Synergy of mica and inorganic UV filters maximizes Blue Light Protection as first defense line

Marina Lefort, Jutta zur Lage, Lilia Heider, Frank Pfluecker
MERCK, Frankfurter Str. 250, 64293 Darmstadt, Germany

INTRODUCTION:

Blue Light and its potential damage to skin is a concern that has become extremely widespread. Reasons for this new interest are manifold, ranging from recent studies showing that HEVL (high energy visible light, 400-500 nm) penetrates the dermis causing generation of reactive oxygen species (ROS) [1-3], exponential usage of mobile device emitting high proportion of these short, high-energy wavelengths, and uncertainty as to whether our modern sunscreen and skin care products that are designed to grant well-balanced UV-A/B protection provide any protection from blue light.

There is an obvious need for efficient defense against HEVL within cosmetic products, and consequently a need for a suitable easy-to-use test method to assess it. There are two ways of considering protection: ingredients that help counteract the production of radicals in/on skin such as antioxidants acting as second defense line; and ingredients that prevent/minimize free radical formation from the beginning through absorbing, reflecting and scattering properties, thus acting as first defense line.

In previous investigations using photometric measurements of cosmetic formulations on different substrates in vitro, we could show that UV filter grade titanium dioxides with different coatings and particle sizes may offer excellent first defense from high energy visible light (HEVL) and IR-A light [4].

Now we present new findings showing that combinations of appropriate TiO$_2$ UV filters with a selected range of mica based functional fillers owing a special coating of inorganic oxides can provide tremendous first level protection against harmful HEVL, and represent herewith an innovative concept for modern and protective skin care.

Furthermore, we propose a new in vitro method to assess the blue light protection efficacy of cosmetic formulations based on transmission measurements on PMMA plates.

MATERIALS & METHODS:

Selected micronized titanium dioxide UV filters (at 3-10 % use level) with various coatings and particle sizes and/or skin color correcting functional fillers (at 3-5 % use level) were incorporated in standard o/w and w/si emulsion systems (Tab. 1; See Rozman et al. (2017) for composition of emulsions). Their performance was analyzed by two different spectrophotometric methods – measurements in short cut cuvettes and on PMMA plates – by determining the transmission rate (T) of HEVL through the respective test emulsions.
The base emulsions serving as placebo (which did not contain any scattering nor absorbing nor antioxidative ingredients) were normalized to 100 % transmission and the reduction in transmission i.e. the protection provided by the test materials was evaluated. The read out was defined as follows:

Protection (%) = \[1- \frac{T(\text{emulsion with TiO}_2/\text{Filler})}{T(\text{base emulsion})}\] x 100.

**Broad spectrum inorganic UV-A/UV-B filters**

<table>
<thead>
<tr>
<th>Code</th>
<th>INCI</th>
<th>Properties</th>
</tr>
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<tbody>
<tr>
<td>T-AS</td>
<td>Titanium Dioxide (EU: nano), Alumina, Silicic acid</td>
<td>Amphilic, versatile and high SPF efficient</td>
</tr>
<tr>
<td>T-ASA</td>
<td>Titanium Dioxide (EU: nano), Alumina, Stearic Acid</td>
<td>Hydrophobic, vegetable derived coating</td>
</tr>
<tr>
<td>T-AMn</td>
<td>Alumina, Manganese Dioxide</td>
<td>Amphilic, with anti-radical properties</td>
</tr>
<tr>
<td>T-Si</td>
<td>Titanium Dioxide (EU: nano), Silica</td>
<td>Hydrophobic, alumina free, increased compatibility and synergy with Avobenzone</td>
</tr>
<tr>
<td>T-SiCP</td>
<td>Titanium Dioxide (EU: nano), Silica, Cetyl Phosphate</td>
<td>Amphilic, best compatibility with challenging ingredients</td>
</tr>
</tbody>
</table>

**Skin color correcting functional fillers**

<table>
<thead>
<tr>
<th>Code</th>
<th>INCI</th>
<th>Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>FF-Go</td>
<td>Titanium Dioxide, Mica, Tin oxide</td>
<td>White pigment, low coverage, with gold interference</td>
</tr>
<tr>
<td>FF-Re</td>
<td>Titanium Dioxide, Mica, Tin oxide</td>
<td>White pigment, low coverage, with red interference</td>
</tr>
<tr>
<td>FF-BI</td>
<td>Titanium Dioxide, Mica, Tin oxide</td>
<td>White pigment, low coverage, with blue interference</td>
</tr>
<tr>
<td>FF-Gr</td>
<td>Titanium Dioxide, Mica, Tin oxide</td>
<td>White pigment, low coverage, with green interference</td>
</tr>
</tbody>
</table>

Tab. 1: Test substances

Spectroscopic measurements in short cut cuvettes (with a defined film thickness of 0.1 mm) were conducted as previously described [4]. For the measurements on PMMA plates, four molded plates (HD6, HeliScreen) were prepared for each sample. Product spreading was performed according to the method depicted in ISO 24443 (*in vitro* UVA-PF) with an amount of 1.3 mg/cm². A glycerol coated PMMA plate (0.58 mg/cm²) served as base line. Transmission measurements in the HEVL range (400-500 nm) were performed with and UV-VIS spectrophotometer (Cary 300 Bio, Agilent).

