

IFSCC 2025 full paper N° IFSCC2025-1804

Surface Coatings: A Critical Determinant of Photostability in TiO₂-Based Sunscreens

Stephany Araki¹, Michelle Barão de Aguiar¹, Fabiana Pessoa², Maria Valéria Velasco¹ and André Rolim Baby^{1,*}

¹ Pharmacy, Faculty of Pharmaceutical Sciences – USP, São Paulo, Brazil; ² Universidade Federal do Espírito Santo, São Mateus, Brazil

Abstract

Inorganic ultraviolet (UV) filters, typically composed of semiconductor materials, necessitate surface coatings to mitigate reactive oxygen species (ROS) generation under UV irradiation. These coatings enhance dispersibility, facilitating their incorporation into cosmetic formulations and ensuring stability and efficacy. Photostability is another critical parameter for real-world applications. Our study evaluated the photoprotective effectiveness and photostability of TiO₂-based inorganic UV filters under UV irradiation, considering the influence of particle coatings and time. Ten commercially available TiO₂ samples were investigated. Samples were formulated as 10.0 wt% TiO₂ dispersions in oil-in-water emulsions. In vitro sun protection factor (SPF) and critical wavelength (nm) were determined using diffuse reflectance spectrophotometry with a integrating sphere (Labsphere UV2000S; UV2000 software) in the 290-400 nm range. Samples (1.3 mg/cm²) were evenly applied to polymethylmethacrylate plates (Helioplate®) and dried at room temperature for 20 minutes in the dark. In vitro SPF and critical wavelength were then measured in triplicate at five locations on each plate. Photostability tests were conducted by measuring SPF values every 30 minutes for 120 minutes under UV artificial irradiation (580 W/m²) in a solar chamber (Atlas Suntest CPS+). Results revealed that photostability and photoprotective efficacy were strongly influenced by the particle coating composition, with some samples exhibiting up to a 90% decrease in SPF after two hours of irradiation. The silica-coating-derived samples had the best performance. Statistical analysis demonstrated that UV filters from different manufacturers with identical core materials, but varying coatings exhibited statistically similar photostability profiles, strongly suggesting that the coating is the primary determinant of photostability. These findings underscore the critical role of surface coating characteristics in defining the photoprotective performance of TiO₂-based UV filters and emphasize that selecting suitable materials for sunscreen formulations cannot solely rely on the type of core material.

Key-words: sunscreen; inorganic UV filters; titanium dioxide; surface coating

1. Introduction

The exposure of unprotected skin to ultraviolet radiation (UV) leads to many complex chemical and morphological reactions which are related to the development of skin disorders, including the formation of reactive oxygen species (ROS), histochemical conditions, thickening of the *stratum corneum*, and alterations of the dermo-epidermal junction, compromising the barrier function of the skin [1,2]. A variety of photoprotective strategies/methods are suggested by the CDC (Center of Disease Control and Prevention) and the WHO (World Health Organization), which include limiting the time of solar exposure, especially in midday sun, seeking shade when outdoors, wearing a brimmed hat, the use of adequate photoprotective clothing and sunglasses, and applying broad-spectrum sunscreens with SPF equal or greater to 30 with critical wavelength of at least 370 nm on the exposed sites of the body [3,4].

Sunscreens are topical dermocosmetic formulations used to protect the skin from the UV radiation and its harmful effects. Generally, they are constituted of UV filters, which is the active compound of the formulation, associated with an adequate vehicle, such as an emulsion, gel, aerosols and/or sticks, among others. The UV filters can be classified as organic (chemical) or inorganic (physical), being capable of transforming, dispersing, scattering and/or absorbing the incident UV radiation. The organic UV filters are molecules that absorb the incident UV radiation due to the presence of chromophore groups, transforming it into less harmful radiation, e.g. infrared radiation (heat) or fluorescence. In contrast, the inorganic UV filters are insoluble metal oxide particles, typically zinc oxide (ZnO) and titanium dioxide (TiO_2), which disperse, scatter, and absorb part of the incident UV radiation [1]. Due to their intrinsic characteristics, these metal oxide particles should stay suspended in the cosmetic formulation, and their particle size determines the photoprotective efficacy, along with the product's appearance and sensorial attributes on the skin surface [5].

The importance of sunscreens is undeniable, however, there are some concerns regarding their safety. For example, the literature reports that organic UV filters and their byproducts may be related to the development of skin rashes, allergic reactions and endocrine dysfunctions [6,7]. These compounds can also affect the environment, potentially contributing to coral reef bleaching and disrupting the hormonal balance of aquatic organisms [8,9]. The inorganic UV filters can be an alternative to develop safer sunscreens, as they are broad spectrum and cause less cutaneous irritation than their organic counterparts. Thus, they are the first option to lower the allergenic potential of formulations and develop products that are more suitable for children and individuals with sensitive skin [1,10–12]. In addition, this type of UV filter is considered to be safer to the environment, being labeled as “reef-safe”, attracting the attention of consumers seeking for more eco-friendly cosmetic products [8,13].

