Comprehensive Analysis of Zinc Oxide and Titanium Dioxide in Mineral Sunscreen Formulations

Jaden C. Bonfietti and Dhia A. Habboush
Department of Chemistry, Sacred Heart University, Fairfield, Connecticut

ABSTRACT

The inorganic materials of zinc oxide and titanium dioxide were analyzed through *in vitro* and physical tests to show their significant role in a sunscreen formulation scope. On-market formulas and lab-made prototypes were tested together to understand the relationship of finalized products and the formulation creation process, while highlighting sustainability efforts within personal care and cosmetic formulations. With a UV Spectrophotometer, Sun Protection Factor (SPF), broad spectrum UVA/UVB protection, and critical wavelength were explored, while skin-like substrate and a UV light visualized the differences between formulas.

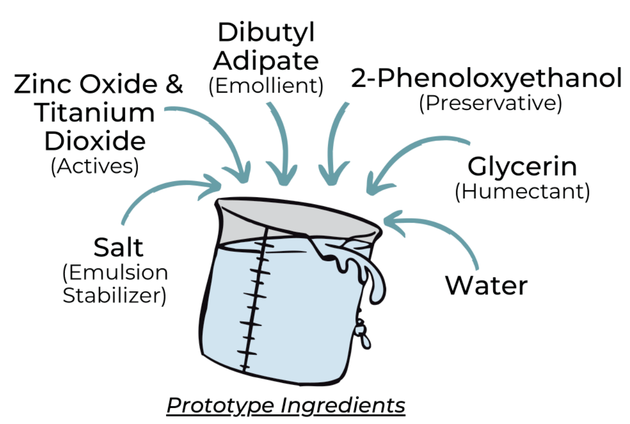
METHODOLOGY

Five prototypes were created with the same base formulation, yet with varying ratios of zinc oxide and titanium dioxide. These prototypes were compared alongside three on-market formulas with different ratios.

Formula	Zinc Oxide (ZnO)	Titanium Dioxide (TiO_2)	$ZnO:TiO_2$ Ratio
A	4%	4%	1:1
B	6.50%	4.50%	6.5:4.5
C	7%	9%	7:9
1	5%	5%	1:1
2	10%	0%	1:0
3	0%	10%	0:1
4	2.50%	7.50%	1:3
5	7.50%	2.50%	3:1

On-market Formula (A–C)
Lab-made Prototype (1–5)

Table 1. *Showcases each formula and the percentages of each active ingredient and the ratio between the actives.*



Prototype Ingredients

Using polymethyl methacrylate (PMMA) cuvettes and a Shimadzu UV-1800 UV-Spectrophotometer, the COLIPA *in vitro* test method prepared by The European Cosmetic Trade Association for determination of SPF and critical wavelength was conducted.

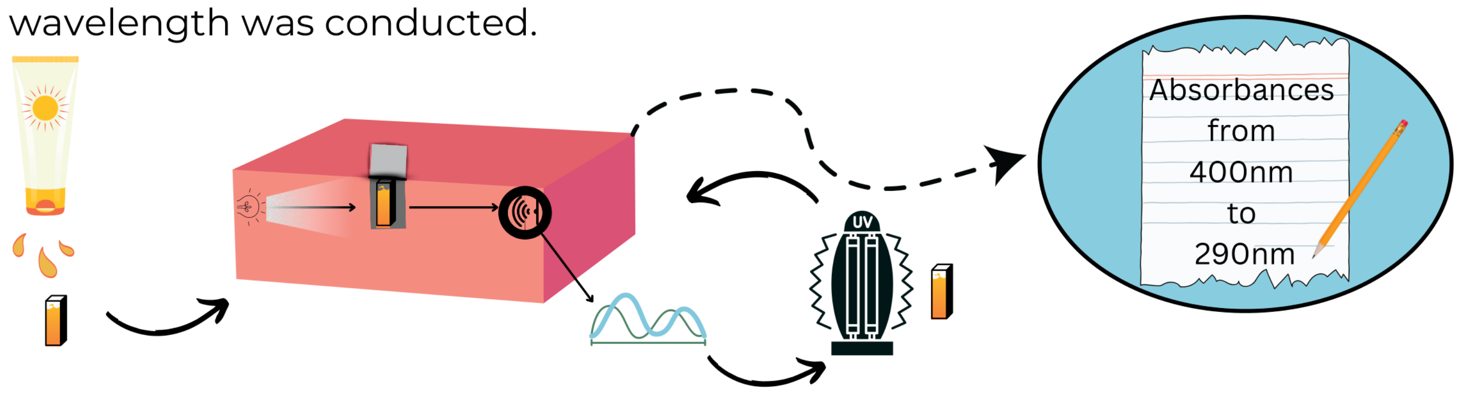


Figure 1. *Each formula was added to a cuvette and put into the UV-Spectrophotometer. The absorbances were collected against the wavelengths from 400nm to 290nm, covering both the UVA/UVB spectrums. Then, the cuvettes were exposed to the UV light source and put back into the UV-Spectrophotometer to collect the post-irradiation absorbances against the wavelengths.*

With IMS Vitro-Skin® testing substrate, another test was done to visualize the differences of the ratios on a surface similar to human skin.

