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In Vitro Photoprotection and Functional Photostability of Sunscreen Lipsticks Containing Inorganic Active Compounds

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Abstract: Titanium dioxide (TiO_2) is a safe inorganic ultraviolet (UV) filter with activity against UV damage. However, the recombination of the carrier's charge and the tendency for TiO_2 aggregation are the main disadvantages. Substrate supports, such as mesoporous silica, are biocompatible strategies to incorporate TiO_2, altering its interaction with the skin. Since the lips are sensitive to the adversities of the environment, including UV radiation, the application of lipstick sunscreens is of great importance and expected to provide protection for this particular area against sunburn and photoaging, among other unfavorable responses unprotected UV exposure. We investigated the in vitro photoprotective efficacy and photostability of lipstick formulations containing TiO_2 incorporated into mesoporous silica (SBA-15). The samples were the lipstick base; SBA-15; TiO_2 (free form); and TiO_2 incorporated into SBA-15. The photoprotective efficacy was characterized in vitro using a Labsphere UV2000S. Lipsticks were irradiated in a Suntest CPS+ chamber to evaluate functional photostability. Lipstick base and SBA-15 alone did not display photoprotective efficacy. The sample containing 10.0% TiO_2 incorporated into the mesoporous silica generated greater photostability and sun protection factor (SPF) value compared to the one containing only 10.0% TiO_2 (free state). Our findings suggest that TiO_2 + SBA-15 can be considered a broad-spectrum ingredient for innovative sunscreens, particularly for the photoprotection of the lips.

Keywords: photostability; lipstick; sunscreen; titanium dioxide; mesoporous silica

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1. Introduction

Excessive and unprotected exposure to ultraviolet (UV) radiation causes multiple injuries to the skin, such as erythema, edema, wrinkles, dryness, collagen loss, dilation of blood vessels, melasma and skin cancer, among others [1]. Unfortunately, the regular use of sun protection is still sporadic in the most underdeveloped countries, especially among men. The World Health Organization has estimated that daily use of sunscreen can minimize such harmful effects [2,3].

Most photoprotective formulations may contain a combination of various types of organic and inorganic UV filters to provide a broad-spectrum protection, i.e., the efficacy of the product is ensured against the UVB and UVA radiation [4]. Inorganic UV filters can be considered safe and effective for protection of the cutaneous tissue due to their low potential to cause irritation and rare cases of photosensitization [5]. They are also the first option for use in children and patients with a history of allergy. These UV filters are classified as metal oxides, such as zinc oxide and titanium dioxide [6]. They are pigments that, besides reflecting and dispersing the UV rays, can, depending on their particle size, absorb UV and visible radiation in the opaque film that is formed over the skin surface. Iron and zinc oxides, talc, red petrolatum, kaolin and titanium dioxide (TiO_2) are examples of inorganic UV filters. In addition to the aforementioned examples, Nery and coworkers published a review that presented and discussed nontraditional possible substitute compounds or technologies being considered as potential inorganic UV filters, such as hydroxyapatite, cerium oxide, hydrotalcite and the use of nanotechnology [5].

TiO_2 is widely used as an inorganic UV filter. It is an opaque, insoluble, semiconductor powder capable of reflecting and dispersing UV radiation and visible light through a film formed by particles over the skin surface [7]. The application of methods to incorporate inorganic filters to develop photoprotective formulations was increased not only because of their high acceptability, but also through the development of transparent sunscreens after application, which maintained strong protection against the UV rays [8]. In the case of TiO_2 specifically, the recombination of cargo conveyors and tendency for aggregation are the main disadvantages that can be prevented by its incorporation into mesoporous silica. This material is ideal for the incorporation of TiO_2, besides presenting photocatalytic capacity [9].