Developing formulations containing inorganic UV filters pose a challenge, as they tend to leave a chalky white texture film on skin, which can be solved by the use of nanoparticles (NPs), as the decrease in particle size reduces the visible light scattering effect [14,15]. However, TiO_2 NPs may cause the generation of reactive oxygen species (ROS), which can damage the genetic material, potentially leading to mutations, formation of melanoma and the development of actinic keratosis [16]. *In vitro* studies demonstrated that TiO_2 extracted from commercially

available sunscreen formulations can generate ROS, which confirms the importance of methods to reduce the photoactivity of such materials [17].

The application of coated particles can reduce the photocatalytic properties of these metal oxides, as they inhibit the occurrence of redox reactions when UV-irradiated. Typically, the particle coating is composed of inert materials, such as aluminum oxide (Al_2O_3), silicon dioxide (SiO_2), polymers, among others [18,19]. In addition, the particle coating is important to facilitate the incorporation of inorganic UV filters into the cosmetic formulation [20,21], conferring a better dispersion and stability, also reducing the agglomeration/aggregation of the particles [22,23]. Also, the coating determines the affinity of the particle with the dispersing medium, influencing the manufacturing process [19].

Currently, a large variety of TiO_2 particles are available in the market for cosmetic usage. They vary on many factors such as the particle size, crystal structure, morphology of the particles, presence of doping, and surface coating. These characteristics may influence their photoprotective efficacy and safety profile [21]. Besides its effectiveness as a UV filter, it is important to evaluate whether the particle's surface coating is capable of withstanding UV irradiation and other forms of stress, since a damage on the coating may expose the core material, leading to a potential generation of ROS on skin [24]. The aim of this study was to evaluate the photoprotective efficacy and photostability of TiO_2 -based inorganic UV filters with different particle coatings by *in vitro* SPF evaluation methods, as there is lack of information in the literature regarding these properties.

2. Materials and Methods

2.1. TiO_2 samples

For this investigation, ten samples from various manufacturers with different surface coatings were evaluated. All samples and their characteristics of particle coating and percentage of active are described in Table 1.

Table 1: List of commercially available TiO_2 samples analyzed in the present investigation and their characteristics of particle coating and percentage of active.

Sample	Particle coating	% active
S1	Uncoated	NI
S2	Triethoxycaprylylsilane	NI
S3	Hydrogen dimethicone	93%
S4	Isopropyl Titanium Tiisosterate	96%
S5	Aluminium hydroxide, stearic acid	77%
S6	Alumina, jojoba esters	79%
S7	Alumina, silica	92%
S8	Silica	NI
S9	Triethoxycaprylylsilane	96%
S10	Silica, cetyl phosphate	75%

NI: Not informed by manufacturer.

2.2. Sunscreen samples containing TiO_2

The samples were formulated as 10.0 wt% TiO_2 dispersions, considering the percentage of active, in oil-in-water (O/W) emulsion for each TiO_2 sample. The quantitative and qualitative composition of the O/W emulsion is described in the Table 2. The concentration of 10.0 wt% was stipulated after formulation tests with different concentrations of TiO_2 , which concluded that this concentration was the highest possible to maintain an acceptable SPF value and sensorial characteristics. In addition, it was observed that the sensorial aspect of the formulations is considerably affected by the intrinsic characteristics of the particles, as they have different coatings and size, which influences the interaction between the inorganic UV filters and other components of the cosmetic formulation.

Table 2: Quantitative and qualitative composition of the O/W emulsion.

Ingredients	Function	Composition % w/w
Cetearyl alcohol (and) dicetyl phosphate (and) ceteth-10 phosphate	Self-emulsifying base	3.0
Caprylic/capric triglycerides	Emollient	15.0
BHT	Antioxidant	0.05
Xantham gum	Thickening agent	0.1
Ammonium Acryloyldimethyltaurate/VP Copolymer	Thickening agent	0.2
Phenoxyethanol (and) caprylyl glycol	Preservative	1.0
TiO_2	Inorganic UV filter (active compound)	10.0
Purified water	Vehicle	Enough to 100.0

2.2. In vitro photoprotection efficacy and photostability assay

The *in vitro* sun protection factor (SPF) and critical wavelength (nm) were determined by diffuse reflectance spectrophotometry with integrating sphere (Labsphere UV2000S, North Sutton, US) in the 290-400 nm range, accordingly to Marcelino et al. [11]. The samples (1.3 mg/cm²) were spread evenly on polymethylmethacrylate (PMMA) plates (Helioplate®), then dried at room temperature, for 20 minutes, protected from light exposure. The *in vitro* SPF and critical wavelength values were measured in triplicates with at least five transmittance records determined for different locations on the plate. Photostability tests were performed with the evaluation of SPF values every 30 minutes until reaching 120 minutes under artificial UV irradiation (580 W/m²) of the samples in a solar chamber (Atlas Suntest CPS+). The photostability assay process is depicted in Figure 1.

