Innovation in inorganic UV filters in sunscreen

WHY SUN PROTECTION IS IMPORTANT?

There are many benefits that are brought by sun, such as positive feeling and mood and trigger the production of vitamin D in skin. But giving to the skin an overdose of ultraviolet rays (UV) may be harmful to our bodies and result in premature skin ageing, skin cancers, eye damage and photo-immunosuppression.

UV radiation is made up of three types of rays with different wavelength (λ): ultraviolet A (UVA) (λ = 315–380 nm), ultraviolet B (UVB) (λ = 280–315 nm), and ultraviolet C (UVC) (λ = 100–280 nm). The UVA is weaker than UVB but passes further into the skin. Lately, it was defined the Near-UV (HEV) light is just beyond the cut-off from the UVA to the visible region of the electromagnetic spectrum (380 nm-500 nm), being related directly to the degradation of collagen and elastin resulting in formation of wrinkles and premature aging.

IMPORTANCE OF THE INORGANIC SUNSCREENS

Sunscreens are a form of photo-protection most widely used by the public to reduce UV damage. They contain UV filters, organic and inorganic, aiming specifically to filter the UV light to a certain level to protect the human skin from the harmful affections of sunlight. The sunscreen consisting of inorganic UV filter such as titanium dioxide (TiO₂) and zinc oxide (ZnO) has long been considered safe and effective. They are particularly preferred by individuals having high propensity for skin irritation from sunscreens containing organic UV filters. Despite these advantages, the use of this type of filter has been limited because of their poor aesthetics due to their large particle size. The decrease in size results in the formation of wrinkles and premature aging.

TYPES OF INORGANIC SUNSCREENS: ZnO AND TiO₂ AND OTHER METALLIC INORGANIC SUNSCREENS AND DERIVATIVES

The more commonly used inorganic UV filter are titanium dioxide (TiO₂) and zinc oxide (ZnO). Due to their large particle size, they leave on the skin a white film. They also have a low dispersity, leaving users with a gritty feeling. Since 90-thies ZnO and TiO₂ nanoparticles gradually replaced the large TiO₂ and ZnO particles in order to overcome these drawbacks. However, the decrease in the size results in photo-catalysis and generation of reactive oxygen species.

In this respect, some surface modifications were made for TiO₂ and ZnO in order to reduce the photo-catalytic activity at the surface of nanoparticles, to alter their hydrophobic/hydrophilic character to improve their dispersibility in various media, or to enhance their compatibility with organics matrix by introducing new functional groups that can react with organic molecules. These modifications require coating the particles with certain substances. There are direct coating and indirect coating. Direct coating is a passive protection. A protective film of organic or inorganic material envelops the nanoparticle to prevent direct contact with the viable cells and generate dangerous free radicals. Although the inner part of the nanoparticles is quite active and might generate electrons under UV irradiation, these generated electrons cannot migrate to the particle surface and therefore avoid any contact with the aqueous solution or oxygen to create free radicals.

KEYWORDS: inorganic filter, metallic inorganic UV filters, sunscreen
Some inert materials such as Al₂O₃ (1) and SiO₂ are used to coat the particles to suppress their photo-catalytic activity. Metal-doped nanoparticles showed a decrease in the degradation of ingredients in the final products under the effect of sunlight. Other suitable dopants for the oxide particles include manganese (especially in form of Mn³⁺), vanadium, chromium, cerium, selenium, iron, nickel, copper, tin, aluminium, lead, silver, zirconium, zinc and cobalt.

It has been found that an UV protection obtained by hydrothermal treatment of a particulate metal oxide and subsequent application of a manganese-containing coating is possible to suppress the pro-oxidative properties. The hydrothermal treatment leads to the formation of stable nanocrystallites of uniform size and shape, resulting in a reduction in reactivity and photo-activity. It is preferred for the metal oxide parent substance to carry a first coating essentially consisting of manganese compounds and a second coating essentially consisting of aluminium and/ or silicon compounds or vice versa. It may be furthermore preferred for the particulate UV protection agent to be hydrophobicized by application of a further organic coating or layer. The organic outer coating or layer can consist, for example, of silicone oils, alkylsilanes, olefinic acids, polyols or organophosphonic acids, or mixtures thereof (2).