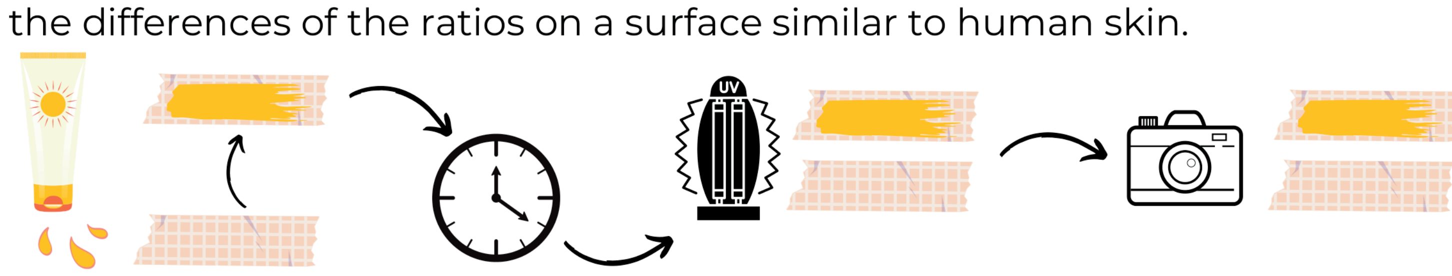


Figure 2. *The formulas were added at 2mg/cm² to the substrate plates of 6cm by 3cm. After 30 minutes of absorbing, the plates were exposed to the UV light source and photographed.*

MATHEMATICS

① $$SPF_{in\ vitro} = \frac{\int_{\lambda=290nm}^{\lambda=400nm} E(\lambda)\times I(\lambda)\times d\lambda}{\int_{\lambda=290nm}^{\lambda=400nm} E(\lambda)\times I(\lambda)\times 10^{-A_0(\lambda)} \times d\lambda}$$

Equation 1. *Sun Protection Factor*

- $E(\lambda)$ = Erythema action spectrum
- $I(\lambda)$ = Spectral irradiance of the UV source
- $A_0(\lambda)$ = Mean monochromatic absorbance measurements per plate of the test product layer *before* UV exposure
- $d\lambda$ = Wavelength step (1 nm)

② $$UVA_{PF} = \frac{\int_{\lambda=320nm}^{\lambda=400nm} P(\lambda)\times I(\lambda)\times d\lambda}{\int_{\lambda=320nm}^{\lambda=400nm} P(\lambda)\times I(\lambda)\times 10^{-A_0(\lambda)\times C} \times d\lambda}$$

Equation 2. *UVA Protection Factor (for UVB 290nm to 320nm)*

- $P(\lambda)$ = PPD action spectrum
- $I(\lambda)$ = Spectral irradiance of the UV source see Appendix I)
- $A_0(\lambda)$ = Mean monochromatic absorbance of the test product layer before UV exposure
- C = Coefficient of adjustment previously determined
- $d\lambda$ = Wavelength step (1 nm)

③ $$\int_{290}^{\lambda_c} A_\lambda d\lambda = 0.9 \int_{290}^{400} A_\lambda d\lambda \quad \text{where} \quad A_\lambda = \log\left(\frac{C_\lambda}{P_\lambda}\right)$$

