

## Article

# Criticisms in the Development of High-Protection and Broad-Spectrum “Natural/Organic” Certifiable Sunscreen

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**Abstract:** Attention to environmental issues has become increasingly important in recent years and also massively affects the cosmetics sector. In this context, sunscreens are questioned due to the proven or believed ecotoxicity of organic ultraviolet (UV) filters. This has pushed developers increasingly towards the use of inorganic filters, which can prove difficult to spread with low compliance. We faced the problem by proposing a rational approach based on the evaluation of the morphology of the inorganic material, as the real dimension does not often correspond to the characteristics declared by the producers because the material itself tends to aggregate. A combination of a specially selected inorganic filter is required to formulate Cosmetic Products with a Natural and Sustainable Connotation (CPCNS) standards.

**Keywords:** inorganic sunscreen filters; ZnO; TiO<sub>2</sub>; SPF; UVA-PF; COSMOS; ISO-16218; safe-by-design; SBD4Nano



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## 1. Introduction

Attention to environmental issues has become increasingly important in recent years, and is also affecting the cosmetics sector in a massive way, and thus consumer interest in natural and/or sustainable products is still increasing. According to Statista [1], a German website for statistics, the global sales of organic cosmetic products is still in the nascent stage and is predicted to increase to USD 54.5 billion by 2027 from USD 34.5 billion in 2018 [1].

The trend is confirmed in Italy by the economic figures of the last 3 years, from Cosmetics Italia, the Italian association of cosmetic companies: in 2019, before the COVID-19 pandemic, the turnover based on natural and sustainable cosmetics amounted in Italy, to 1654 million euros. Out of these, 572 million euros were generated by companies with at least one certification or compliance audit relating to sustainability [2].

In 2020, due to the impact of the COVID-19 pandemic, the entire Italian cosmetic turnover decreased by 12 percentage points. There were sudden changes in purchasing habits both in terms of point-of-sale and the type of products. However, some trends have consolidated, such as the purchase of cosmetics with a natural and sustainable connotation, with an estimated sale in 2020 of over 1650 million euros, distributed in all sales channels, even those not specialized in natural.

Moreover, the analysis of the main ten claims of cosmetic products launched on the world market between 2019 and 2020, set in first place “Ingredients with natural

connotations”, with a frequency ranging from 39.9% in 2019 to 41.4% in 2020. Sustainability claims also increased, both relating to the product (with an increase from 15.7% to 21.6% from 2019 to 2020) and to packaging (with an increase from 10.6% to 14.6% from 2019 to 2020) [3].

Preliminary data of the Italian cosmetics sector at the end of 2021 confirmed, for the cosmetics sector, a recovery in turnover to pre-COVID levels; however, the new consumption trends for cosmetics also suggest the need of new strategies to face the market. For the macro trend of natural and sustainable, it is necessary to demonstrate the effectiveness of the actions taken and measure them against specific objectives. Furthermore, one should be able to narrate the cosmetic product, especially on issues increasingly closer to the consumer, such as the knowledge of supply chains and their functioning in terms of ethics and ingredients [4].

This is particularly important for the new generation of those born after 2000, the largest potential purchasing group, representing approximately 32% of the world’s population. They seek label transparency, they are curious to know where the ingredients come from and how the products are made, and they buy through product information related to contents rather than traditional marketing. They are health- and environmentally conscious consumers who are motivated to buy natural cosmetics that are clean, natural, and “free from” undesirable chemicals; however, there is considerable confusion over the definition of what is desirable, and the idea of “green” cosmetics is somewhat simplified [5].

A product based on ingredients of plant origin, not containing petrochemicals or substances considered critical for health and environment, such as preservatives and silicones, to name a few, is largely perceived as ecological and environmentally friendly, however, these generic “green features” are not able to substantially define this class of Cosmetic Products with a Natural and Sustainable Connotation (CPCNS) as far as the formula, packaging and production process, nor is there a mandatory legal regulation defining natural and organic cosmetics.

As a result of this lack of legislation, over the years, we have seen the birth of several private certification bodies worldwide, of which Cosmos and Natrue can be considered the most representative ones that aim to support this type of claim by setting criteria and definition requirements for natural and organic cosmetics. More recently, the need to adopt a single international standard to define cosmetics as natural or organic also led the International Organization for Standardization (ISO) to develop the project ISO 16128: Guidelines on technical definitions and criteria for natural and organic cosmetic ingredients and products [6,7].

Private certification bodies and the ISO have followed different approaches in defining natural and organic cosmetics. ISO 16128 Guideline adopts a quantitative criterion that aim to identify the content in natural or organic components of any cosmetic product and the degree of naturalness of each individual ingredient within it; it does not specifically define which ingredients are allowed in natural or organic cosmetics and their minimum contents in the finished product, and it does not adopt a list of prohibited ingredients or production processes.

On the other hand, the general criteria established by private certification bodies do not focus on the products themselves but involve the entire cosmetics sector in a project of sustainable development and social responsibility, having as their object the maintenance of the balance of our planet. Despite the fact that ISO 16128 represents an important step forward in the international standardization of the concept of natural and organic cosmetics, the main international certification bodies, as well as many companies operating in the sector, have taken a critical detached stance toward it. They consider ISO 16128 a source of confusion and a step backward compared to the achievements of the various standards already on the market over the years [8].

According to Cosmos and Natrue, which are widely followed in Europe, in order to stimulate the process of transition to sustainable consumption and production, organic and natural cosmetics must follow some simple rules governed by precautionary and safety

principles at all levels of the production chain, from the production of raw materials to the distribution of the finished product, promoting organic farming and respect for biodiversity, facilitating the responsible use of natural resources, using “clean” processes and production methods that are respectful of human health and the environment, and developing “Green Chemistry,” that is, an ecological and sustainable approach to the chemical industry.

Therefore, where there is evidence or even suspicion that an ingredient or manufacturing process may pose a risk to human health or the environment, such ingredients or processes will not be allowed. Although there are some similarities, the ISO 16128 standard and private certifications have substantial differences in the way raw materials and finished products are classified, making it necessary for the formulator to choose in advance which certification to follow in the development of the cosmetic formula.

In this complex scenario, and for the purpose of this study, we decided to approach the field of Cosmetic Products with a Natural and Sustainable Connotation (CPCNS) by developing high-protection, broad-spectrum sunscreen formulations that comply with EC Regulation No. 1223/2009 and are “certifiable” according to the COSMOS (Natural) Standard.

COSMOS was chosen because it is the first voluntary standard (established in 2002) on natural and organic cosmetics harmonized at the European level and supported by the existing certification bodies Ecocert and Cosmebio (France), BdiH (Germany), Soil Association (UK) and Icca (Italy) and because it has the highest number of approved ingredients among the certified bodies. Finally, we also calculated the percentages of naturalness of each individual ingredient and determined that for all formulas, the resulting total percentage of natural origin, according to ISO 16128, was greater than 99%.

The active ingredients in the sunscreen formulations are UV filters. Although they are essential for sunscreen activity, they cannot be considered the only ingredients responsible for the effectiveness of a sunscreen product; the overall UV protection depends on the formulation as a whole. Parameters, such as the stability of the formula to radiation, its spreadability on the skin and its ability to remain on the skin surface without being absorbed, contribute to the overall effectiveness of a sunscreen [9]. However, the main challenge in this study was the limitation placed by COSMOS on the use of active ingredients with a sunscreen function [10].

According to EC Regulation No. 1223/2009, UV filters allowed in cosmetic preparations are listed in Annex VI and consist of a number of 31 molecules [11]. According to their mechanism of action, they can be classified as organic (also improperly called chemical) (c-UVf) or inorganic (also improperly called physical) (p-UVf) UV filters. Organic UV filters are aromatic organic molecules with highly conjugated structures that can absorb ultraviolet electromagnetic radiation by causing reversible conformational changes in the molecules. The energy absorbed can be re-emitted in the form of longer wavelength radiation or be dissipated in the form of heat [12].

