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abstract

Disrupting changes in the sun care field that signal the avoidance of Octocrylene (OCR) and Ethylhexyl Methoxycinnamate (EHMC) in newer sunscreen developments express a real challenge in terms of performance achievement. Ethylhexyl Triazone (EHT) and Bis-ethylhexyloxyphenol Methoxyphenyl Triazine (BEMT) are often used as replacements but the achievement of higher Sun Protection Factors (SPF) requires additional UVB filters. This paper aims to evaluate the benefits of using Tris-Biphenyl Triazine (TBPT) as additional UV filter in comparison to Phenylbenzimidazole Sulfonic Acid (PBSA) and Titanium Dioxide (TiO₂) seeing that TBPT is organic like PBSA and particulate like TiO₂. We measured the UV absorbance and photostability as product specific performance criteria, and evaluated the risk of the production of free radicals under UV exposure since this is closely linked to photostability and can impact the irritation potential of sunscreens. Their effect in market relevant UV filter combinations was further assessed in view of their contribution to SPF, UVA-PF, blue light protection, and water resistance. We evaluated the ocular acceptability of a sunscreen containing TBPT and proposed solutions for environmentally friendly sunscreens. In this contribution, we show the broadness of the benefits gained in using TBPT in the future production of sunscreens. As a whole, this work reveals the huge potential of TBPT in modern sunscreens.

Introduction

Disrupting changes in the sun care field include the avoidance of Octocrylene (OCR) and Ethylhexyl Methoxycinnamate (EHMC) in new sunscreen developments due to rising concerns regarding their safety profile for humans and for the environment. The number of products without OCR and without EHMC rose from 15% in 2015 to 39% in 2020 in Europe [1]. These new UV filter systems express a real challenge in terms of performance achievement and a real split with the UV filter systems of past decades where sunscreens contained either EHMC or OCR. Ethylhexyl Triazone (EHT), Diethylhexyl Butamido Triazone (DBT) and Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine (BEMT) are very often used as replacement of OCR and EHMC, and create the core of the UVB and broad-spectrum protection. The three belong to the efficient 1,3,5-Triazine filter type, and they are supplied as a powder and require appropriate solubilization. Salicylate-based UV filters including Ethylhexyl Salicylate (EHS) and Homosalate (HMS) are efficient solubilizers and rather used for this feature than for their mere absorbing performance. Recently, the SCCS (Scientific Committee on Consumer Safety) published a new final opinion on the UVB filter HMS after a reevaluation in view of its endocrine disrupting potential. Earlier, HMS was evaluated twice in 2001 and 2007 (SCCP/1086/07) and was considered as safe for the consumer up to a concentration of 10%. The final opinion of June 2021 regards the use of HMS as safe for the consumer up to a maximum concentration of only 0.5% in the final product [2]. HMS was used in approximately 30% of sunscreens launched in Europe in 2020. Formulating out salicylate-based

filters might become an effect of this new final opinion. Other available filters are more effective in absorbing UV rays than salicylate-based UV filters and comprise essentially Phenylbenzimidazole Sulfonic Acid (PBSA), Titanium dioxide (TiO₂), and Tris-Biphenyl Triazine (TBPT). The purpose of the present study is to evaluate the benefits and effects of using TBPT in comparison to PBSA and TiO₂ in sunscreens seeing that TBPT is a water dispersion of organic particles, thereby combining the properties of both the organic-like PBSA and particulate-like TiO₂ filters. We measured the UV absorbance spectrum and photostability profile which consisted of product specific performance features. We evaluated the potential to produce free radicals under UV exposure, which is closely linked to the photostability profile and can impact the irritation potential of sunscreens [3]. We further investigated the effect of studied UV filters in market-relevant UV filter combinations in terms of SPF, UVA PF, blue light protection, and water resistance. We evaluated the benefit of using TBPT for the sensitive eye area and for eco-friendly sunscreens.

Materials and methods

UV filters

We analyzed the benefits of using TBPT in sunscreens by comparing the efficacy and effects of TBPT to PBSA and to TiO₂, since TBPT is added to the water phase like PBSA and is in particulate form like TiO₂. **Table 1** provides the properties of the three UV filters.