Among the commonly studied inorganic mesostructures are Mobil Composite of Matter no. 41 (MCM-41) and Santa Barbara Amorphous no. 15 (SBA-15). The later mesoporous silica has a pore size of between 2 and 30 nm and is named by their structure: SBA-11 (cubic), SBA-12 (hexagonal 3D), SBA-15 (hexagonal) and SBA-16 (cubic cage-shaped) [10]. SBA-15, the most well-studied material in the series, displays a certain structural similarity to MCM-41, as they both have a hexagonal structure [11]. However, SBA-15 has a larger pore size, thicker pore walls and pore interconnectivity, which gives it greater hydrothermal, thermal and mechanical stability. Its surface area can vary between 690 and 1040 $m^3.g^{-1}$, pore volume close to 2.5 $cm^3.g^{-1}$, pore diameter between 4.6 and 30 nm, and wall thickness between 3.1 and 6.4 nm. Due to these characteristics, SBA-15 has interesting properties for application as adsorbents, catalysts and encapsulation of drugs and other bioactive molecules [12–16]. These materials have been investigated for the encapsulation or incorporation of UV filters, since they have unique mesostructural characteristics such as high surface area, high loading of active molecules and ability to interact with light that may improve the efficacy, as well as the safety, of photoprotective preparations [9,17].

Since the lips are more sensitivity to the adversities of the environment, including UV radiation, and the lack of additional defense mechanisms in comparison to the cutaneous tissue (pigmentation and elevation of the stratum corneum layers, for example), the application of lipstick sunscreens is of great importance and expected to provide protection of this particular area against sunburn and photoaging, among other unfavorable responses to unprotected UV exposure. According to Sarruf and coworkers, sunscreens in the form of sticks, particularly a lipstick, for this purpose, are important photoprotective formulations and an affordable strategy to prevent damage on the lips induced by outdoor exposure to sun rays, including the prevention of cancer of the lips [18]. This class of dermocosmetic is developed with waxes, as consistency agents; lipophilic liquids (oils and esters, for example), as emollients and solvents; preservatives; antioxidants; fragrance(s); colored pigments, if applicable; and active ingredients, with UV filters being those for sunscreen lipsticks [19].

We investigated the in vitro photoprotective efficacy and photostability of TiO_2 incorporated into a mesoporous silica (SBA-15) in a lipstick sunscreen formulation vehicle. For our lipstick prototype samples, the efficacy parameters (sun protection factor and critical wavelength) were determined by diffuse reflectance spectrophotometry with an integration sphere, with the functional photostability observed after the samples were exposed to an artificial UV irradiation source in a Suntest CPS+ solar simulator.

2. Material and Methods

2.1. TiO_2 Incorporation into Mesoporous Silica

The synthesis of SBA-15 was performed as already described in the specialized literature [11,20,21]. The process of encapsulation/incorporation of TiO_2 into the mesoporous silica was performed with approximately 150 mL of acetone (1:1, SBA-15: TiO_2) and conducted under gentle magnetic agitation at 25 °C for 48 h. After this step, the supernatant was discarded. The remaining solid portion was transferred to a glass container and dried at 80 °C for 2 h.

2.2. Formulation of the Lipsticks

Photoprotective lipsticks are described in Table 1.

Table 1. Quantitative and qualitative composition (% *w*/*w*) of the photoprotective formulations prepared as lipsticks.

Composition	F1	F2	F3	F4
Candelilla Wax Extract		4.00		
Ceteareth-20		2.50		
Alba Wax		4.00		
Ozokerite		4.00		
Paraffin (and) Isopropyl Palmitate (and) *Euphorbia cerifera* (Candelilla) Wax (and) Butyl Stearate (and) Ethylene/VA Copolymer		3.53		
Acetylated Lanolin Alcohol		4.00		
Butylene Glycol Cocoate **		19.00		
Tocopheryl Acetate **		0.05		
BHT		0.10		
Propylparaben		0.10		
Lanolin **		4.41		
Ricinus communis (Castor) Seed Oil **		q.s. 100.00		
Titanium dioxide (TiO_2)	0.00	10.00	0.00	0.00
Mesoporous silica (SBA-15)	0.00	0.00	0.00	10.00
Mesoporous silica (SBA-15) + TiO_2	0.00	0.00	10.00	0.00

F1 = Lipstick base; F2 = TiO_2; F3 = SBA-15 + TiO_2; F4 = SBA-15/q.s. = enough quantity to.

For the base sample, all components of the formulation except those described with **, were initially weighed and transferred to glass beaker. The mixture was heated up to 75–80 °C to melt the fatty agents. After the mixture reached 60–65 °C, the other components were added. Manual agitation was continued until a homogeneous mixture was obtained. The lipstick mold was lubricated with volatile silicone with the help of a brush. After it was heated to 45 °C, the homogeneous mixture was poured onto the mold and taken to the refrigerator for 30 min in order to promote the cooling and hardening of the lipsticks. The samples were manually removed from the mold and packed in parchment paper. Lipsticks weighed approximately 3.5 g.