According to COSMOS [10], the use of organic filters in cosmetic products is prohibited because their degradation products might be persistent and toxic to the aquatic environment. Moreover, recent studies revealed that the organic filters Butyl Methoxydibenzoylmethane, Octocrylene and Benzophenone-3 are able to provoke skin sensitization by interaction with different skin proteins [13]; nevertheless, their use can be considered within a specific range of concentration as seen in the recent opinion of SCCS [14].

These data have raised alarms regarding toxicity towards humans and the environment [15], which have led some tropical places to ban four organic filters, thus, generating an alarm towards this type of substance [16]. An approach pursued in recent times is the search for new, natural, environmentally friendly molecules of an organic nature that can perform as sunscreen (UV) filters.

However, this process is still in its infancy because of a number of issues related to the harmonization of tests used in the experiments to demonstrate effective filtering ability. This topic was covered by some of us extensively, in a recent review [17]. Inorganic UV filters are mineral particles that provide UV protection through absorption, reflection and

scattering processes. ZnO and TiO<sub>2</sub> reflection/scattering and absorption largely depends on the size: with small particles, more is based on the absorption mechanism [18].

Within inorganic UV filters, EC regulation no. 1223/2009 allows the use of ZnO and TiO<sub>2</sub> (also in nano form) at the maximum concentration of 25% [11]. TiO<sub>2</sub> is primarily a UVB filter but is able to offer a significant UVA protection depending on its particle size. The efficacy of TiO<sub>2</sub> as a filter is quite good, and it is possible to formulate high-SPF products with only TiO<sub>2</sub> as an active ingredient but with a narrower spectrum.

ZnO is less efficient than TiO<sub>2</sub> in terms of UVB protection, and consequently of overall SPF but has a broad and constant absorption profile up to wavelengths of 360–370 nm, and thus it is typically better suited than TiO<sub>2</sub> in protection against so-called “UVA long rays”(UVA I) [19,20]. Moreover, the combined use with TiO<sub>2</sub> may increase ZnO performance in the field of UVB and UVA. ZnO partly owes its popularity also to the lower refractive index (1.9–2.0), which gives it more transparency compared with TiO<sub>2</sub> (2.5–2.7) [21].

Compared to organic filters, inorganic filters are perceived as safer because they cause less irritation to the skin. However, depending on the particle sizes (above 200 nm), they can reflect not only UV radiation but also visible light, causing an unpleasant whitening effect in sunscreen [20]. The use of inorganic filters with nano particle size enhances radiation absorption and gives the advantages of transparency; however, concerns remain present about their safe use in cosmetics [22].

Regulation EC 1223/2009 defines a nanomaterial as “insoluble and bio-persistent material, intentionally manufactured having one or more external dimensions, or an internal structure, measurement from 1 to 100 nm” [11]. Nanomaterials, as defined above, are generally seen with suspicion and prohibited by EU cosmetic regulation given the potential danger of high reactivity due to the reduction of the particle size and the ability to penetrate tissues. Exceptions are permissible if requests are supported by technical documentation to the EU Scientific Committee on Consumer Safety (SCCS).

COSMOS position regarding minerals is that, although necessary in cosmetics, they are not a renewable source; therefore, to admit their use COSMOS requires methods of well-defined production. Appendix IV of Cosmos Standard lists pure minerals present in nature and treated only according to the physical processes listed in Appendix I, which include ZnO and TiO<sub>2</sub>. As far as nanomaterials concerns, in a communication of August 2016 [10], COSMOS acknowledged that, although the precautionary principle generally excludes nanomaterials a priori for “certifiable” cosmetics, TiO<sub>2</sub> and ZnO represent the only effective alternatives to ultraviolet (UV) filters of petrochemical origin regarding photoprotection, and they contribute significantly to the safety of consumers who use them.

Their use is then admitted; however, specific requirements are introduced to minimize the potential risk: the raw material must comply with the requirements of the Cosmetic Regulation (EC) 1223/2009, specifically the regulations (EU) 2016/1143 and (EU) 2016/621 which implement annex VI of Regulation (EC) 1223/2009 regarding TiO<sub>2</sub> and ZnO: the number of particles with dimensions below 100 nm must be less than 50%; the mass of the particle fraction below 100 nm must constitute less than 10% of the total mass; and in any case, TiO<sub>2</sub> and ZnO cannot be used in applications under pressure with possible inhalation (cylinders).

Recently, new “inorganic (UV) active” molecules have been proposed as potential sunscreen (UV) filters—for example, Calcium Phosphate, Hydroxy Apatite, Tinted UV filters, metal oxides and more. These materials are promising and represent a possible valuable alternative to the well-known ZnO and TiO<sub>2</sub>. Up to now, they have not been recognized in Annex VI to the EC regulation; however, they are often used and mentioned in the INCI and label as coloring agents or UV boosters [23–26].

## 2. Materials and Methods

### 2.1. Chemicals

We used citric acid monohydrate FU-E 330 (Acef, Fiorenzuola d'Arda, PC, Italy), Glycerol vegetable 99.7% Ph.Eur. E422 COSMOS, (Acef, Fiorenzuola d'Arda, PC, Italy), ACTICIRE MB (Gattefossé, Saint-Priest Cedex, France), PDS300 (Applechem, Parsippany, NJ, USA), KELTROL<sup>®</sup> (CP Kelco France, Levallois-Perret, France), Magnesium Sulfate Eptahydrate EP (Acef, Fiorenzuola d'Arda, PC, Italy), PolyAquil<sup>™</sup> OS2 (Lincoln Fine Ingredients, A Maroon Group, LLC Co, Lincoln, RI, USA), Potassium sorbate RC (Acef, Fiorenzuola d'Arda, PC, Italy), Sodium benzoate granular E211-EP-FCC-USP (Giusto Faravelli S.p.A., Milano, Italy), Salpur Sale Fine, (Südwestdeutsche Salzwerke AG Heilbronn, Germany), Myritol<sup>®</sup> 318 (BASF, Ludwigshafen, Germany), TEGOSOFT AC MB (Evonik Nutrition & Care GmbH, Essen, Germany), Natural Tocopherol 1000 UI IP (Sunflower) (Acef, Fiorenzuola d'Arda, PC, Italy), ZinClear<sup>®</sup> XP (Antaria, Perth, Australia), ASL-1 ZnO-300 (Daito Kasei Kogyo Co., Ltd., Osaka, Japan), SUNZnO-SA (Sunjin Beauty Science Co., Ltd., Ansan, Gyeonggi-do, Korea), and T-80JJ (Sunjin Beauty Science Co., Ltd., Ansan, Gyeonggi-do, Korea), MT-100TV (Tayca Corporation, Osaka, Japan).

### 2.2. Instruments

We used an electron microscope Zeiss EVO 40XVP (Carl Zeiss Pty Ltd., Oberkochen, Germany), Transmission electron microscope Zeiss EM 910 (Carl Zeiss Pty Ltd., Oberkochen, Germany), pH meter Sension+ pH 31 (Hach Lange S.r.l, Lainate, Italy), Centrifuge RE.MI NEYA 10R (REMI, Mumbai, India), Spectrophotometer SHIMADZU UV-2600 provided of integrating sphere ISR 2600 60 mm (Shimadzu Corp., Kyoto, Japan), WW5 PMMA Plates (Schonberg GmbH, Munich, Germany), Suntest CPS+ (Atlas, Linsengericht, Germany), Viscosimeter Brookfield DV2T (Brookfield, Toronto, ON, Canada), Portable density meter DMA 35 (Antoon Paar Italia s.r.l, Rivoli, Italy), Galli 2800 High Performance Incubator (F.lli Galli G.&P. snc, Fizzonasco, Italy), DV-I<sup>™</sup> Prime Viscometer coupled with T-E Bar Spindle and RV Spindle (Brookfield, Toronto, ON, Canada), Magnetic stirrer (Heidolph, Schwabach, Germany), Laboratory glassware Kalsse, L5M-A Laboratory Mixer (Silverson Machines, Inc., East Longmeadow, MA, USA), Microscope OPTIKA B-510PH (OPTIKA S.r.l. Ponteranica (BG)-Italy), and Nikon Digital Camera D3200 18-55 VR (Nikon Corporation, Tokyo, Japan), Lamp D-65, 6500 Kelvin, Osram GmbH, Berlin, Germany.