UV absorbance

To evaluate the UV performance of Tris-Biphenyl Triazine (TBPT), we measured the extinction from 290 to 400 nm of a 1% (active amount w/v) dispersion at an optical thickness of 1 cm using a UV/Vis spectrophotometer Perkin Elmer Lambda 25. These conditions provide the so-called E_{1,1} value for each wavelength which allows a direct performance comparison between different UV filters. We compared the spectrum of TBPT with the spectra of PBSA and TiO₂.

| Abbreviation | TBPT | TiO ₂ with coating | PBSA |
|--|--|---|-----------------------------------|
| INCI | Tris-Biphenyl Triazine (nano) | Titanium Dioxide (nano) | Phenylbenzimidazole sulfonic acid |
| Nature | Water dispersion of particles | Particles (powder or dispersion) | Water soluble |
| pH in formulation | No limitation | No limitation | > 7 |
| Molecular weight (g/mol) ⁽¹⁾ | 538 / molecule 1.7·10 ⁹ / particle | 80 / molecule 2.3·10 ⁸ – 4.5·10 ⁹ / particle | 274 |
| Median particle size (D50) as given in SCCS dossiers | 81 nm (FOQELS) ⁽²⁾ | 28 to 75 nm (disc centrifuge) | < 1nm |
| ⁽¹⁾ [4] | | | |
| ⁽²⁾ Fiber-optic quasi-elastic light scattering. | | | |

Table 1: Properties of TBPT, PBSA and TiO₂

Photostability

The recovery (%) after UV irradiation of 1% TBPT and 1% PBSA without or with 5% Butyl Methoxydibenzoylmethane (BMDDBM) or 5% Diethylamino Hydroxybenzoyl Hexyl Benzoate (DHHB) was determined with HPLC measurements (Agilent 1100 Series, Agilent Technologies, Santa Clara, CA, USA). In this methodology, the studied UV filter/UV filter combination was formulated in an oil-in-water (O/W) base which was spread on a sand-blasted quartz plate at an amount of 5.6 mg (thickness layer of 2 mg/cm²) followed by 30 minutes of equilibration time. The plates were irradiated with UV light (Suntest CPS+ irradiation chamber, Atlas, Illinois, USA) with increasing exposure times of 0h, 1h, 2h, 4h and 10h corresponding to 0, 5, 10, 20 and 50 MED (Minimal Erythral Dose respectively), 1 MED equaling 59.8 kJ/m². After irradiation, the formulation was washed off the quartz plate with a solvent (in a 5 ml volumetric flask) and the remaining parent UV filter concentration evaluated via HPLC. The averaged peak area of the probe without irradiation was set to 100% and the ones after irradiation related to the one without irradiation. Analysis wavelengths were chosen as 314 nm for TBPT, 300 nm for PBSA, 357 nm for BMDDBM and DHHB.

Measurement of free radicals

The formulations were the same as for the evaluation of the photostability. Photostability of a UV filter is a key factor for its potential to generate free radicals under UV exposure. We evaluated the percentage of UV-induced free radicals in the O/W emulsion containing 1% TBPT or 1% PBSA, either alone or combined with 5% BMDDBM or 5% DHHB via electron spin resonance (ESR) spectroscopy (MiniScope MS300, Magnetech GmbH Berlin, Germany). The measurement was performed following the method described earlier, referred to as study 1 in Sohn et al. [5]. In this methodology, the spin probe PCA, (2,2,5,5-tetramethyl pyrrolidine N-oxyl, Sigma-Aldrich, Munich, Germany) is added to the probe (0.01 mM).

It is stable over time but reacts with free radicals produced in the formulation under UV irradiation (UV solar simulator 300 W Oriel, Newport) to be reduced to the ESR-silent hydroxylamine. The integrated irradiances values were 23.5 W/m² for the range 280 to 320 nm and 180 W/m² for the range 320 to 400 nm. The signal intensity decay of PCA was measured as a function of UV exposure doses, and the samples were exposed up to 10 minutes of UV irradiation (= 13.9 J/cm²). The amount of reduced PCA can be measured and the percentage of UV-generated free radicals deduced.