For the other formulations, a step was added to the process in order to allow the incorporation of the mesoporous silica (SBA-15) or encapsulated/incorporated material. Butylene glycol cocoate, lanolin and castor oil were weighed separately in a glass beaker and transferred to a porcelain grail. To this mixture, SBA-15 or encapsulated/incorporated material was added, according to each formulation, under manual agitation with the aid of a pistil until a homogeneous dispersion was obtained, which was then reserved (Phase A). The other components of the formulation, except vitamin E, were weighed, transferred to a glass beaker and heated up to 75–80 °C for the fusion of fatty agents (Phase B). After the fusion of Phase B, Phase A was gradually added under manual agitation with the aid of a glass rod, maintaining the heating until complete homogenization. After the mixture of Phases A and B reached 60–65 °C, vitamin E was added and, again, agitation was performed until homogenization. The mixture was poured into the mold for lipsticks. The mold was placed in the refrigerator for 30 min in order to promote sample cooling and hardening. The lipsticks were manually removed from the mold while still cooled and packed in parchment paper, as previously described.

2.3. In Vitro Photoprotective Efficacy

The in vitro photoprotection efficacy was evaluated using the diffuse reflectance spectrophotometer with an integration sphere (Labsphere UV-2000S Ultraviolet Transmittance Analyzer), in the spectral wavelength interval between 250 and 450 nm at the progression rate of 1 nm. Polymethylmethacrylate (PMMA) plates (5.0 × 5.0 cm, Helioplate HD6, Helioscreen) were used as substrates to which samples were individually and manually applied in the form of a thin and uniform film (1.3 mg.cm^{-2}). The PMMA plates were selected for their easy handling and access, in addition to their reproducible surface roughness. After application, the samples were dried at room temperature for 20 min and protected from light [20,22].

The in vitro efficacy of the formulations was based on the sun protection factor (SPF) and the critical wavelength (λ_{crit}) values [23] and they were presented as mean ± standard deviation. The analyses were performed in triplicate and nine different points per plate were measured for each sample [20]. The calculation of the in vitro parameters was performed by the UV-2000 software. Equations (1) and (2) describe the mathematical approach to calculate the in vitro SPF and the critical wavelength (nm) [24].

$$\text{SPF} = \frac{\int_{290\text{ nm}}^{400\text{ nm}} \text{E}\lambda\text{S}\lambda\text{d}\lambda}{\int_{290\text{ nm}}^{400\text{ nm}} \text{E}\lambda\text{S}\lambda\text{T}\lambda\text{d}\lambda} \quad (1)$$

In vitro sun protection factor (SPF). Eλ = spectral irradiance effectiveness according to Commission Internationale de l'Eclairage (CIE); Sλ = solar spectral irradiance; dλ = range of wavelengths; and Tλ = sample spectral transmittance.

$$\int_{290\text{ nm}}^{\lambda_{crit}} \text{A}(\lambda)\text{d}\lambda = 0.9 \int_{290\text{ nm}}^{400\text{ nm}} \text{A}(\lambda)\text{d}\lambda \quad (2)$$

Critical wavelength (nm). λ_{crit} = critical wavelength; dλ = range of wavelengths; and Aλ = sample spectral absorbance.

2.4. Photostability Test

After the in vitro photoprotection test, the formulations were irradiated for 1 h in a solar simulator (Suntest CPS+, Atlas, Mount Prospect, IL, USA) equipped with a xenon lamp, an optical filter to remove wavelengths lower than 290 nm, and an infrared filter, aimed at reducing thermal damage. The emission of the solar simulator was maintained at 580.08 W.m^{-2} (irradiation dose = 198 kJ.m^{-2}) [3,20]. The SPF and λ_{crit} were analyzed after irradiation and compared with the results of pre-irradiation. The tests were also performed in triplicate with nine different reading points per plate for each sample.

2.5. Statistical Analysis

Results were evaluated in Minitab, version 16, using ANOVA (generalized linear model), with significance level of 5.0% ($p < 0.05$) for the determination of statistically significant responses.