### 2.3. Analysis of Surface Morphology

Sunscreen formulas examined in this study were prepared using five different inorganic UV filters. Given the importance of the particle size of the filters, we performed scanning electron microscopy (SEM) analysis on each one. Before SEM analysis, the materials were treated with gold sputtering, and then images were collected in a vacuum.

The results of the SEM analysis are compared with the particle size data provided by suppliers. Table 1 lists the INCI names of the five filters used with a brief description.

It is important to emphasize that the three types of ZnO used fall into the characteristics required in Annex VI of Regulation (EC) 1223/2009. Regarding the two different TiO<sub>2</sub>, the producers declare that the first, Titanium Dioxide (Nano), Aluminum Hydroxide And Stearic Acid, have a Primary Particle Size of 15 Nm, while the second, Titanium Dioxide, Silica and Jojoba Esters, are 10 nm. This latter however displays an aggregate particle size of 500 nm. This is a quite common phenomenon: nanoparticles always aggregate, thereby, reducing the overall area with strong interactions.

### 2.4. Formulations

We created five different sunscreen emulsions proceeding as follows. On a chassis with a pre-established formula a water-in-oil emulsion, (W/O), which is preferred in sunscreen products because more water resistant than oil-in-water (O/W), the three different types of ZnO were tested at their maximum permitted concentration (25%). Sunscreen formulas obtained are identified as sunscreen formulas A, B and C (Table 2).

**Table 1.** Inorganic UV filters selected for this study.

INCI Name	Description	CAS Number	Ratio of Solid (%)	Average Particle Size Declared by the Producer
ZINC OXIDE	Uncoated zinc oxide powder	1314-13-2	100	500 nm
ZINC OXIDE, SODIUM LAUROYL GLUTAMATE, LYSINE, MAGNESIUM CHLORIDE	Zinc oxide coated sodium lauroyl glutamate and lysine and Magnesium Chloride	1314-13-2 29923-31-7 70-54-2 7786-30-3	N.A.	294 nm
ZINC OXIDE, STEARIC ACID	Zinc oxide coated with stearic acid	1314-13-2 57-11-4	N.A.	150 nm
TITANIUM DIOXIDE (NANO), ALUMINUM HYDROXIDE, STEARIC ACID	highly micronized titanium dioxide coated with aluminum hydroxide and stearic acid	13463-67-7 21645-51-2 57-11-4	78	15 nm
TITANIUM DIOXIDE, SILICA, JOJOBA ESTERS	Titanium dioxide coated with silica and jojoba esters	13463-67-7 7631-86-9 61789-91-1	76-81	500 nm (aggregate size)

**Table 2.** Sunscreen formulas A, B and C.

Phase	Ingredient (INCI Name)	Function	Sunscreen Formula A % in Formula	Sunscreen Formula B % in Formula	Sunscreen Formula C % in Formula
A	CAPRYLIC/CAPRIC TRIGLYCERIDE	Emollient	10.00	10.00	10.00
A	ISOAMYL COCOATE JOJOBA ESTERS	Emollient	10.00	10.00	10.00
A	HELIANTHUS ANNUUS SEED CERA	Emollient	5.00	5.00	5.00
A	POLYGLYCERIN-3 ACACIA DECURRENS FLOWER CERA TOCOPHEROL HELIANTHUS ANNUUS SEED OIL	Antioxidant	0.20	0.20	0.20
A	POLYHYDROXYSTEARIC ACID CAPRYLIC/CAPRIC TRIGLYCERIDE ISOSTEARIC ACID LECITHIN POLYGLYCERYL-3 POLYRICINOLEATE	Dispersant	1.25	1.25	1.25
A	ZINC OXIDE	UV Filter	25.00	0	0
A	ZINC OXIDE SODIUM LAUROYL GLUTAMATE LYSINE	UV Filter	0	25.00	0
A	MAGNESIUM CHLORIDE ZINC OXIDE, STEARIC ACID POLYGLYCERYL-2 OLEATE	UV Filter	0	0	25.00
B	POLYHYDROXYSTEARIC ACID POLYGLYCERYL-2 STEARATE	W/O Emulsifier	5.00	5.00	5.00
C	AQUA		to 100	to 100	to 100
C	GLYCERIN	Humectant	5.00	5.00	5.00
C	SODIUM CHLORIDE	Stabilizer	0.60	0.60	0.60
C	MAGNESIUM SULFATE	Stabilizer	0.60	0.60	0.60
C	BENZYL ALCOHOL	Preservative	0.90	0.90	0.90
C	DEHYDROACETIC ACID	Preservative	0.10	0.10	0.10
C	XANTHAN GUM	Viscosity modifier	0.10	0.10	0.10
C	CITRIC ACID	pH regulator	0.03	0.03	0.03

In vitro SPF analysis of the three formulas was conducted according to ISO 24443:2012 [27]. Of these three formulas, the most promising in terms of UVA protection was sunscreen formula B. It was selected, and two further formulas were tested by adding to sunscreen formula B, respectively, two different types of TiO<sub>2</sub> at the 8% concentration, obtaining sunscreen formulas D and E (Table 3).

**Table 3.** Sunscreen formulas D and E.

Phase	Ingredient (INCI Name)	Function	Sunscreen Formula D: % in Formula	Sunscreen Formula E: % in Formula
A	CAPRYLIC/CAPRIC TRIGLYCERIDE	Emollient	10.00	10.00
A	ISOAMYL COCOATE	Emollient	10.00	10.00
A	JOJOBA ESTERS HELIANTHUS ANNUUS SEED CERA	Emollient	5.00	5.00
A	POLYGLYCERIN-3 ACACIA DECURRENS FLOWER CERA	Emollient	5.00	5.00
A	TOCOPHEROL HELIANTHUS ANNUUS SEED OIL	Antioxidant	0.20	0.20
A	POLYHYDROXYSTEARIC ACID CAPRYLIC/CAPRIC TRIGLYCERIDE ISOSTEARIC ACID LECITHIN	Dispersant	1.25	1.25
A	POLYGLYCERYL-3 POLYRICINOLEATE	Dispersant	1.25	1.25
A	ZINC OXIDE SODIUM LAUROYL GLUTAMATE LYSINE	UV Filter	25.00	25.00
A	MAGNESIUM CHLORIDE TITANIUM DIOXIDE (nano)	UV Filter	8.00	0
A	ALUMINUM HYDROXIDE STEARIC ACID	UV Filter	8.00	0
A	TITANIUM DIOXIDE, SILICA, JOJOBA ESTERS	UV Filter	0	8.00
B	POLYGLYCERYL-2 OLEATE	W/O Emulsifier	5.00	5.00
B	POLYHYDROXYSTEARIC ACID	W/O Emulsifier	5.00	5.00
C	POLYGLYCERYL-2 STEARATE	W/O Emulsifier	5.00	5.00
C	AQUA		to 100	to 100
C	GLYCERIN	Humectant	5.00	5.00
C	SODIUM CHLORIDE	Stabilizer	0.60	0.60
C	MAGNESIUM SULFATE	Stabilizer	0.60	0.60
C	BENZYL ALCOHOL	Preservative	0.90	0.90
C	DEHYDROACETIC ACID	Preservative	0.10	0.10
C	XANTHAN GUM	Viscosity modifier	0.10	0.10
C	CITRIC ACID	pH regulator	0.03	0.03

In vitro SPF analysis according to ISO 24443:2012 was performed to evaluate how the SPF and UVA varied regarding sunscreen Formula B. Each formulation (A, B, C, D and E) was made by melting phase A ingredients, at 60 °C, in the main container, taking care to disperse the powders in order to obtain a fluid and completely homogeneous phase. Phase B, at 60 °C, was then added to phase A and mixed until completely dispersed. In a separate beaker, phase C was prepared by adding water at room temperature and dissolving in it the other ingredients in sequence and mixing until complete solvation of the gelling agent. Phase C was slowly inserted into phase A + B, with continuous mixing. Finally, we stirred with turbo emulsifiers until homogeneity.

