigmentation. The extract also protects collagen from infrared light, which has the ability to deeply penetrate the skin and stimulate the formation of free oxygen radicals.[28, 5] New grades of titanium dioxide have also appeared on the market, which show a greater ability to protect against infrared radiation than conventional UV filters or pigments currently used in colour cosmetics. These grades of titanium dioxide have been shown to limit the rise of skin temperature when exposed to IR irradiation, indicating that IR light is being blocked.[29]

Sunless Tanning

It is difficult to achieve a 'dream tan' when using products with high sun protection. Self-tanning products are an increasingly important segment of the sun care market, as consumers want to achieve a tanned look without compromising their health. Self-tans are considered safe and are a perfect solution for those who want to enjoy a tan without having to expose themselves to UV radiation. The base component of self-tans is dihydroxyacetone (DHA), which reacts with amino acids in the stratum corneum of the epidermis and gives a brown colour a few hours after application. However, as DHA does not

stimulate melanin synthesis and does not protect against UV radiation, sunscreens should still be used to protect the skin. The addition of pigments is desirable in self-tan formulations because it provides an instant bronzing effect and improves the immediate appearance of the skin. However, DHA requires a fairly low pH and is incompatible with iron oxides, so many cosmetics manufacturers have so far struggled with the introduction of pigments, ordinary or pearlescent, for self-tanning products. The solution can be to separate the pigments from DHA, placing them in separate phases of the emulsion and using pigments with extra surface modification. This makes it possible to achieve a more stable product, limiting DHA degradation.[30]

Conclusion

It is not always easy to balance aesthetics with efficacy in sun care products. Cosmetics that provide sun protection help to reduce the risk of skin cancer and slow down 'photo-ageing'. Educating consumers about the need for frequent and correct use of protective sun care products is undoubtedly very important, but introducing new ingredients to improve their ease of application and pleasant feel is also key. The constant misuse of sun care products raises questions about the way consumers have been informed about sun care as well as the efficacy of the SPF system. Modern consumers are concerned not only about the harmful effects of UV radiation, but also about the effects of pollution, blue light and IR. They also pay attention to the impact of the products they buy on the environment, through both the product packaging and also the product's ingredients. The growing list of consumer requirements: their active lifestyles, pro ecological attitudes, and desire for high protection against a wide range of factors mean that the development of sun care products is becoming quite a challenge. Technological advancements and multifunctional materials such as those discussed in this article should help formulators in the development of modern sun care formulations that meet both consumers' aesthetic and safety needs. PC

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