3. Results and Discussion

Some important common properties of sunscreens involve the product stability and photostability, the safety and efficacy, resistance to water removal, the sensorial properties and aspect of the film formed over the skin surface and, if possible, the ability to deliver multiple cosmetic attributes to the cutaneous tissue [25]. Improving sunscreen formulations to provide a photostable profile associated with a broad-spectrum protection has become an utmost relevant issue in the cosmetic science and dermocosmetics in general [26]. The development of safe, effective and innovative active ingredients elevates the competitiveness of the related industries, to offer the consumers more alternatives to be adopted as sun care protection strategies.

The SPF parameter of a photoprotective product is widely known to consumers as the efficacy measure of a sunscreen against sunburn and in vitro methods, principally the ones that use the reflectance spectrophotometry with integrated spheres, are advantageous, providing results in a short time as well as being cheaper and ethical [27]. The in vitro assays were developed on the fundamental assumption that the UV protection of a photoprotective sample would simply be a response from the UV light attenuation by the UV filtrating compounds, through their absorption properties, concentrations and type of vehicle they would be incorporated into; however, those in vitro assays do not take into account in vivo biological effects, such as antioxidative and anti-inflammatory activities [28]. To shed more light on the emerging active ingredients for more effective and photostable sunscreens to be applied over the lips, we investigated the performance of a mesoporous material associated with TiO_2.

Lipsticks with TiO_2 (free state) or TiO_2 encapsulated/incorporated into the mesoporous silica were prepared to evaluate the impact of this type of technology on the photoprotection and photostability of this widely used inorganic UV filter in a less explored/studied cosmetic form. Table 2 describes the aspect of the lipstick samples. Since the lipstick ingredients impact several attributes of the final product, a search for signs of instability (cracks, deformation and aeration, for instance) was required to guarantee the efficacy evaluation of the most adequate stable samples. All formulations presented satisfactory stability after the preparation that was macroscopically homogenous, independent of the active in the composition (TiO_2; mesoporous silica; or TiO_2 encapsulated/incorporated into the mesoporous silica).

Prior to the establishment of the concentration of the active ingredients at 10.0%, we performed preliminary tests with samples containing the actives at 5.0% (data not shown). Our results obtained in these conditions indicated no differences (p-value > 0.05) between the TiO_2 in the free and the one encapsulated/incorporated into the mesoporous silica, being the in vitro SPF values equal to, approximately, 4.7 and 5.3, respectively. Those samples' performances justified the use of the active concentrations at 10.0% which, at least, doubled the in vitro SPF.

The sample containing TiO_2 incorporated into the mesoporous silica (SBA-15 + TiO_2) presented greater absorption in the UVB (290–320 nm) and UVA (320-400 nm) regions when compared to the sample containing 10.0% TiO_2 (Figure 1). Similar results were obtained with the encapsulation of avobenzone and TiO_2 in SBA-15 reported in the literature [29]. TiO_2 (free state) had better absorption in the UVB than in the UVA region, and its presence in the formulation was not able to offer broad-spectrum protection, even at the concentration of 10.0%. However, when the inorganic UV filter was incorporated into the mesoporous silica, the sample was indicated to develop a broad-spectrum sunscreen property, since it had an SPF value greater than 15 and a critical wavelength (λ_{crit}) value above 370 nm [30,31] (Table 3). The highest SPF value was found for the sample containing 10.0% TiO_2 incorporated into the SBA-15, as shown in Table 3, in which we found an interesting result profile suggesting a synergistic effect.

Table 2. Aspect and organoleptic properties of the lipstick samples.

Formulation	Aspect	Organoleptic Characteristics
Lipstick base		Homogeneous stick, yellowish and characteristic odor
Mesoporous silica (SBA-15)		Homogeneous stick, white and characteristic odor
TiO_2		Homogeneous stick, white and characteristic odor
SBA-15 + TiO_2		Homogeneous stick, white and characteristic odor

