

## Environmental Fate and Toxicity of Aged Titanium Dioxide Nano-Composites Used in Sunscreen

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**Abstract :** In the assessment and management of cosmetics and personal care products, sunscreens are of emerging concern regarding both human and environmental health. Organic UV blockers in many sunscreens have been evidenced to undergo rapid photodegradation, induce dermal allergic reactions due to skin penetration, and to cause adverse effects on marine systems. While mineral UV-blockers may offer a safer alternative, their fate and impact and resulting regulation are still under consideration, largely related to the potential influence of nanotechnology-based products on both consumers and the environment. Nanometric titanium dioxide (TiO<sub>2</sub>) UV-blockers have many advantages in terms of sun protection and aesthetics (i.e., transparency). These UV-blockers typically consist of rutile nanoparticles coated with a primary mineral layer (silica or alumina) aimed at blocking the nanomaterial photoactivity and can include a secondary organic coating (e.g., stearic acid, methicone) aimed at favouring dispersion of the nanomaterial in the sunscreen formulation. The nanomaterials contained in the sunscreen can leave the skin either through a bathing of everyday usage, with subsequent release into rivers, lakes, seashores, and/or sewage treatment plants. The nanomaterial behaviour, fate and impact in these different systems is largely determined by its surface properties, (e.g. the nanomaterial coating type) and lifetime. The present work aims to develop the eco-design of sunscreens through the minimisation of risks associated with nanomaterials incorporated into the formulation. All stages of the sunscreen's life cycle must be considered in this aspect, from its manufacture to its end-of-life, through its use by the consumer to its impact on the exposed environment. Reducing the potential release and/or toxicity of the nanomaterial from the sunscreen is a decisive criterion for its eco-design. TiO<sub>2</sub> UV-blockers of varied size and surface coating (e.g., stearic acid and silica) have been selected for this study. Hydrophobic TiO<sub>2</sub> UV-blockers (i.e., stearic acid-coated) were incorporated into a typical water-in-oil (w/o) formulation while hydrophilic, silica-coated TiO<sub>2</sub> UV-blockers were dispersed into an oil-in-water (o/w) formulation. The resulting sunscreens were characterised in terms of nanomaterial localisation, sun protection factor, and photo-passivation. The risk to the direct aquatic environment was assessed by evaluating the release of nanomaterials from the sunscreen through a simulated laboratory aging procedure. The size distribution, surface charge, and degradation state of the nano-composite by-products, as well as their nanomaterial concentration and colloidal behaviour were determined in a variety of aqueous environments (e.g., seawater and freshwater). Release of the hydrophobic nanocomposites into the aqueous environment was driven by oil droplet formation while hydrophilic nano-composites were readily dispersed. Ecotoxicity of the sunscreen by-products (from both w/o and o/w formulations) and their risk to marine organisms were assessed using coral symbiotes and tropical corals, evaluating both lethal and sublethal toxicities. The data dissemination and provided risk knowledge from the present work will help guide regulation related to nanomaterials in sunscreen, provide better information for consumers, and allow for easier decision-making for manufacturers.

**Keywords :** alteration, environmental fate, sunscreens, titanium dioxide nanoparticles

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