### 2.5. In Vitro Evaluation of Filtering Parameters

The in vitro sun protection factor determination method used in this work was conducted taking into consideration the requirements of the ISO 24443:2012 guideline and the

requirements of the European recommendation EC 647/2006 of 22 September 2006 relating to the efficacy of sun protection products [28].

The UVA protection factor (UVAPF) of each sunscreen formulation was instrumentally verified before and after a period of controlled UV irradiation, using a spectrophotometric technique in accordance with the ISO 24443:2012 guideline. A thin film of product (1.3 mg/cm<sup>2</sup>) was applied to an artificial support which must have physical characteristics as similar as possible to human skin. The substrate chosen for the test corresponds to those described in the ISO 24443:2012 guideline and consists of polymethylmethacrylate (PMMA) plate of 25 cm<sup>2</sup> area, with a roughness of 5 µm. We applied 15 mg of glycerin on the support that served as blank reference.

Irradiation of each sample was conducted using the Atlas SUNTEST CPS + solar simulator, equipped with a Xenon lamp, an optical filter to cut off wavelengths shorter than 290 nm and an IR-block filter to avoid thermal effect, and set to operate between 40–200 W/m<sup>2</sup> in accordance to ISO 24443:2012 guidelines

Instrumental determinations of the UV absorbance (calculated from transmittance) were conducted using a Shimadzu UV-2600 spectrophotometer, provided of integrating sphere ISR 2600 60 mm and coupled with an SPF determination software, with emission of wavelength from 290 to 400 nm and 1 nm increment. This test is informative for the determination of two significant parameters: the critical lambda and the SPFlabel/UVAPF ratio. Critical lambda describes the amplitude of the protection across all the UV spectra (280–400 nm). It is the wavelength at which 90% of the area under the absorbance curve (AUC) is reached starting from 290 nm. The SPFlabel/UVAPF ratio relies on the ability of the formula to specifically protect in the UVA range, in relation to the global SPF value declared on the label.

Similarly, to the Critical Lambda, this ratio provides an evaluation of the amplitude of the protection across the UV spectra without considering the amount of the filtering activity. Values near to 1 are indicative of a broad-spectrum activity. EC 647/2006 suggests that all solar products have a critical lambda value greater than 370 nm and a UVAPF value of at least 1/3 of the SPF value declared on the label (SPFlabel).

The in vitro SPF was calculated as follows:

$$\text{InVitroSPF} = \frac{\int_{\lambda=290 \text{ nm}}^{\lambda=400 \text{ nm}} E(\lambda) I(\lambda) d(\lambda)}{\int_{\lambda=290 \text{ nm}}^{\lambda=400 \text{ nm}} E(\lambda) I(\lambda) 10^{-A(\lambda)} d(\lambda)}$$

$E(\lambda)$  = erythema action spectrum (CIE-1987) at a wavelength  $\lambda$ .

$I(\lambda)$  = spectral irradiance received from the UV source at a wavelength  $\lambda$ .

$A(\lambda)$  = a monochromatic absorbance of the test product layer at a wavelength.

$d(\lambda)$  = wavelength step (1 nm).

The UVA protection factor UVAPF0 has been calculated for each non-irradiated plate individually:

$$\text{UVAPF0} = \frac{\int_{\lambda=290 \text{ nm}}^{\lambda=400 \text{ nm}} P(\lambda) I(\lambda) d(\lambda)}{\int_{\lambda=290 \text{ nm}}^{\lambda=400 \text{ nm}} P(\lambda) I(\lambda) 10^{-A(\lambda)^C} d(\lambda)}$$

$P(\lambda)$  = Persistent Pigment Darkening (PPD) action spectrum.

$I(\lambda)$  = spectral irradiance received from the UV source (UVA 320–400 nm for PPD testing).

$A(\lambda)$  = Mean monochromatic absorbance of the test product layer.

$C$  = Coefficient of adjustment.

$d(\lambda)$  = Wavelength step (1 nm).

## 2.6. Stability of the Formulas

All formulas were subjected to a preliminary stability test, based on the accelerated ageing upon exposure to increased temperature. One sample of each sunscreen formula was stored in an oven at 45 °C for 1 month, while a second sample of each sunscreen

formula was kept at room temperature. The two samples for each sunscreen formula were then evaluated.

### 2.7. Optical Analysis

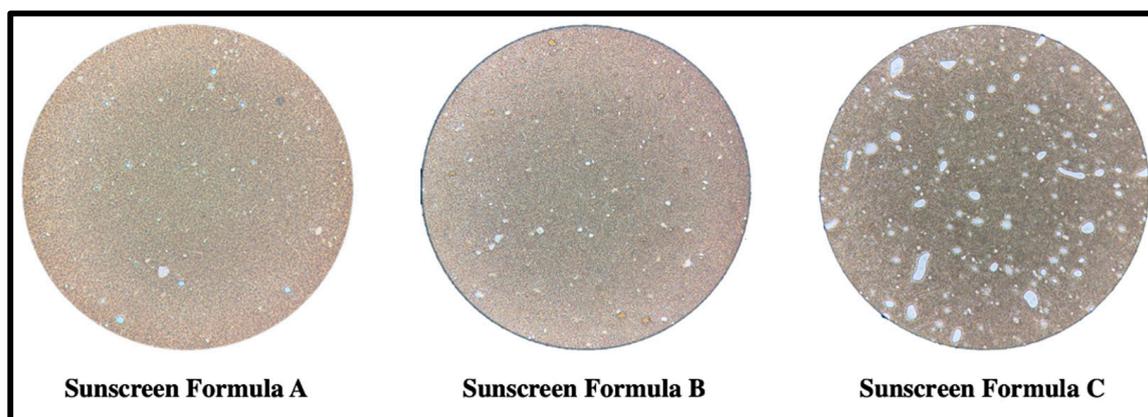
Each sunscreen formula was evaluated under optical microscope coupled with image analysis software (Optika Proview). A slide covered by a coverslip was loaded with the sunscreen formula and observed on three different regions of the slide in order to randomize the evaluation and verify the homogeneity of the sample. Evaluations were conducted at room temperature (25.0 °C).

### 2.8. Sunscreens' Appearance and Transparency

The transparency of the formulas was evaluated through visual observation and by means of spectrophotometric analysis. In both cases samples were prepared as follows: 2.0 mg/cm<sup>2</sup> of each sunscreen formulation was spread on a polymethylmethacrylate (PMMA) plate of 25 cm<sup>2</sup> area with a roughness of 5 µm.

For visual investigation all plates were placed on a black paper background, located into a specially designed and closed box. The box measured 110 cm in length, its height was 44 cm and depth 65 cm. It was internally illuminated with solar lamps (D-65, 6500 Kelvin, Osram GmbH, Berlin, Germany), which corresponds to "average daylight from the northern sky" and is the reference illuminant in DIN 6173-2 "Colour matching" and a referenced illuminant in ASTM D1729. Images of the PMMA plates were taken through a slit centrally located in the upper part of the box.

The digital camera (Nikon D3200 18-55 VR) was adjusted to cover the entire slit in order to exclude the entry of other light sources so that images of the samples were taken under the same constant lighting conditions (Figure 1).



**Figure 1.** The coating based on Sodium Lauroyl L Glutamate, Lysine that covers this type of commercial ZnO (Formula B) is able to optimize the wettability and dispersion of the powder in the chosen oily phase, as compared to uncoated ZnO (Formula A) or Zinc Oxide, Stearic Acid (Formula C).