Inorganic layer with metal oxides or silicon oxides produces stable coating. But the density of the film seems to be a problem that decreases UV-shielding ability of original particles powder (3). Thus, the efficient inhibition of photo-catalytic activity with less coating amounts will be essential. The organic substances are preferred for coating the particles because they form a thinner layer covering the surface of particles. There are many agents that are proved to be able to decrease the photo-catalytic activity of particles without much affecting its capacity to protect against the UV. It helps also improving the compatibility between the particles and the surface of the polymers and increasing the dispersion stability of particles in various organic media.

The most popular are silane coupling agents used for particle modifying, 3-aminopropyltriethoxysilane, n-propyltriethoxysilane (4) 3-methacyloxypropyl trimethoxy-silane, γ-methacryloyloxy-propyltrimethoxysilane (5), 3-amino propyltrimethoxysilane, 3-isocyanatopropyltrimethoxysilane (6), 3-glycidoxypropyltrimethoxysilane (7), 3-methacloxypropyl trimethoxysilane (8) and some other silane coupling agents have been developed to modify the surface of nanoparticles used in sunscreen (Z-Cote and Z-Cote HP1 from BASF) (UV-TITAN M160, M212, M262, M195 from Merck, (SOFTITAN 85 from SUNJIN).

Besides an enhanced aesthetic light formulation of Solaveil ST-100 that offers transparency to the skin due to the silane coating (Croda, INCOSMETCS, Innovation 2013), this technology provides an excellent UVB protection due to the tightly controlled particle size distribution of the new Titanium Dioxide (TiO₂) dispersion.

Coating of a specific organic phosphorus compound was also developed for UV protection particles that are used in self-tanning products containing dihydroxyacetone (example: RonaCare® Bronzy™, MERCK). This innovation came from a trend of combination of self-tanning products with UV inorganic filters. However, the presence of metal oxides like TiO₂ causes many unwanted effects such as degradation of dihydroxyacetone, colour reactions of the TiO₂ particles with dihydroxyacetone and with further organic molecules in the composition, or greying of the formulations upon UV irradiation. Organic phosphorus compounds selected from the group of the hydroxalkyldiphosphonic acids, alklyphosphonic acids, aminoalkylisophosphonic acids or organic phosphoric acid esters help reduce or prevent the degradation of the dihydroxyacetone in the cosmetic formulations. The titanium dioxide particles post treated by this method have also the property of preventing colour reactions (9).

The surface of nanoparticles is also modified by grafting or anchoring polymers such as polymethacrylic acid (10) poly(methylmethacrylate) (11), polystyrene (12) and polivinylpyrrolidone (13). These polymers can penetrate the aggregated nanoparticles and react with the activated sites on the nanoparticle surface. The interstitial volume inside the nanoparticle aggregates becomes partially filled with grafted macromolecular chains, and the aggregated nanoparticles become further separated. In addition, the surfaces of the nanoparticles become hydrophobic which is important for the miscibility of the filler and matrix (14).

Contrary to the direct coating, the method of indirect coating is based on the addition of semi-stable radical scavengers such as MeO – MnO, MgO, nitroxides NO, antioxidants-phenols to the nano-filter composition. They provide an active intervention in the radical generating process at the surface of the crystal filter. However, it is recommended to combine direct and indirect coating in which the indirect coating can act as a second defense line against a generation of free radicals caused by an imperfect direct coating (15).

A good example is SOLAVEIL SPEXTRA (Croda, INCOSMETCS) Innovation 2013), providing protection across the UVA and near-UV (HEV) light. The innovative dispersion of TiO₂ in a mixture of Polyglyceryl-2 caprate / Sucrose Stearate /Simmondsia chinesis (Jojoba) Seed oil / Stearic Acid /Alumina /Glycerol caprylate / Squalane is giving a talc-like feel on skin and protection against free radicals damage in the near-UV part of the spectrum.