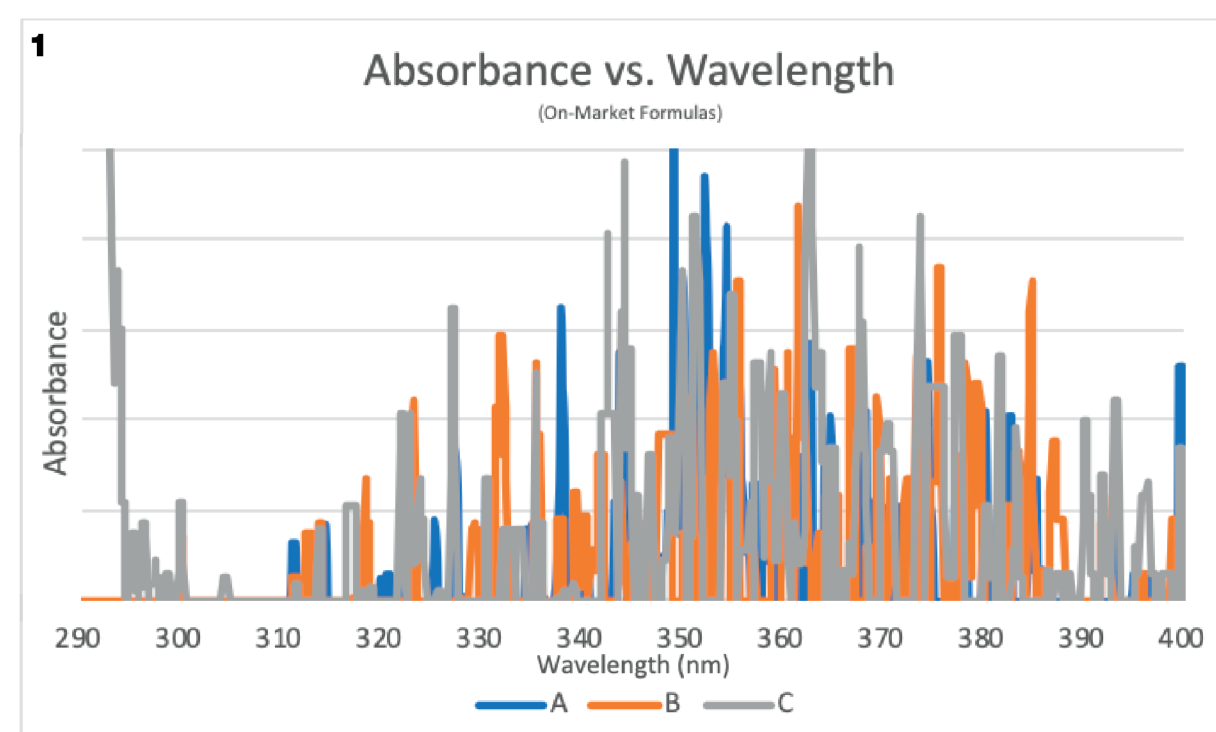
Equation 3. *Critical Wavelength formula defined as the wavelength where the area under the absorbance spectrum for the irradiated product from 290nm to the critical wavelength is 90% of the Integral of the absorbance spectrum from 290nm to 400nm.*

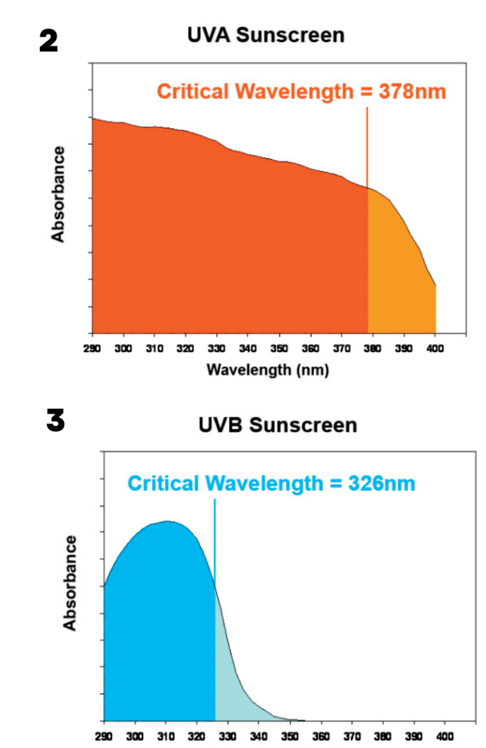
IMPORTANCE

Solar ultraviolet (UV) radiation causes many health effects that can be a burden financially or cosmetically. (There are 3 major types of skin cancer, and in order of most to least common they are basal cell carcinoma (BCC), squamous cell carcinoma (SCC), and the potentially fatal melanoma. Prolonged exposure to UV radiation causes all 3 types. The sun emits UVA and UVB radiation, where UVA rays affect the deepest layers of skin and cause fine lines and wrinkles, and UVB rays mainly affect the top layer of skin and cause sunburn. Protection against both is critical to an optimal formulation, as studies prove that regular application of sunscreen protects against sunburns/cancer.