We investigated the transmittance parameter of each sample using spectrophotometric analysis, conducted using a Shimadzu UV-2600 spectrophotometer, provided of integrating sphere ISR 2600 60 mm, we set the emission of wavelength from 290 nm to 700 nm and 1 nm increment.

## 3. Results

### 3.1. Chemical-Physical Parameters

The viscosity and density were determined on each sunscreen formula at discharge time, at 25°. The viscosity was also determined 1 month later on two different samples in order to assess stability (Table 4).

**Table 4.** Chemical-physical parameters for each formulation.

Formulation	Density (g/mL)	Viscosity (cP), 25 °C, Discharge Time	Viscosity (cP), RT, 1 Month after	Viscosity (cP), 45 °C, 1 Month after
Sunscreen Formula A	1.23	24,000 (spindle RV06, 10 rpm)	250,000 (spindle RV06, 10 rpm)	390,000 (spindle RV06, 10 rpm)
Sunscreen Formula B	1.22	40,000 (spindle RV06, 10 rpm)	74,000 (spindle RV06, 10 rpm)	110,000 (spindle RV 06, 10 rpm)
Sunscreen Formula C	1.23	125,000 (spindle T-E95, 10 rpm)	360,000 (spindle T-E95, 10 rpm)	540,000 (spindle T-E95, 10 rpm)
Sunscreen Formula D	1.31	38,000 (spindle RV06, 10 rpm)	135,000 (spindle RV06, 10 rpm)	380,000 (spindle RV06, 10 rpm)
Sunscreen Formula E	1.30	32,000 (spindle RV06, 10 rpm)	72,000 (spindle RV06, 10 rpm)	260,000 (spindle RV 06, 10 rpm)

### 3.2. Stability

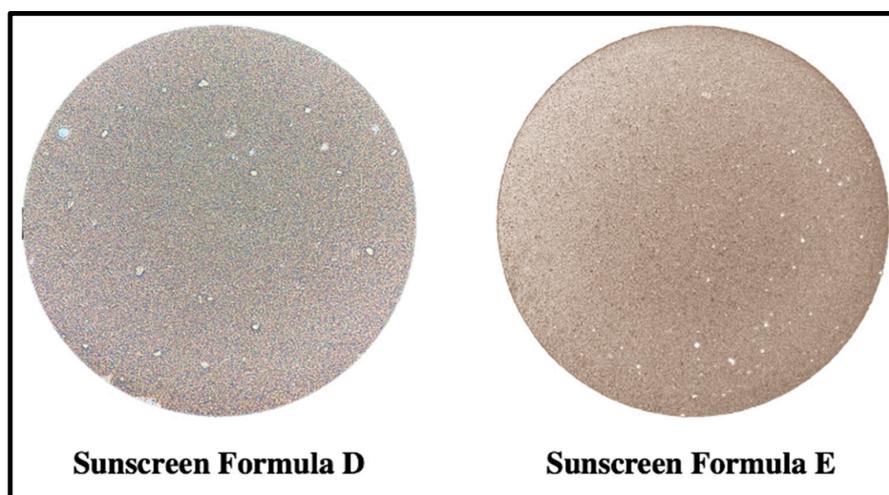
All formulas showed no structural instability after 1 month at 45 °C in the oven, no oozing or significant change in the reference olfactory note. The most significant variation observed was the increase in viscosity recorded over time, a phenomenon that occurs both in the reference sample and in the tests subjected to thermal stress where this effect is further amplified (Table 4).

We also observed an increase in viscosity over the observation period that was not itself a structural problem but rather related to a loss of pleasantness in application. This may result in possible problems of dosing and dispensing, and it is probably related to the needs of longer time for the complete wetting of the powders. Although minor, it is important to take this into account in the product development phase.

### 3.3. Optical Microscopy

The optical microscope images (40× magnification) reveal that among the emulsions containing 25% zinc oxide, sunscreen formula B, containing Zinc Oxide, Sodium Lauroyl Glutamate, Lysine, does not show visible aggregates and gives the best dispersion of powders (Figure 1).

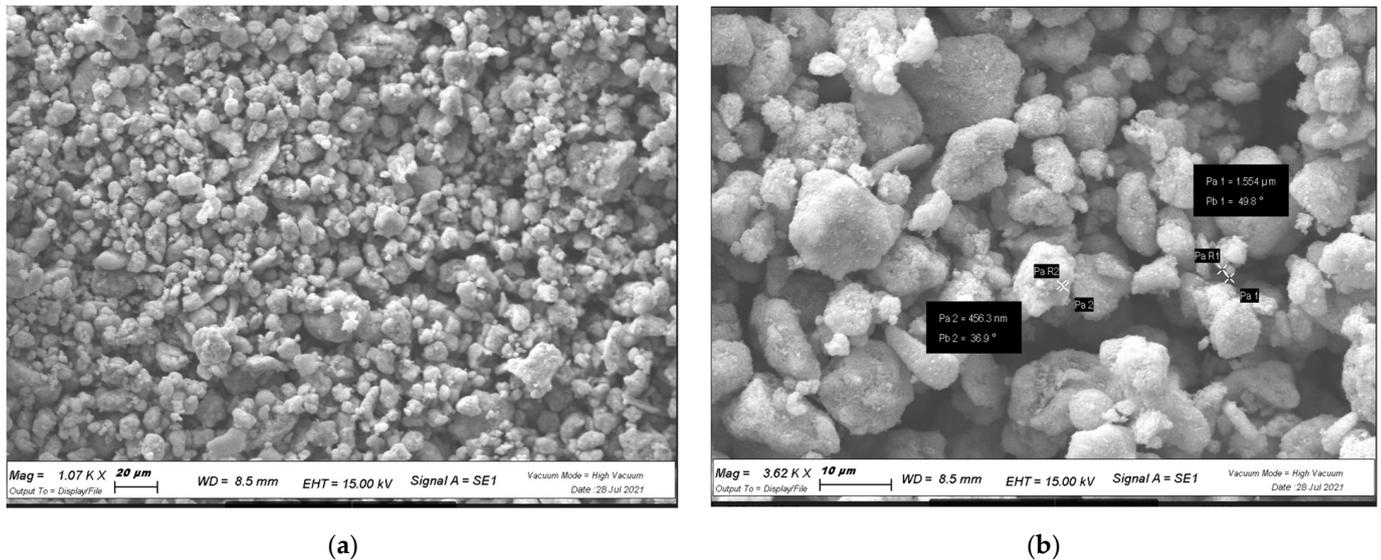
The optical microscope analysis (40× magnification) of the two emulsions containing both ZnO and TiO<sub>2</sub> clearly shows how in the case of the sunscreen formula D the micronized TiO<sub>2</sub> (particle size 15 nm) is finely dispersed, while in sunscreen formula E, it creates clearly visible and irregular agglomerates (Figure 2).



**Figure 2.** The data reflect the particle size of the two types of TiO<sub>2</sub> used: in Sunscreen Formula D it is nanometric, while in Sunscreen Formula E the size of the aggregates (about 500 nm) is comparable with the wavelengths of visible light.