Another example is the UV-TITAN M040 (Merck) in which the TiO₂ is coated with silica and glycerin for a perfect dispensability in water phase and a good stability versus antioxidants and proteins. Kobo company developed the TiO₂ (KSL-0261) and ZnO (KSL-0161) with particles sized over 100 nm after surface treatment with jojoba esters. Nevertheless we should mention the new ecological combination of TiO₂/ZnO with coconut oil in the mixture VEGELIGHT TiO₂/ZnO (30 dispersion) by the Grant Industries, that is an innovation product with a biodegradability (ECOCERT) and water resistance presented at INCOSMETICS in 2013. The particle size is about 150 nm in the coconut oil, presenting low whitening and a silky touch along with a high SPF value with a guaranteed UVA protection. SUNJIN Company obtained the non-nano TiO₂ (SOSTITAN 60) with silica, alky sylane and lauroyl-lysine for an ECOCERT grade.

NEW INORGANIC SUNSCREENS AND DERIVATIVES:

HYDROXYAPATITE, TRICALCIUM PHOSPHATE, CERIUM, SILICON MICROSPHERES, GLASS MICROSPHERES AND HAIRY ROOTLES OF ENGLISH IVY

Besides the development of conventional filter TiO₂ and ZnO, many new filters are being also developed to meet the high
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demands of consumers. These advanced filters are proven to be more efficient, safer not only for the health of users but also for the environment, and can be replacements for TiO₂ or ZnO to be used in future sunscreens.

Hydroxyapatite is one of the potential candidates. It is a compound already present in the human body, being the main mineral constituent of bone tissue. Its nature leads to a complete dermal and systemic tolerance. More important, hydroxyapatite is found to be highly effective as a physical sunscreen agent to protect the skin from UV rays. This effectiveness is even greater than that shown by zinc oxide and titanium dioxide. Besides being an excellent physical UV filter, it also acts as an SPF booster that advantageously helps to reduce the concentration of chemical agents typically used in known sunscreen products. In addition, hydroxyapatite shows an extremely low whitening effect, thus overcoming aesthetic drawbacks and problems of proper skin transpiration (16).

The optical absorption of hydroxyapatite can be further improved by doping with Zn²⁺ and Mn²⁺ ions (17). Tricalcium phosphate Ca₃(PO₄)₂ is another phosphate particle which has the potential to be an active ingredient in sunscreens as it is non-toxic, non-mutagenic, and non-irritating (18). The particles of Ca₃(PO₄)₂ alone are not able to absorb UV rays. However, when they are doped with metal ions, they can play a role of UV filter. Fe³⁺ is a metal that may generate optical absorption bands in the UV range when incorporated in a crystalline matrix. The biocompatibility of Ca₃(PO₄)₂ with the optical activity of the Fe³⁺ makes it very interesting as an active ingredient for inorganic sunscreens (19).

Nano-sized particles of TiO₂-doped SiO₂ gels have been used as composites to enhance the UV absorption efficiency (20). SiO₂ gels having mesoporous morphology have been synthesized via a sol-gel processing route from rice husk. Some studies have shown that amorphous SiO₂ particle have not only a size in the nano-scale range, but also the typical characteristics of the particles (21). Nano-structured CeO₂ appears to be a promising inorganic material for use as a UV filter in sunscreen cosmetic products (22). Lima has suggested that ZnO:CeO₂ systems are promising candidates to be used as optical materials in UV-filters that present higher UV absorption and better transparency in the visible region and less photo-catalytic activity than the conventional system TiO₂:ZnO (23).

Although cerium manifests a lower photocatalytic activity than that of zinc and titanium oxides, it still has an important catalytic behaviour for the oxidation of organic compound (24). It can oxidize under light and degrade the other compounds present in the product. This characteristic feature makes the pure material incompatible with a use in commercial cosmetic products. Additionally, it also slightly absorbs in the visible range producing a yellowish colouring in the products, mostly undesired in specific applications.