SPF and UVA protection

To assess the benefits of TBPT in a product without OCR and EHMC, we measured the SPF *in vivo* [6] and the UVA protection of an O/W formulation containing a core UV filter system of 3.0% EHT, 4.0% DHHB, and 1.0% BEMT. In addition, we added either 3% TBPT or 3% PBSA or 3% TiO₂. For the UVA protection, the ratio UVA-PF/SPF expressed as superior or inferior to the value of 1/3 was given. The criterium of 1/3 is recommended by the European Commission so that the minimum UVA protection factor afforded by a sunscreen should be at least equal to or higher than 1/3 of the SPF [7].

Water resistance

Water resistance became a standard performance claim; 65% of sunscreens launched in Europe in 2020 claimed water resistance [8]. We measured the *in vitro* water resistance of two sunscreens based either on TBPT or on PBSA as additional UVB filters according to a method described earlier referred to as the "solution method" [9]. In this methodology, 2 mg/cm² of the tested sunscreen was applied on four plates made from Ethylene Methacrylate Acid Copolymer named M14 EMA in [9]. Two of them were immersed in a water bath, and, after immersion, each of the four plates (immersed and not immersed) was rinsed off with a solvent mixture (THF/Ethanol/Neutrol TE (50:48:2)). The solvent/formulation solution was diluted (1:40) and measurements of the UV absorbance were

performed from 290 to 400 nm using a Lambda 20 device. The static SPF *in silico* value was deduced from the UV absorbance spectra of the non-immersed plates and the wet SPF *in silico* from the UV absorbance spectra of the immersed plates using a computational method developed for this purpose. The percentage of water resistance is calculated from the ratio between the average wet and average static *in silico* SPF.

The composition of tested formulations is given in **Table 2**. The SPF *in silico* was 16 for the UV filter composition without PBSA and without TBPT, and increased to 30 with an additional 3% PBSA or 2.5% TBPT [10].

Blue light protection

Blue light protection was measured with the same formulations as for the water resistance test (**Table 2**). The blue light transmittance of the probe applied on PMMA plates (SB6 from HelioScreen Labs, FR) with an amount of 1.2 mg/cm² was measured using a Labsphere UV-2000S device (Labsphere Inc, USA) between 400 and 450 nm. Three plates were prepared per probe and 5 transmittance measurements were performed per plate. The average transmittance value was used to calculate the blue light protection. The blue light protection factor given in percentage corresponds to the reduced transmitted light between 400 and 450 nm.

Sensitive eye area

The stinging potential on eyes of a formulation containing TBPT was evaluated in a clinical test (Eurofins, DermScan, Gdansk, Poland) performed in accordance with the Helsinki declaration and successive updates. The methodology consisted in a single-blind and intra-individual test involving 20 subjects with a phototype I to IV and an average age of 43 ± 4. An amount of 0.5 ml of the tested probe was applied by the subject on the contour of one of its eyes as in normal conditions of use, under the control of the technician. A saline solution used as a comparison product was applied on the

other eye contour by the technician using a soaked cotton pad and by wiping 3 times. The panelists were asked to blink several times. A clinical examination of the eyes and contours was performed by an ophthalmologist before and after a single application of the probe. The observation included the examination of the state of the cornea, bulbar and palpebral conjunctiva and eyelids using a slit lamp. After product application, the same examination was performed by the same