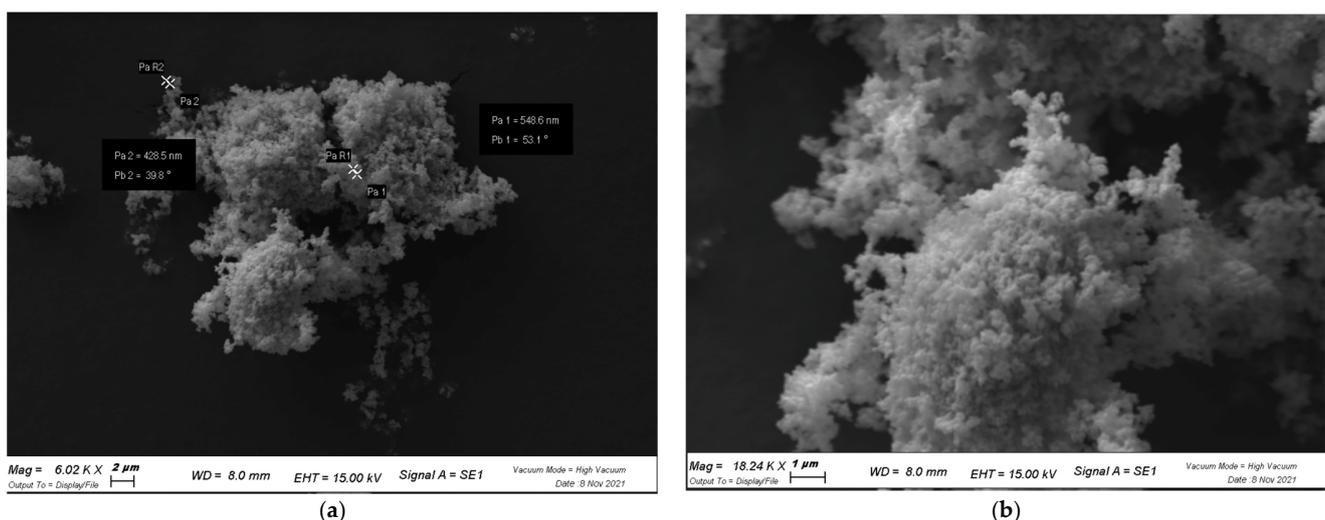
### 3.4. Morphological Study

The inorganic filters were evaluated for their morphology with SEM analysis. Uncoated ZnO is present in the form of porous particles having sizes mostly in the micrometer range (Figure 3a). Aggregates are in the order of a few tens of micrometers formed by primary particles with sizes in the nanometers range (Figure 3b). These results confirm data from the producer.



**Figure 3.** SEM image of Zinc Oxide at different magnifications. (a) 1007 $\times$  magnification; (b) 3620 $\times$  magnification.

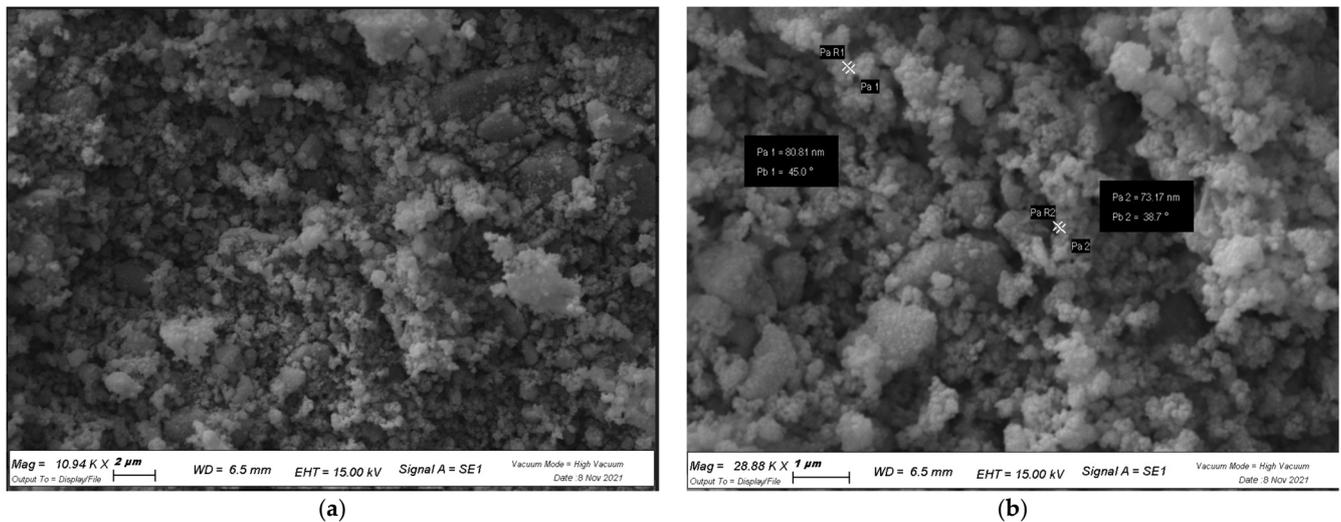
In Figure 4, SEM image of Zinc Oxide, Sodium Lauroyl Glutamate, Lysine, Magnesium Chloride is reported. This material is less aggregated than the corresponding uncoated that was sized about 500 nm and different from the following coated one with a more porous amorphous surface.



**Figure 4.** SEM image of Zinc Oxide, Sodium Lauroyl Glutamate, Lysine, Magnesium Chloride at different magnifications. (a) 6000 $\times$  magnification; (b) 18,240 $\times$  magnification.

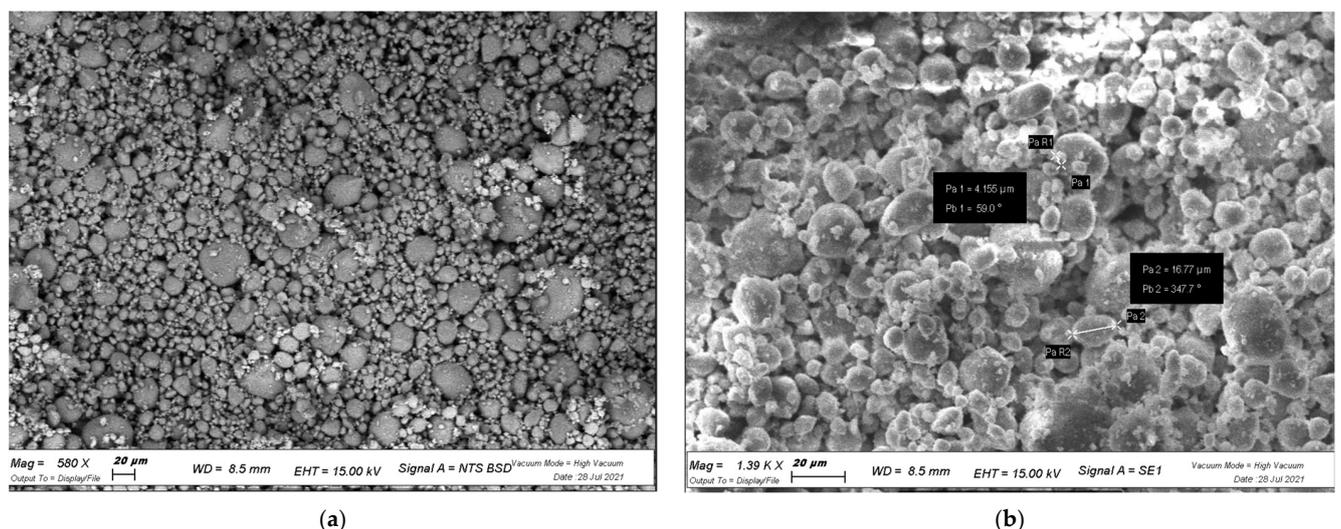
In Figure 5, SEM image of Zinc Oxide, Stearic Acid shows an average size of about 90 nm in line with data reported by the producer (declared 150 nm primary particle size); however, the morphology is more that of an aggregate and heterogeneous solid, than

an uncoated metal oxide. Also, the aggregate range is more variable than that of the corresponding uncoated form.



**Figure 5.** SEM image of Zinc Oxide, Stearic Acid at different magnifications. (a) 10,900× magnification; (b) 28,880× magnification.

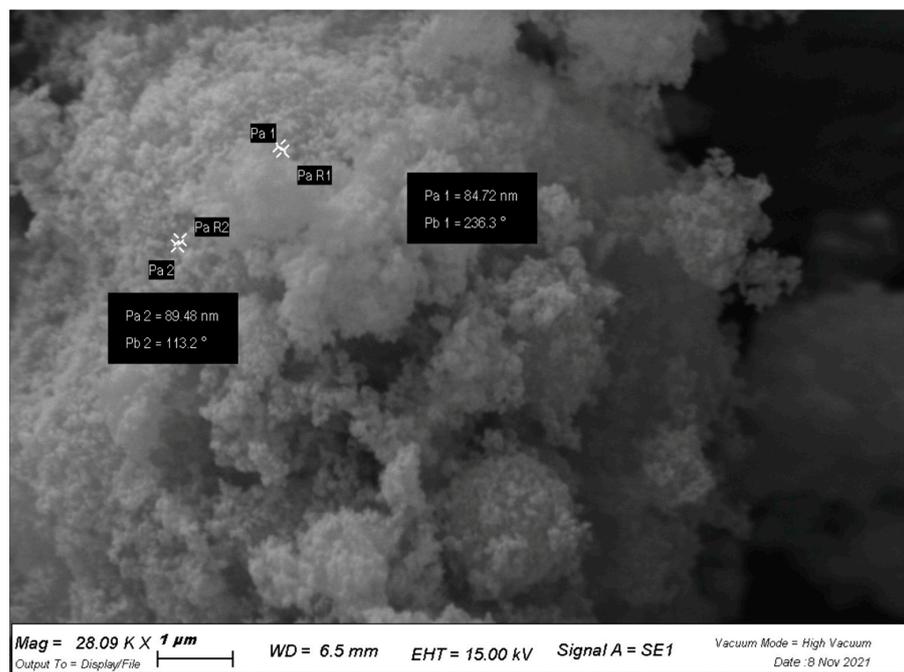
In Figure 6, SEM image of non-nanometric Titanium Dioxide, Silica, Jojoba Esters is reported, the morphology of Titanium Dioxide, Silica, Jojoba Esters is almost regular but not perfectly spherical. SEM reveals a non-porous system, thanks to the presence of a coating that reduces the characteristic surface roughness of TiO<sub>2</sub> and increases its size. At Mag = 1390× (Figure 6b) the fine grain of the sample under analysis was observed. In addition, an heterogeneity of the particle size can be observed with small and large aggregates probably due to variability of TiO<sub>2</sub> core size in the coating process. In fact interaction between metal oxide and coating agent play a key role in the final granule organization. In this case the appearance of the product is that of a coated one.



**Figure 6.** SEM image of non-nanometric Titanium Dioxide, Silica, Jojoba Esters at different magnifications: (a) 500× magnification; (b) 1390× magnification.

Figure 7 reports SEM image of nanometric Titanium Dioxide (Nano), Aluminum Hydroxide, Stearic Acid that appears as an aggregate of particles having a medium size of 72–86 nm (15 nm declared by the producer). In this case the porous surface looks as not

completely coated thus maintaining a smaller size in the respect of the previous sample of Figure 6.



**Figure 7.** SEM image of nanometric Titanium Dioxide (Nano), Aluminum Hydroxide, Stearic Acid, 28,000× magnification.

### 3.5. Analysis of UV Absorption Performance

All three formulations containing only ZnO have a good absorption in the UVA portion of the spectrum. They all show a quite low SFP, also considering the percentage of ZnO used, which is equivalent to the maximum allowed by the EU regulation. For all formulations the UVA/UVB ratio is approximately 1:1 and the critical lambda is greater than 370 nm (Table 5). Because the main ZnO shielding mechanism of UV radiation is absorption [20], a smaller particle size (therefore a greater specific surface area for the same quantity) should correspond to higher SPF and UVAPF.

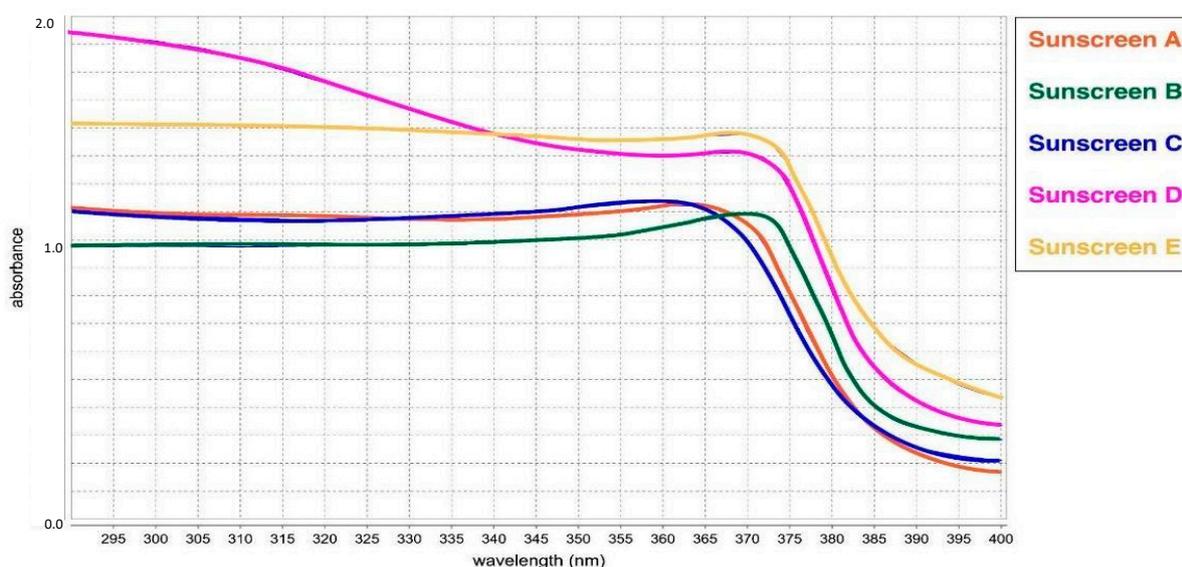
**Table 5.** SPF analysis for each formulation.

Formulation	SPF	UVAPF	SPF Label	SPF Label/ UVAPF	$\lambda$ Critical (nm)
sunscreen formula A	12.26	7.52	10	1.33	374
sunscreen formula B	11.23	8.82	10	0.89	377
sunscreen formula C	11.86	7.29	10	1.37	374
sunscreen formula D	35.42	12.44	30	2.41	375
sunscreen formula E	25.79	19.16	30	1.57	379

Smaller oxide particles expose a larger surface to the incident radiation and are thus supposed to contribute more effectively to the absorption of the latter. Indeed, SunScreen Formula B shows the highest UVAPF values, while the SPF values are substantially the same. This could be explained by the fact that the coating of the ZnO particles introduces an important variable allowing an optimal dispersion of the filter and increases its effectiveness.

Data relating to UVAPF and SPF of the latter two formulations reflect the great differences between the two kinds of TiO<sub>2</sub> used: for sunscreen formula D, containing a highly micronized titanium, the SPF obtained is about 35, with compliant UVAPF (UVA/UVB ratio of about 1/3); for sunscreen formula E containing a much larger TiO<sub>2</sub> particles, the SPF obtained is lower (25); however, the UVAPF is decidedly higher (i.e., the UVA/UVB ratio is much higher than 1/3). Apparently, in the study formulation, titanium micronization increases SPF and reduces UVA absorption.

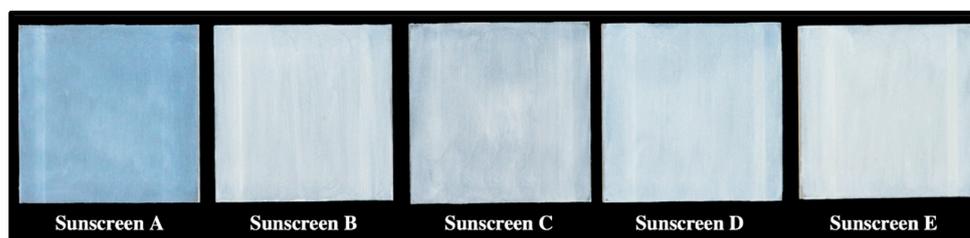
The UV absorption curves (Figure 8) confirm what state above: Titanium Dioxide (Nano), Aluminum Hydroxide, Stearic Acid absorbs much more intensively in the UVB; in comparison Titanium Dioxide, Silica, Jojoba Esters, which has a larger particle size, absorbs less in the UVB range but more in the UVA and visible, so it is expected to have less transparency, less UVB protection but more UVA protection. Therefore, to achieve adequate UVA protection, the TiO<sub>2</sub> particle size cannot be too small, although this involves a partial loss of SPF and transparency, as seen in Figure 1.



**Figure 8.** Absorption curves of the different formulations (A–E).

### 3.6. Sunscreens' Appearance and Transparency

An evaluation on a PMMA plate was conducted in the range of visible radiation through direct observation of images and the spectrophotometric analysis, according to the methods described above (Section 2.8). The results of both analyses confirmed that sunscreen formula E was the least transparent (Figure 9).



**Figure 9.** Order of transparency:  $A < C < B \leq D < E$ .

## 4. Discussion

The formulation of effective and pleasant sunscreen, having a natural, organic, sustainable (CPCNS) connotation, is getting a more and more complex approach for the paucity of suitable ingredients. Broad protection and a broad spectrum “green” sunscreen require a careful selection of suitable filters; the choice of coated pigments with an appropriate

surface treatment is essential to obtain a formulation that is both attractive and stable over time and also accepted by most of the certified bodies. In order to develop an example of approach to certifiable sunscreens, in the present study, we decided to follow the widely adopted COSMOS standard which has the largest number of approved ingredients among certified bodies. For this standard, organic ultraviolet (UV) filters are not allowed and thus we investigated inorganic filters.

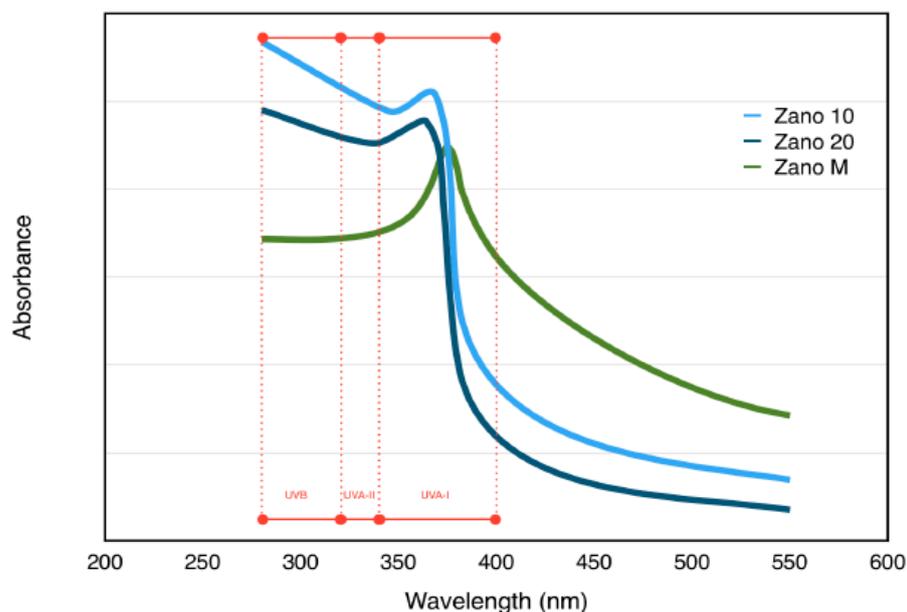
ZnO and TiO<sub>2</sub> reflection/scattering, and absorption largely depends on the size: as little as more is the absorption mechanism [29]. In particular, ZnO (nano) provides wider protection in UVA and UVB range (SPF and UVA-PF) but with less intensity in regards TiO<sub>2</sub>(nano), as it protects more strongly at UVA wavelengths; however, if the particle size of TiO<sub>2</sub> is appropriately calibrated, it can also achieve satisfactory results in the UVB area.

UVB attenuation by TiO<sub>2</sub> is mainly due to absorption, so its particle size should be minimized to increase SPF, and thus UVB protection, and achieve a pleasant appearance in view of its transparency. As it can be observed in Figure 9, formula D, which uses the smaller TiO<sub>2</sub> (Titanium Dioxide (Nano), Aluminum Hydroxide, Stearic Acid), shows better absorbance in the UVB in the respect of formula E containing aggregated TiO<sub>2</sub> (Titanium Dioxide, Silica, Jojoba Esters) but maintaining the same Zinc Oxide, Sodium Lauroyl Glutamate, Lysine, Magnesium Chloride.

To balance UVA protection, however, the size of TiO<sub>2</sub> should not be too small, because in this portion of the spectrum, its scattering activity makes a substantial contribution to shielding; this activity decreases with the TiO<sub>2</sub> size. In our case this behavior was not observed to be likely for the difficult dispersion of the aggregate for (about 500 nm) of the Titanium Dioxide, Silica and Jojoba Esters. Moreover, in our case, most of the UVA protection is attributable to the ZnO present in formulation.

ZnO attenuates UV primarily by absorption, regarding both UVA and UVB; it absorbs UVA effectively; however, the levels of protection in terms of SPF factor that it can achieve, even at very high concentrations, are rather low.

Regarding ZnO, three different commercial products were used and corresponding formulations were prepared in order to select the better candidate for combination with different TiO<sub>2</sub> candidates. As for Figure 10 Zinc Oxide, Sodium Lauroyl Glutamate, Lysine, Magnesium Chloride absorbs at longer wavelength in the UVA field in the respect of the ZnO naked itself and of the corresponding Zinc Oxide, Stearic Acid.



**Figure 10.** UV/VIS absorbance curves of a solution 0.1% of ZnO (Zano, courtesy from EVERZINC group SA, Liege, Belgium) particles of different dimension in caprylic/capric triglyceride.

Moreover, as stated above, an increase in viscosity was observed during the time. Indeed, this phenomenon frequently occurs in W/O formulation containing a high level of powders, probably because the powders tend, over time, both to re-aggregate [30] into larger agglomerates, and to adsorb part of the oily phase, effectively removing it from the formulation. The use of coated oxides, particularly with suitable lipophilic coating, allows the emollients to penetrate the agglomerates and wet the particles more easily, and can be effective in limiting and/or slowing down the adsorption and re-aggregation phenomena.

## 5. Conclusions

In conclusion, the pressure from consumer opinions and media toward a natural but sustainable cosmetic product has a deep impact in the field of sunscreen because of the different and sometimes opposite needs regarding human and environmental safety conjugated with a pleasant and effective application. Sunscreen, which is a cosmetic in the EU regulation but an “over the counter drug” in the United States and Japan, has to satisfy specific requisites of protection against sun ray damage. The current perception regarding the potential toxic effects of organic filters pushed toward the development of sunscreen products based on inorganic filters and recently also incurred worries about the impact of intentionally manufactured insoluble and bio-persistent nanomaterials with restrictions in use.

This is particularly true for the TiO<sub>2</sub> molecule, whereas ZnO (because of its solubility and biodegradability) might be the best candidate but with certain limitations in performance. Therefore, the combination of the two filters, TiO<sub>2</sub> and ZnO, appears as the best choice at the moment in the formulation of CPCNS sunscreen, while newer organic natural and inorganic synthetic sunscreen (UV) filters are recognized by EC regulation as safe and effective.

In this plethora of materials, it is difficult for the formulator to orient his choice, risking formulas that are overloaded with filters, that are difficult to spread and that do not meet the compliance of consumers. This may lead to the final result of lower use of the sunscreen product. This is an attitude to be avoided in relation to the risks connected with the onset of skin neoplasms.

In this complex scenario, we propose a safe and sustainable approach (SBD) to formulation to reach the best compromise combining the right concentration and the right material to be used as an inorganic ultraviolet (UV) filter.

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