Doping with metal ions is a solution for the drawbacks of ceria. Yabe et al. have shown that the substitution of larger and/or less positively charged cations (Ca²⁺, Sr²⁺, Ba²⁺, Mg²⁺, Zn²⁺) for Ca⁴⁺ can reduce the oxidation catalytic activity. Furthermore, the presence of the dopant ions caused significant absorption shifts into the visible region that significantly improves their optical activity (25). The most preferred metal ion for doping is Ca²⁺. With Ca-doped particles, the photo-catalytic activity of CeO₂ can be nearly removed without loss of UV shielding ability and transparency in the visible light region (25). Free radicals are not generated in totally stripped dermis if CeO₂ formulations are applied (3). A blue shift of the absorption is observed for the doped CeO₂. This blue shift allows for better screening of short UVA, the most harmful UVA wavelengths that are involved in skin cancers (22). In sunscreen preparation, Ca-doped CeO₂ can be used in association with TiO₂ as an alternative to ZnO. The combinations TiO₂/Ca-doped CeO₂ gave better photo-protection than the classical combination TiO₂/ZnO (22). In 2004, nanoparticles of calcium-doped ceria were coated with amorphous silica that was proved to be safe when used to provide high UV-shielding ability while maintaining a natural appearance when applied to the human skin (26).

Recently, it was shown (27) that cerium phosphate (CePO₄) is a new UV filter with excellent morphological characteristics, high UV absorption features, low toxicity, low photocatalytic activity and ideal particle size for application in sunscreen formulations which can substitute the currently employed inorganic UV filters ZnO and TiO₂ (27).

Silicon microspheres with the size from 0.3 to 5.0 micrometers proved to be good candidates for developing effective broad-spectrum radiation filters from UV to visible and IR. These highly refractive materials represent a new generation of solar filters since they are chemically inert, able to absorb UV and visible rays, and they strongly scatter IR radiation. Moreover, the spherical shape and smoothness of the silicon microspheres can impart desirable properties in cosmetic preparations, providing a soft feel when applied onto the skin. Finally, their high IR blocking power enables protection from thermal effects, suggesting new benefits for sun care products (28).

Glass microspheres are also used in the sun care product. Although they are not UV filters, the final formulations containing them are aesthetically elegant and have a soft, non-greasy and non-sticky sensation when applied to the skin, the lips, the mucous membranes and/or the hair, and compared with identical formulations not containing glass microspheres. Their presence in the sun care product also increased in vitro FPS.

Particles extracted from hairy rootlets of English Ivy (scientific name Hedera helix), a popular evergreen plant in gardens, are an exception for inorganic UV filters. They are different from the filters mentioned above because they are organic particles. These particles block ultraviolet light from the sun much better than conventional sunscreens containing nanoparticles. Strong ultraviolet extinction and excellent visible transparency are observed, compared to the inorganic TiO₂ and ZnO nanoparticles at similar concentrations (29). Ivy nanoparticles exhibited much less toxicity than widely used TiO₂ nanoparticles. Ivy nanoparticles with a diameter of 65.3 nm do not reach the bottom of the stratum corneum layer in normal conditions for short periods of time after application. The biodegradability of theseivy nanoparticles also reduces all concerns regarding an environmental contamination and problems arising from the entry into the body (30). They are degradable by common protease. In addition, the ivy particles are...
sticky, and should adhere to skin effectively. For these advantages, the ivy nanoparticles have the potential to act as a very effective sunscreen that is also safer than present inorganic filters like TiO₂ and ZnO.

In conclusion, concerning the classical ZnO and TiO₂ filters, many achievements are reported in the development of their formulation and association with the new inorganic filters such as polymer grafting, TiO₂-doped SiO₂ or TiO₂/Ca-doped CeO₂ to ensure a perfect coating and efficiency for UV rays by overcoming the aesthetic drawbacks and skin transpiration, and no photo-catalytic reaction. Beside these improvements, there are new ways of research and application for new filters such as hydroxyapatite, cerium or roots ivy nanoparticles.

REFERENCES AND NOTES

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