| Trade Name | INCI abbreviation | % in product PBSA based | % in product TBPT based |
|---------------------|--|----------------------------|----------------------------|
| Eumulgin Prisma | Disodium Cetearyl Sulfosuccinate | 0.5 | 0.5 |
| Eumulgin SuCro Plus | Sucrose Polystearate (and) Cetyl Palmitate | 3.0 | 3.0 |
| Cutina GMS SE | Glyceryl Stearate SE | 2.0 | 2.0 |
| Cutina HVG | Hydrogenated Vegetable Glycerides | 2.5 | 2.5 |
| Cetiol OE | Dicaprylyl Ether | 2.0 | 2.0 |
| Cetiol CC | Dicaprylyl Carbonate | 10.0 | 10.0 |
| Cetiol RLF | Caprylyl-Caprylate/Caprates | 5.0 | 5.0 |
| Hydagen CAT | Triethyl Citrate | 5.0 | 5.0 |
| Dermosoft Octiol | Caprylyl Glycol | 0.4 | 0.4 |
| Sensiva SC50 | Ethylhexylglycerin | 0.2 | 0.2 |
| Spherilex 10PC | Hydrated Silica | 2.0 | 2.0 |
| Uvinul A Plus | Diethylamino Hydroxybenzoyl Hexyl Benzoate | 4.0 | 4.0 |
| Uvinul T 150 | Ethylhexyl Triazone | 2.5 | 2.5 |
| Tinosorb S | Bis-ethylhexyloxyphenol Methoxyphenyl Triazine | 1.0 | 1.0 |
| Water | Aqua | Qsp 100% | Qsp 100% |
| Glycerin | Glycerin | 5.0 | 5.0 |
| Rheocare XGN | Xanthan Gum | 0.3 | 0.3 |
| | Phenylbenzimidazole Sulfonic Acid | 3.0 | ---- |
| Tinosorb A2B* | Tris-Biphenyl Triazine (nano), Aqua, Decyl Glucoside, Butylene Glycol, Disodium Phosphate, Xanthan Gum | ---- | 5.0 |

* 50% dispersion, 5.0% Tinosorb A2B corresponds to 2.5% active amount of Tris-Biphenyl Triazine

Table 2: Composition of the products in the water resistance test

| Trade Name | INCI abbreviation | % in product |
|------------------|--|--------------|
| Cetiol B | Dibutyl Adipate | 8.0 |
| Cetiol OE | Dicaprylyl Ether | 7.0 |
| Cetiol Sensoft | Propylheptyl Caprylate | 6.0 |
| Cetiol Ultimate | Undecane, Tridecane | 4.0 |
| Euxyl PE 9010 | Phenoxyethanol and Ethylhexylglycerin | 1.0 |
| Uvinul A Plus | Diethylamino Hydroxybenzoyl Hexyl Benzoate (DHBB) | 5.0 |
| Uvinul T 150 | Ethylhexyl Triazone (EHT) | 3.0 |
| Tinosorb S | Bis-ethylhexyloxyphenol Methoxyphenyl Triazine (BEMT) | 1.5 |
| Water | Aqua | Qsp 100% |
| Glycerin | Glycerin | 3.0 |
| Avicel PC 611 | Microcrystalline Cellulose, Cellulose Gum | 1.0 |
| Rheocare XGN | Xanthan Gum | 0.2 |
| Tinovis GTC UP | Acrylates/Beheneth-25 Methacrylate Copolymer | 1.5 |
| Sodium Hydroxide | Sodium Hydroxide | Qs |
| Tinosorb A2B | Tris-Biphenyl Triazine (nano), Aqua, Decyl Glucoside, Butylene Glycol, Disodium Phosphate, Xanthan Gum | 6.5 |
| Tinosorb M | Methylene Bis-Benzotriazolyl Tetramethylbutylphenol (nano), Aqua, Decyl Glucoside, Propylene Glycol, Xanthan Gum | 4.0 |

Table 3: Composition of the product assessed for ocular acceptability

ophthalmologist to detect any modification and to assess ocular acceptability. In parallel, the subjects made a self-evaluation of the stinging and watering sensation. The tested product shows a SPF *in silico* of 50 [10], and its composition is given in **Table 3**.

Eco-friendly sunscreens

Concerns of the damaging effects of UV filters on ecosystems gained a high level of awareness in public debates, since they are likely to be directly released into the environment. To meet the demand of eco-conscious consumers, some manufacturers focus their promotion on the biodegradability of their product with a protocol which was developed for the testing of the biodegradability of raw materials and not of finished formulations [11]. Besides, describing the eco-friendliness of a UV filter combination with the isolated biodegradability factor is inadequate; it should encompass all ecological relevant compartments. We used the EcoSun Pass value to characterize the eco-friendliness of UV filter combinations with Tris-Biphenyl Triazine [12,13]. The EcoSun Pass value considers the individual environmental hazard profile of the UV filters plus the efficacy of the composition using the SPF and UVA-PF in relation to the total UV filter concentration. The environmental hazard profile of a UV filter is determined individually using representative criteria of the environmental fate and ecotoxicological profile of the corresponding UV filter. These criteria encompass the biodegradation, bioaccumulation, acute and chronic aquatic toxicity, chronic terrestrial toxicity, and sediment toxicity. The EcoSun Pass aims to facilitate the selection of the most appropriate UV filter combination in respect of eco-friendliness.

Results

UV absorbance

Figure 1 displays the E(1,1) absorbance profile of TBPT, PBSA and TiO₂ (coating; Aluminum Hydroxide (and) Dimethicone (and) Dimethicone/Methicone Copolymer).

From the absorbance curves, we can deduce that the maximum E(1,1) value is 1110, 875, 945 for TBPT, PBSA, TiO₂ at the wavelength of 310, 305, and 290 nm, respectively. Also, the area under the curve (AUC) is used as an indicator factor of the efficacy of the UV filter since it provides information on the UV coverage effectiveness obtained with 1% active of UV filter. The AUC obtained from the absorbance data equals 580 for TBPT, 245 for PBSA and 450 for TiO₂ over the UV range 290-400 nm. The E(1,1) and the AUC values express the efficacy and anticipate the impact of the UV filter on the

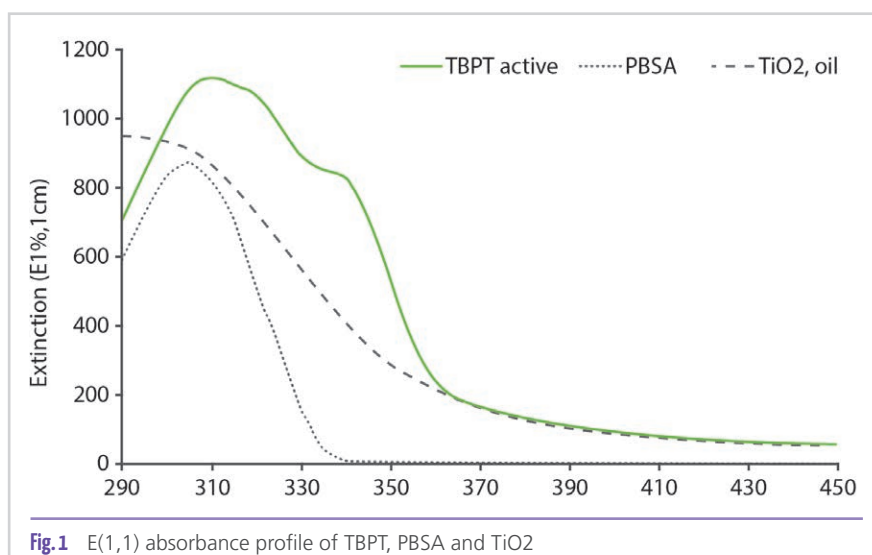


Fig. 1 E(1,1) absorbance profile of TBPT, PBSA and TiO₂

SPF. The higher the values, the higher the impact on the SPF is expected to be. **Figure 1** also reveals that the shape of the absorbance curves varies between the UV filters; the profile of TBPT is unique since it shows a shoulder in the UVAII range extending up to 340 nm with a value of E(1,1) of 825. Sayre et al. showed that a UVB-loaded sunscreen blocking exclusively radiation from 290 to 320 nm would assumably reach a maximum SPF of 11 because a continuous amount of UVAII radiation, which is likewise erythemally active, is transmitted [14]. From its absorbance profile, TBPT should positively impact the SPF and UVA protection versus PBSA and TiO₂ whose efficacy is lower in the UVB range and lacking the UVAII shield.

Photostability

The recovery (in %) of PBSA and TBPT, alone and in combination with either 5% BMDDBM or 5% DHHB, after increasing irradiation doses is shown in **Figure 2** and **Figure 3**.

TBPT is sensibly more photostable than PBSA, with 100% of the parent molecule that is recovered for TBPT versus 91% for PBSA after an irradiation of 14400 s (corresponding to 20 MED) and 85% for TBPT versus 68% for PBSA after an irradiation of 36000 s (corresponding to 50 MED). The photostability profiles of TBPT and PBSA highly differ when combined with BMDDBM. Whereas TBPT remains photostable in combination with BMDDBM, PBSA is photodegraded when combined with BMDDBM (**Figure 2**). By contrast, PBSA is photostabilized in combination with DHHB with a recovery of 97% after 14400 s UV irradiation. DHHB remains fully photostable (data not shown).

Measurement of free radicals

The percentage of free radicals generated in an O/W formulation after UV irradiation was determined by electron spin resonance (ESR) spectroscopy. The formulations were the same as for the photostability test and differed only with the filter

composition. The results are given in **Table 4**. A value of 0% would signify that the spin probe PCA remained as is in the formulation and no free radicals are generated with UV irradiation; by contrast, a value of 100% would signify that the spin probe PCA is immediately and totally reduced into ESR silent hydroxylamine because it reacted with the free radicals generated intensively and immediately after starting the irradiation of the formulation with UV light.

Table 4 indicates that PBSA actively initiates the production of free radicals upon UV irradiation. This is in line with the investigations of *Inbaraj et. al* and *Bastein et al.* who studied the photophysical and photochemical properties of PBSA and showed its ability to photogenerate reactive oxygen species and free radicals capable of damaging DNA [15,16]. In combination with DHHB, the number of UV-generated free radicals produced in the formulation is decreased by 40%, which is most probably related to the improved photostability of PBSA in combination with DHHB (**Figure 2**). Compared to PBSA, the number of free radicals produced in the formulation containing TBPT is approximately 80% lower, which is further reduced to a very small number when TBPT is combined with DHHB. Free radicals might also be generated by some of the formulation excipients, but it is not possible here to specifically distinguish the effect of each excipient.

SPF and UVA protection

To substantiate the observations regarding the absorbance spectra, we investigated the impact of TBPT in comparison to PBSA and TiO₂ on the UV efficacy in a realistic UV filter combination. **Table 5** provides the SPF *in vivo* value [6] and the ratio UVA-PF/SPF expressed as superior or inferior to the value of 1/3 of a UV filter combination containing EHT, DHHB, BEMT plus PBSA, or TiO₂, or TBPT.

As expected, the SPF *in vivo* of the base was increased by the addition of a further UVB filter, but the level of increase differed highly between investigated UV filters. An SPF increase of 70% and 47% was achieved by adding PBSA and TiO₂ to the base, respectively. In compar-