**RESULTS:**

**Measurements in short cut cuvettes**

The reproducibility of the method was checked with 5 repeated measurements for both placebo emulsion systems: A standard deviation (SD) of ± 1 % transmission of HEVL was found for the o/w emulsion (mean 55 %) and ± 2 % transmission for the w/si emulsion (mean 73 %).

Titanium dioxides formulated in these two different emulsions systems showed an outstanding performance in reducing light transmission in the range of 400- 500 nm. In the o/w emulsion, the most efficient grades were T-AMn and T-Si that could reduce the
transmission by up to 80 % and 67 % respectively compared to placebo (Fig. 1). In the w/si emulsion, an optimized effect could be achieved with T-ASA at its highest tested concentration of 25 % for which a transmission reduction of 85 % was measured. However, even at lower use level of 5 % TiO₂, high protection levels of 50 – 60 % were also observed for T-ASA, T-AMn and T-Si (Fig. 2).

Following these first very encouraging results obtained with titanium dioxide UV filters, we had a look at further scattering, absorbing and reflecting systems. We selected a range of mica based functional fillers owing a special coating of inorganic oxides like titanium dioxide and tin oxide (Tab. 1). O/w formulations with 3 – 5 % fillers were evaluated for their ability to reduce HEVL transmission.

A nice protective effect could be observed as well, even if to a slightly lower extent than with micronized TiO₂ UV filters. Best impact was measured for the blue interference filler FF-Bl at 5 % use level achieving 42 % transmission reduction. FF-Go, FF-Re and FF-Gr provided similar protective effects of approx. 25 % (Fig. 3). All results showed that concentration of the inorganic test materials and transmission rate are inversely proportional. The type of formulation and the distinct characteristics of the test substances (particle size distribution, particle shape, coating) may also influence the overall performance.

Our next approach was to combine above mentioned systems to understand the physical aspects of the first defense line created by these inorganic systems in the HEVL range. A combination of T-AMn (10 %) and FF-Bl (5 %) in o/w was tested as proof of concept. The tandem T-AMn / FF-Bl achieved an exceptional transmission reduction of 89 %, which even outperforms the addition of protective effects of both single materials – 72 % for T-AMn and 42 % for FF-Bl; i.e. a theoretically calculated transmission reduction of 83 % (Fig. 4).
Measurements on PMMA plates:

4 plates per test sample were used to ensure measurement accuracy. With an application amount of 1.3 mg/cm², both o/w and w/si base emulsions showed high transparency after spreading on the plates: indeed, transmission values of 92 ± 1% for the o/w and 90 ± 0% for the w/si were measured.

Transmission measurements on PMMA plates resulted in a similar picture as for measurements in short cut cuvettes. All tested TiO₂ UV filters could reduce the HEVL in a dose-dependent manner. In the o/w system, the most efficient grades were T-Si and T-AMn offering protection levels of up to 44 % and 38 % respectively (Fig. 5). On the other hand, no differentiation with regard to performance was observed in the w/si emulsion: all tested titanium dioxides provided a similar protection level of approx. 20 % (Fig. 6).
The functional fillers formulated in the o/w emulsion could lower the transmission of HEVL as well, even though the effect was quite moderate. The highest result was obtained with the blue interference pigment FF-Bl which provided up to 15 % protection from HEVL (Fig.7).

Fig. 6: Transmission of HEVL through TiO2 UV filters (5 % in w/si formulation; PMMA method)

Fig. 7: Transmission of HEVL through functional fillers (3-5 % in o/w formulation; PMMA method)

The next step was to assess the previously identified outstanding mix of T-AMn (10 %) and FF-Bl (5 %) by means of the PMMA method. We could confirm that the combination of these different inorganic systems generates additive protective effects with regard to HEVL defense. The transmission of HEVL was highly reduced by 46 %, fully in line with the addition of the protection levels provided by both single materials – 39 % for T-AMn plus 15 % for FF-Bl; i.e. a theoretically expected transmission reduction of 48 % (Fig. 8).