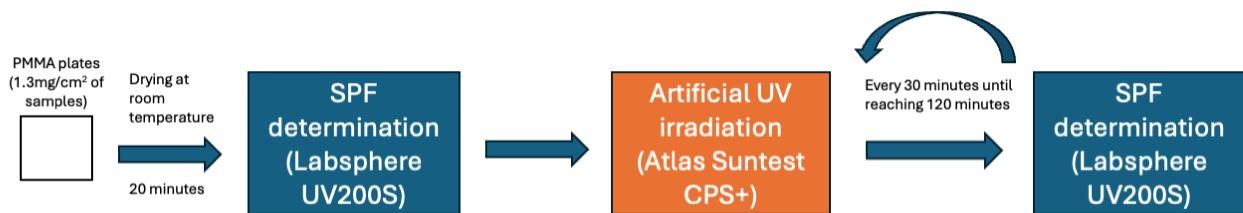


Figure 1: Photostability assay process.

3. Results

3.1. In vitro SPF

The *in vitro* SPF of the samples were determined by spectrophotometer of diffuse reflectance with integration sphere. The results indicated that the samples with particle coating of triethoxycaprylylsilane had the highest SPF value among all samples, followed by the ones containing silica. The other samples presented similar SPF values among them, however were lower in comparison to the aforementioned ones.

3.2. Photostability assay

The photostability assay was performed for all samples, determined after 120 minutes irradiation in the solar chamber (Atlas Suntest CPS+). The SPF loss percentage was calculated considering the initial SPF and the SPF obtained after the total time irradiation.

Table 3: Percentage of SPF loss after 120 minutes irradiation in solar chamber.

Sample	% of SPF loss after 120 minutes irradiation
S1	58%
S2	89%
S3	61%
S4	45%
S5	26%
S6	28%
S7	44%
S8	11%
S9	91%
S10	8%

4. Discussion

The *in vitro* SPF analysis indicated that samples containing triethoxycaprylylsilane coating had the highest SPF, however, they appeared unstable, exhibiting up to a 90% decrease in SPF after two hours of irradiation. Both samples (S2 and S9) with same particle coating and core, but from different manufacturers, presented similar photoprotective and photostability performance, confirming the critical role of the particle coating for the maintenance of photostability. Although having an inferior SPF value in comparison to the triethoxycaprylylsilane-

coated particles, silica-coating-derived samples (S8 and S10) had the best photostability performance among all samples, with less than 12% of SPF loss after UV irradiation. Statistical analysis revealed that the photoprotective efficacy and photostability of sunscreen samples containing TiO₂ were strongly influenced by the particle coating composition, suggesting that the coating is a key factor in determining these properties.

5. Conclusion

Sunscreens are used to reduce the risks associated with unprotected exposure to UV irradiation, which can cause skin and eye disorders. The development of effective and environmentally safe sunscreen products poses a significant challenge. Inorganic UV filters provide a promising alternative, as they are suitable for children and individuals with sensitive skin, while also presenting a reduced environmental impact in comparison to organic filters.

Although being adequate for the development of broad-spectrum sunscreens, the inorganic UV filters are difficult to be incorporated to the cosmetic formulation due to their intrinsic characteristics, also leaving a white chalky texture when applied on skin, which can be solved by the application of nanoparticles. Surface coatings can reduce the photocatalytic properties of NPs by covering the particles' surface and preventing redox reactions when exposed to UV radiation.

The present study revealed that the composition of the particle coating has a critical role in the photostability and photoprotective efficacy of inorganic UV filters, with some samples exhibiting up to a 90% decrease in SPF after two hours of irradiation. Therefore, the characteristics of the surface coating have a crucial role in determining the photoprotective performance of TiO₂-based UV filters, emphasizing that the choice of appropriate materials for sunscreen formulations cannot be based solely on the type of core material used.

Acknowledgments: This research was funded by Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq, Process 303862/2022-0); Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP, Process 2024/01920-0); and Coordenação de Aperfeiçoamento de Pessoal de Nível Superior-Brasil (CAPES, Finance Code 001).

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