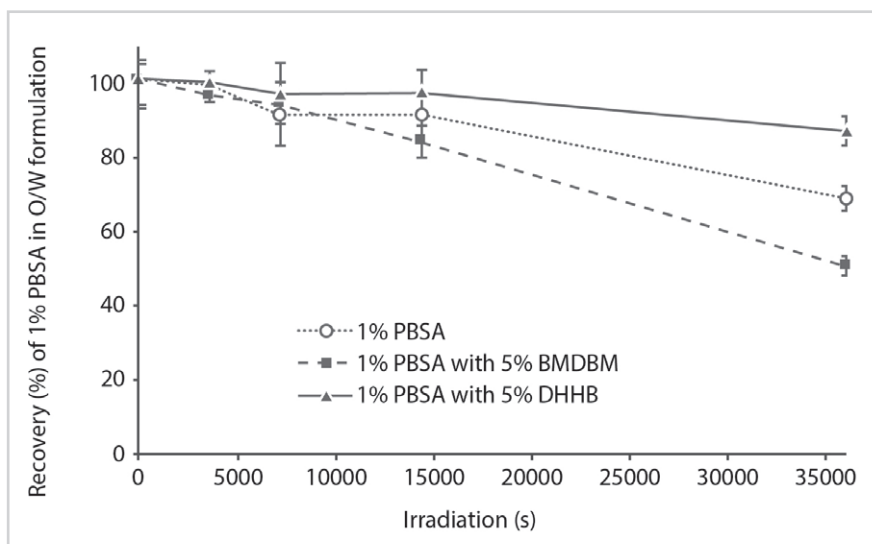


Fig.2 Recovery (%) of 1% PBSA without and with 5% of BMDMB or 5% DHHB

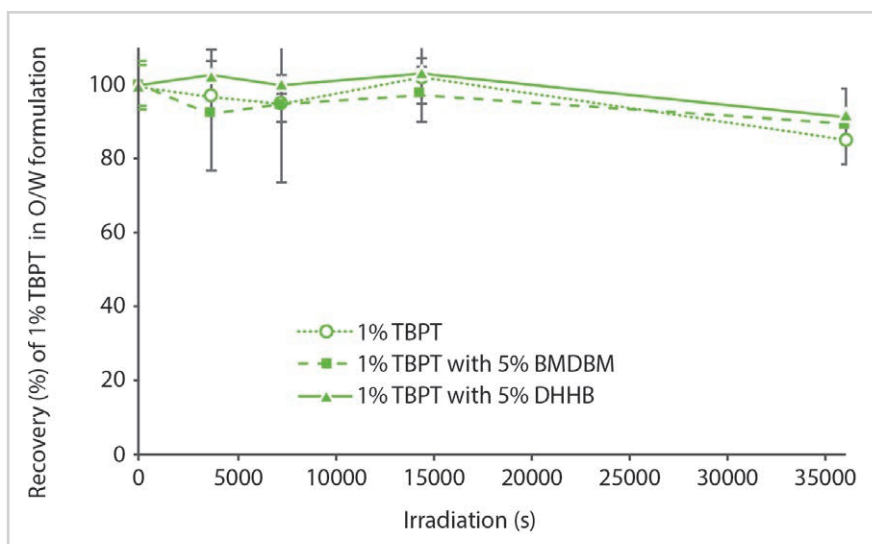


Fig.3 Recovery (%) of 1% TBPT without and with 5% of BMDMB or 5% DHHB

| UV filter combination | Free radicals (%) |
|-----------------------|-------------------|
| 1% PBSA | 75.7% (+/-0.05) |
| 1% PBSA + 5% DHHB | 45.3% (+/-0.35) |
| 1% TBPT | 12.7% (+/-0.54) |
| 1% TBPT + 5% DHHB | 3.7% (+/-0.18) |

Table 4: Free radicals (%) generated in the formulation after UV irradiation, n=2

| UV combination | SPF <i>in vivo</i> | UVA-PF / SPF |
|--|--------------------|--------------|
| Base (3% EHT + 4% DHHB + 1% BEMT) | 17 | > 1/3 |
| Base + 3% PBSA | 29 | < 1/3 |
| Base + 3% TiO ₂ (Aluminum Hydroxide (and) Stearic Acid) | 25 | < 1/3 |
| Base + 3% TBPT | 43 | > 1/3 |

Table 5: SPF *in vivo* and UVA-PF/SPF criterium

ison, the addition of TBPT resulted in a SPF push of 150%. Looking at the UVA protection, only TBPT was able to maintain the ratio UVA-PF/SPF superior to 1/3 like for the base. This overall and strong boosting can be explained by three of its features. The SPF is directly and positively impacted by the higher UVB absorbance seen for TBPT versus PBSA and TiO2. The extended absorbance in the UVAII benefits both to the SPF and UVA-PF, which explains the safeguarding of the UVA protection. Furthermore, the presence of TBPT in the water phase of the emulsion is an additional advantage to avoid the formation of un-protected areas of the non-volatile water part, remaining after spreading of the product [17]. Finally, its particulate nature accounts a lot in the boosting properties of TBPT. When UV light hits a TBPT particle, one part is absorbed and another part is scattered; the pathlength of the scattered light is increased and the likelihood that it is absorbed by a surrounding UV filter molecule is increased. This mechanism was described in detail by Herzog et al [18].

However, nano particulate UV filters currently suffer from a downgrade in the media and by digital consumer apps using a biased evaluation that reaches the end consumer and provokes worries with respect to the human safety of UV filters in nano form. The concern relates to their percutaneous absorption potential, yet all registered UV filters including nano UV filters needed to go through an extensive safety evaluation to obtain a positive SCCS opinion to be marketed [19]. TBPT exhibits a logarithmic octanol/water partition coefficient (log Pow) much higher than 4, a negligible water solubility in the ng/L range, a melting point of 281°C, and a molecular weight over 500 g/mol, not to mention the molecular weight of the particles. Each single of these properties has been determined to decrease the potential for dermal penetration. In combination, they explain the unlikeliness of TBPT to penetrate skin. Taking solely the particle size criterium, implying that several molecules connected to each other to form a particle, comparing TBPT (particle) to the size of a soluble UV filter molecule, basically "Nano means Big". This enlightens us why there is no scientific rationale to downgrade nano UV filters in sunscreens due to their solely particulate nature.