Fig. 8: Transmission of HEVL through combination of T-AMn UV filter (10 %) plus FF-Bl filler (5 %) in o/w formulation (PMMA method)

Fig. 9: Transmission of HEVL through combination of T-AS UV filter (5 %) plus functional filler (3 %) in o/w formulation (PMMA method)

To simulate more market relevant conditions, further combinations were assessed considering 5 % TiO2 UV filter and 3 % functional filler as common use levels in commercial sunscreens and day care products. Example measurements of one specific TiO2 grade (T-AS) combined with distinct fillers offering various skin color correcting properties are shown.
in Fig. 9 while Fig. 10 gives insights on the performance of one selected functional filler (FF-Bi) with different TiO₂ UV filters.

![Normalized transmission [%]](image)

In all cases, the ability to reduce the transmission of blue light was greater for the formulation containing a mix of both type of inorganic materials compared to the respective formulations containing the single ingredients. Furthermore, real additive effects could be observed as the measured values were always very close to the expected calculated transmissions, sometimes even slightly lower. Hence such combinations result in improved first defense against HEVL.

**DISCUSSION:**

Transmission of light can be described as a percolation of electromagnetic waves through a material; in our case through a cosmetic formulation. The penetration or passing of light through the formulation is reduced when light is reflected, scattered or absorbed by particulate matter within the formulation. This can be efficiently realized by titanium dioxides and inorganic particulate functional fillers. When the transmission of the sample containing particulate matter is significantly lower than the transmission of the placebo, a protective effect for the skin can be measured. To realize an optimal protective benefit within a product formulation, parameters like concentration level, particle size plus shape, and selected absorbing systems including respective coatings need to be adjusted. In our systematic approach, a cautious fine-tuning of all these parameters was not realizable as we had to use the same base emulsion to generate comparable results. Therefore, it is challenging to state which is the best performing “blue light protecting” grade among the five tested TiO₂ UV filters and why. All of them showed good dose-dependent efficacy, even though the carrier formulation was not optimized to their very diverse characteristics (color, dispersibility, bulk density, grade of transparency,…). It is expected that the HEVL protection
provided by these titanium dioxides in an optimized formulation chassis might be even higher, like it is the case for the SPF/UVA-PF performance in general. Indeed, homogeneity of the film on the plate or on skin is crucial to ensure best achievable performance. Regarding the evaluated functional fillers specifically designed for skin color correcting purposes, the greatest effect could be obtained by using a pigment with a blue interference color representing a coating of roughly 100 - 140 nm thickness of titanium dioxide. Due to the optimized thickness of the absorbing system on the mica platelet an ideal balance of absorption, reflection and scattering of radiation could be reached, thus enriching the general effect of TiO₂ based UV filters. The final outcome of interaction of reflection, absorption and transmission in-between the two inorganic systems represents an enhanced percolation reduction of light through a representative cosmetic formulation and therefore offers a tremendous first level protection of skin against harmful HEV radiations.

Although measurements in short cut cuvettes are fast and easy to implement, we are aware that they may not reflect realistic application level on skin. Indeed, the thickness of the layer in the short cut cuvette is approximately 5 times higher than a typical amount used for a topical application on skin [5]. This layer thickness may lead to artefacts as the formulation chassis itself - without any particulate active ingredient - may reduce the light transmission up to approx. 50 %. This needs to be considered to assess the real contribution of test substances as first defense against HEVL. Therefore, we decided in a second step to investigate the blue light protection efficacy of cosmetic formulations using a photometric method on roughened PMMA plates – inspired by the ISO 24443 used to assess the in-vitro UVA-PF of sunscreen formulations. Besides the fact that a more realistic application amount is taken into account, a clear advantage of the PMMA method is that the influence of the formulation chassis on the transmission is largely negligible: 92 % transmission was measured on the PMMA plate vs. 55 % in the short cut cuvette for the placebo o/w emulsion and 98 % vs. 73 % for the w/si base emulsion. Hence, the PMMA method allows the assessment and the ranking of the blue light protective effect of market cosmetic formulations, as matrix effects are not expected to play a significant role.

**CONCLUSION:**

Titanium dioxides have been successfully used to protect against UV radiation since years. In addition, we proved in this study an excellent protection extended to wider solar radiations like HEVL by combining appropriate TiO₂ UV filters with functional fillers. As direct consequence, the risk of radical formation on/in skin is minimized. This smart combination represents a beneficial and well-balanced concept: both systems fulfill skin protection demands with regard to photo aging; as further advantage, immediate skin tone correcting aspects for skin care and sun care products can be considered.
The blue light protection efficacy of cosmetic formulations can be assessed in vitro by means of transmission measurements on PMMA plates. This convenient method takes into consideration close-to-reality application conditions on skin and offers a smart solution to evaluate in a simple way the skin protecting efficacy of cosmetics beyond UV.

ACKNOWLEDGEMENTS:

We would like to thank Anett Moschner and Sarah Kögler for their valuable contribution in providing the test formulations, performing the transmission measurements, and for all the fruitful discussions around the HEVL topic.

REFERENCES: