The Role of Titanium Dioxide In Cosmetic Chemistry

Titanium, a metal and element, gets its name from the Titans, the deities in Greek mythology who preceded the Olympians. Titanium was discovered by William Gregor in 1791 in Cornwall, Great Britain and was given its name by German chemist Martin Klaproth who discovered it independently and nearly simultaneously.

From the physical point of view, titanium has an incredibly low density: 4.5 g/cm^3, whereas the density of copper is 8.9, and the densities the of iron, tin, nickel, silver and lead are 7.8, 7.3, 8.9, 10.5 and 11.35, respectively. Having a very high specific strength (the strength to be applied per unit area at failure, divided by the density), Titanium appears to have been appropriately named! Today, it is the element of choice to prepare alloys that are used in the aerospace and military industry, as well as in sport equipment such as tennis racquets, blades for ice skaters, horseshoes and bicycles: to give but one example, a bicycle frame made of Titanium only weighs six pounds!

From the chemical point of view, titanium has several oxidation states and combines with oxygen to form titanium monoxide, titanium dioxide and di-titanium trioxide. Titanium dioxide is a white, water insoluble solid that occurs in nature as rutile, a mineral with very interesting optical properties, such as a very high refractive index. Titanium dioxide can be ground to micronized powders consisting of quasi-spherical particles having a "diameter" of about one micrometer. These powders absorb ultraviolet radiation and their extinction coefficient is very high and practically constant across the UV range. This makes titanium dioxide (TiO_2) a great UV filter and a material of choice for sunscreens.

Titanium dioxide is a key component of many sunscreen formulas.

TITANIUM IN SKIN CARE

Historically, a powder of micronized TiO_2 was first used in sunscreens as a "physical" UV filter. Calling TiO_2 a "physical" UV filter is a misnomer created to differentiate it from the so-called "chemical" UV filters used in other sunscreens. The goal of the misnomer was to point out that, in its micronized powder form, (physical particles) TiO_2 would not penetrate the skin; whereas UV filters, consisting of individually dispersed molecules (chemical particles) have a chance of crossing the stratum corneum, and therefore of being irritants.

The drawback of using micronized TiO_2 is that the topical application of a cream containing micronized TiO_2 results in a white surface. This is the consequence of the relatively large size of the particles in the powder and of the high reflectivity of TiO_2 for visible light. Therefore, the protection offered by TiO_2 against ultraviolet radiation is associated with a white color. This white color on the face is acceptable for instance, when performing outdoor sports but is obviously unacceptable when participating in cocktail parties or other outdoor social events.

Another, more serious drawback of using these powders is that when TiO_2 absorbs ultraviolet radiation, it transfers the absorbed energy to molecular oxygen thus generating singlet oxygen. The Quantum Yield of singlet oxygen formation is quite high, on the order of 0.3. This means that one out of three absorbed photons, generates one molecule of singlet oxygen. Singlet oxygen is a very reactive Oxygen species that reacts with biological molecules such as lipids, proteins and nucleic acids. By doing so it damages cell membranes and cytoskeleton by triggering the peroxidative cascade and inducing protein carbonylation. It also provokes the oxidation of nucleotides in the DNA, with potential mutagenic effects.

NANOMATERIAL ISSUES

Progress in the technologies aimed at manufacturing nanomaterials allowed one to obtain TiO_2 powders consisting of quasi-spherical nanoparticles with "diameters" in the range of one hundred nanometers. Nanoparticles scat-

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ter visible light as in the Tyndall effect. This scattering is strongly dependent on the wavelength and the topical application of these powders does not result in the appearance of the undesired white color. Unfortunately, because of their small dimensions, nanoparticles have a chance of penetrating the skin with, as of yet, unknown consequences.

A way to avoid this inconvenience has been to embed TiO_2 nanoparticles in transparent resins and to grind the resulting material to quasi-spherical microparticles; i.e., with a "diameter" of the order of one micrometer. These particles can be topically applied without providing a white color to the surface and are large enough to be unable to penetrate the skin.[1] This is a convenient methodology to take advantage of TiO_2 nanoparticles while avoiding both the penetration into the skin and the undesired production of singlet Oxygen…provided that toxic heavy metals are not used as catalysts in the preparation of the embedding resins.

TIO_2 IN SUNSCREENS

In the US, UV filters are considered drugs. The US Food and Drug Administration (FDA) issues guidelines to indicate that sunscreens are OTC drugs and that they must be prepared according to a specific legislation. For the FDA, acceptable UV filters must be Generally Recognized As Safe and Effective (GRASE) and are classified in a positive list, with the indication of the maximum concentrations allowed. In recent years the FDA has declared that to be considered GRASE, many UV filters need further proof of safety. The FDA proposes a not-GRASE status for sunscreens containing para-aminobenzoic acid (PABA) and trolamine salicylate, because of documented safety issues. In addition, the FDA proposes a not-GRASE status for cinoxate, dioxybenzone, ensulizole, homosalate, meradimate, octinoxate, octisalate, octocrylene, padimate O, sulisobenzone, oxybenzone and avobenzone, because it insists that additional data is needed to show that these UV filters are GRASE.

As of today, in 2022, the FDA proposes to consider as GRASE only two UV filters: zinc oxide and titanium dioxide. ■

References

1. Sojka MF, et al (2011) UV Protection afforded by gel-trapped TiO_2 particles. Photochem Photobiol Sci. 10: 1146-1151