Water resistance and blue light protection

The water resistance *in vitro* and blue light protection were evaluated with the same formulations (Table 2), and the results are given in Table 6. The formulations differed by the addition of either PBSA or TBPT to achieve an SPF of 30.

| | PBSA-based sunscreen | TBPT-based sunscreen |
|--------------------------------------|----------------------|----------------------|
| <i>In vitro</i> water resistance (%) | 51% | 72% |
| Blue light protection (%) | 7% | 35% |

Table 6: Water resistance and blue light protection of PBSA versus TBPT containing sunscreens with SPF 30





| UV combination | SPF 20 | SPF 30 | SPF 50 | SPF 50+ |
|--|---|---|---|---|
| Ethylhexyl Triazone | 2.00 | 2.50 | 3.00 | 3.50 |
| Tris-Biphenyl Triazine | 1.25 | 2.50 | 3.50 | 4.00 |
| Bis-ethylhexyloxyphenol Methoxyphenyl Triazine | 1.00 | 1.00 | 2.50 | 3.00 |
| Diethylamino Hydroxybenzoyl Hexyl Benzoate | 3.00 | 4.00 | 5.00 | 6.00 |
| EcoSun Pass value | 228 | 246 | 259 | 261 |
| |  |  |  |  |

Table 7: UV filter combinations (in % in finished formulation) fulfilling EcoSun Pass of at least 200 for SPF 20 to 50+ with UVA-PF/SPF > 1/3

The water resistance of the sunscreen containing TBPT is much higher than of the one with PBSA. This is presumably due to the washing off of the water-soluble filter during water contact. The SPF *in silico* of the filter system equaled 16 and 30 without and with PBSA respectively. Since the water resistance is 51%, we may assume that a large portion of PBSA was rinsed off of the plate during water immersion. By contrast, TBPT consists of hydrodispersed but hydrophobic particles and is not dissolved in the water phase which explains the significantly greater water resistance of 71% achieved when adding TBPT in comparison to PBSA. Another advantage of the particulate nature of TBPT versus soluble PBSA is its scattering properties, which leads to the extension of the protection into the blue waveband even as an UVB filter. The transmission in the short visible range could be reduced by 35% with the combination containing TBPT, in comparison to 7% with the combination containing PBSA, the latter being ascribed mostly to the absorption tail of the present UVA filter DHHB.

Sensitive eye area

The clinical ocular assessment of tested cream-gel containing a mixture of 5% DHHB, 3% EHT, 1.5% BEMT, 3.25% TBPT and 2% MBBT did not reveal any modification of the state of the cornea, bulbar and palpebral conjunctiva or eyelids. No undesirable or adverse effects, such as stinging or watering, could be felt by the subjects. The formulation fulfilled the criterium for claiming "does not sting the eyes" and "tear free".

Eco-friendly sunscreens

Table 7 provides UV filter combinations fulfilling the EcoSun Pass criterium optimized with respect to minimal impact on the environment for SPF values of 20 to 50+. The threshold

for satisfying the EcoSun Pass criterium was set to 200, which can be reached with UV filters currently on the market. This criterium, however, also shows that there is room for improvement in the development of optimized eco-friendly sunscreens that respect the environment and nature.

Conclusions

In this contribution, we showed the broadness of the benefits gained in using TBPT in the future production of sunscreens. Compared to the soluble UVB filter PBSA and particulate filter TiO₂, TBPT offers unique absorbance coverage; it highly contributes to an increase in SPF without unbalancing the UVA protection thanks to its unique UVAII shield. Compared to PBSA, its particulate nature allows the upholding of the water resistance and the extension of the protection up to the blue waveband. TBPT is also photostable with both commonly used UVA filters BMDDBM and DHHB, which is essential not to generate free radicals under UV exposure. TBPT has not led to any undesirable skin reaction in an acceptability test around the sensitive eye area. Finally, TBPT allows the development of eco-conscious sunscreens up to SPF 50+. As a whole, this work reveals the huge potential of TBPT in modern sunscreens.

Acknowledgments

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