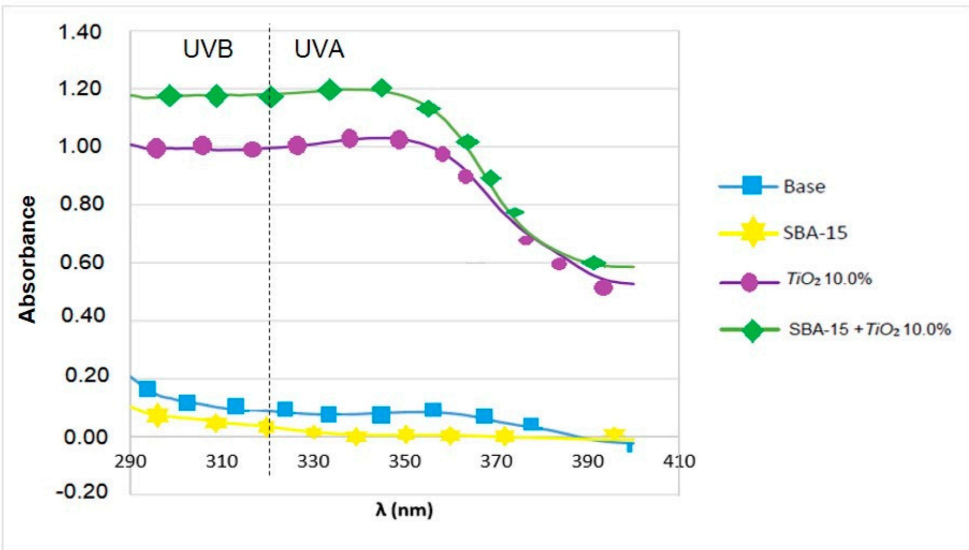

Figure 1. Absorption curves in the UV range of the lipstick base, SBA-15, TiO_2 and SBA-15 + TiO_2 samples generated by the UV-2000 software.

Table 3. Values of in vitro sun protection factor (SPF) and critical wavelength (λ_{crit}, nm) of the samples (lipstick base, SBA-15, TiO_2, and SBA-15 + TiO_2).

Formulations	In Vitro SPF	λ_{crit} (nm)
Base	1.3 ± 0.6^{A}	N.A.
SBA-15	1.0 ± 0.0^{A}	N.A.
TiO_2	10.0 ± 1.7^{B}	382.7 ± 0.6^{D}
SBA-15 + TiO_2	15.0 ± 1.0^{C}	381.7 ± 0.6^{D}

N.A. = not applicable; SPF values expressed in mean ± standard deviation. Results evaluated according to ANOVA, followed by Tukey test for comparison between groups (significance level = 0.05). Groups that share a letter are statistically equal.

So far, only a few studies have been related to SBA-15 as a carrier for UV filters [17,20,32] with the establishment of sun protection parameters, such as in vitro SPF and critical wavelength (nm), for example. However, an increase in the performance was already reported for UV filters encapsulated into mesoporous silica [32]. UVA protection improvement was observed for TiO_2 and avobenzone incorporated into SBA-15 caused the inhibition of cell apoptosis [29]. Silica adsorption ability, promoted by the porosity of SBA-15, was attributed to the improvement in UVA protection and synergistic effect with TiO_2 and avobenzone [29]. Another interesting proposal for the use of mesoporous silica would be as an antipollutant active ingredient, since it is also recognized as a feasible pollutant absorbent due to certain physical properties (porous, surface and stability) [29]. Benzophenone-3, an organic UV filter that absorbs in the UVB and UVA regions, was adsorbed in a high surface area mesoporous silica and incorporated into an emulsified system. The in vitro SPF and UVA values, quantified by a SPF-290S system with transpore tape as the substrate, indicated that the association of the benzophenone-3 with the mesoporus silica had superior performance than the free UV filter [17]. Our research group investigated the effect of the incorporation of avobenzone, oxybenzone (benzophenone-3) and ethylhexyl methoxycinnamate (organic UV filters) into mesoporous silica (SBA-15) and the results demonstrated an increase in the photoprotective efficacy [20]. Our lipstick base and the sample containing the SBA-15 (F4) achieved in vitro SPF values close to 1.0, indicating the absence of relevant photoprotection. Thus, it was found that SBA-15 alone was not able to generate significative SPF. Even as an inorganic material, the mesoporous silica alone did not interact efficiently with UV radiation through its dispersion, scattering and/or absorption. Furthermore, the λ_{crit} (nm) of these samples was considered as non-appropriation, since their absorption curves approached the baseline (Figure 1), shifting them to high values that do not reflect the actual absorption, i.e., the profile of a broad-spectrum sample. The lipstick base and SBA-15 samples also showed no efficiency against the UVA radiation.

The photostability of a sunscreen affects, on several levels of severity, the profile of safety and efficacy as the light-induced degradation reduces the photoprotective system capacity of protection during the outdoor exposure; it is also able to generate potential toxic elements (for instance, free radicals) [1]. Photostability to UV radiation is an important parameter since a sensitive UV-filtering molecule could degrade and induce photoallergy and phototoxicity [33].

Figure 2 and Table 4 reveal that the lipsticks containing only TiO_2 and TiO_2 incorporated into SBA-15 were not statistically significantly changed after irradiation stress, suggesting they were photostable samples, except for the λ_{crit} parameter of the TiO_2 (free state). A slight decrease in the in vitro SPF values was noticed for these samples; however, it had no statistical significance, reinforcing the photostable profile for those formulations observed in our experimental conditions, i.e., the photoprotective efficacy in the UVB region was maintained for the two samples after irradiation. The decrease in λ_{crit} value after irradiation was significant for the lipstick (p-value > 0.05) containing the TiO_2 (free state), although the UV stress condition was not powerful enough to reduce it to less than 370 nm. It is known that photostable products do not form by-products and, therefore, can be considered safer for use [34].

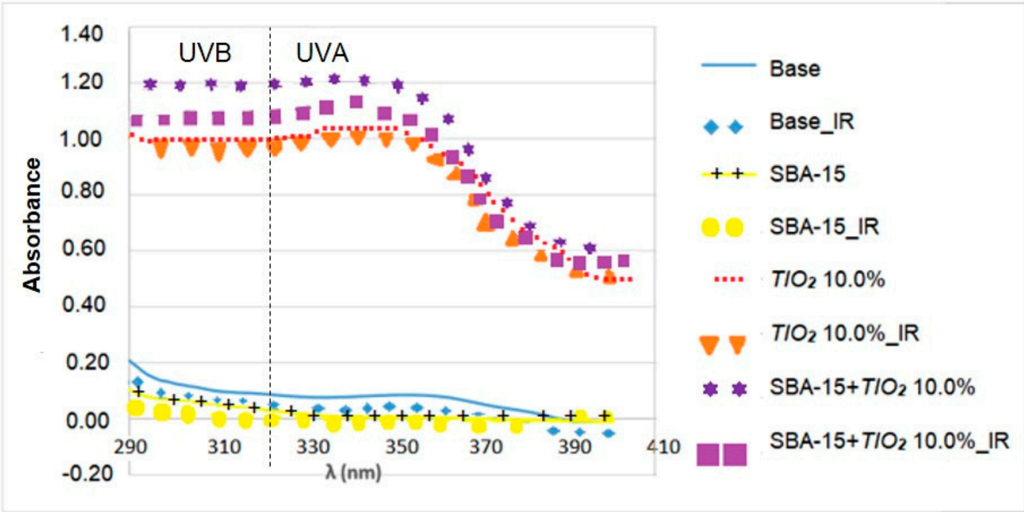

Figure 2. Photostability test. Absorption curves in the UV range, generated by the UV-2000 software, of the lipstick base, SBA-15, TiO_2 (free form) and SBA-15 + TiO_2 samples, before and after irradiation (IR) in the Suntest CPS+.

Table 4. Functional photostability of the formulations (before and after UV irradiation).

Formulation	Irradiation	In Vitro SPF	*p*-Value	λ_{crit} (nm)	*p*-Value
TiO_2	NI	10.0 ± 1.7	0.667	Reduction	<0.05
	IR	9.7 ± 1.5			
Mesoporous silica + TiO_2	NI	15.0 ± 1.0	0.118	Maintenance	0.423
	IR	12.7 ± 2.5			

SPF = sun protection factor; λ_{crit} (nm) = critical wavelength; NI = not irradiated; IR = irradiated. SPF values expressed in mean ± standard deviation. Results evaluated according to ANOVA, followed by Tukey test for comparison between groups (significance level = 0.05).

4. Conclusions

During recent years, there has been growing interest in the development of safer and more effective sunscreens using several strategies (new compounds and technologies; innovative mixtures of traditional and nontraditional actives, such as the association of antioxidants and UV filters, among others). In our experimental conditions, we obtained acceptable lipsticks in terms of aspect and organoleptic properties. The lipstick sample containing TiO_2 associated/incorporated into the mesoporous silica achieved superior performance and photostability compared to isolated compounds and the lipstick base. Mesoporous silica alone was not able to generate satisfactory values of SPF and λ_{crit}. We suggest that TiO_2 + mesoporous silica (SBA-15) could be considered a broad-spectrum ingredient for innovative sunscreens in the future, particularly for photoprotection of the lips.

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