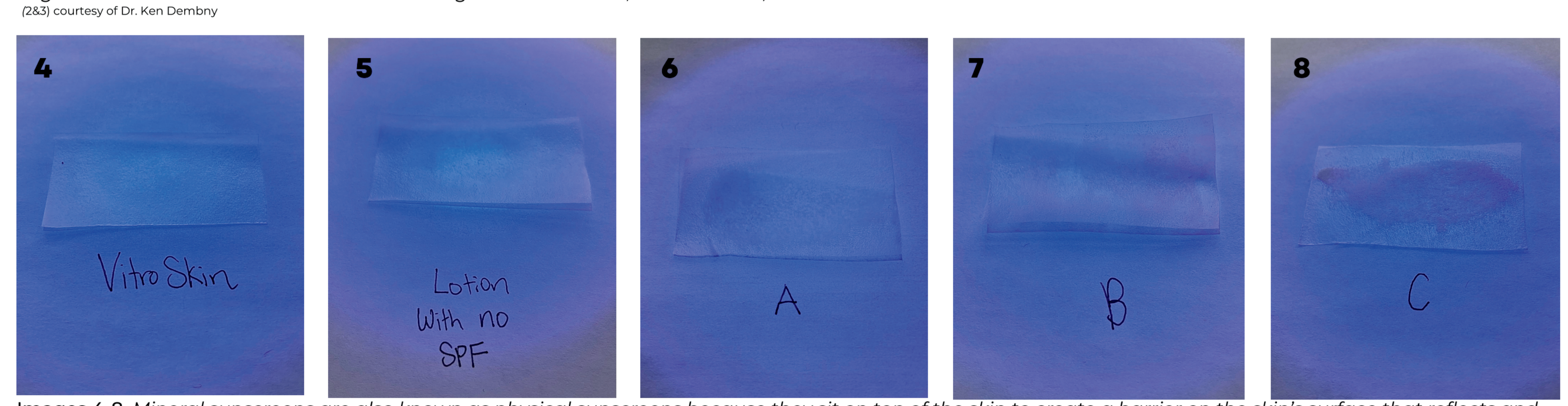
RESULTS

Images 1-3. *After 10 minutes incorporating with an emulsion blender, there is a noticeable difference in cohesion between formula 2 with just zinc oxide on the left and formula 3 with just titanium dioxide on the right (2). This applies to the formulas 4 and 5 as well where there Is more titanium dioxide on the left and more zinc oxide on the right (3). The formula 1 with an equal mix does not have the cohesion issue of formulas 3 and 4.*

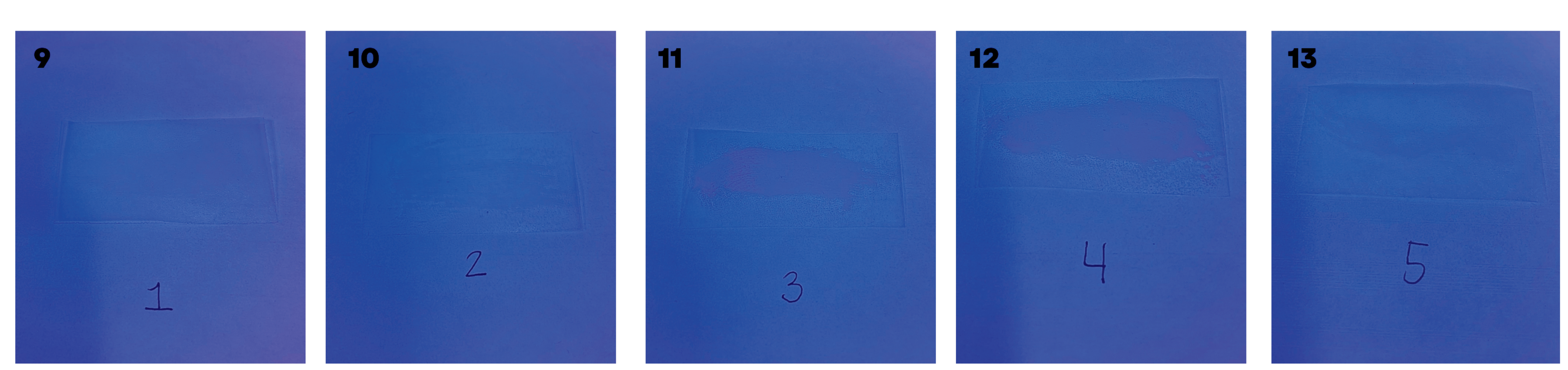




Graphs 1-3. *All formulas had the same SPF of 50, but the similarities stopped there. Formula A had an equal mix of the 2 inorganic compounds, while B had more zinc oxide and C had more titanium dioxide. Zinc oxide is proven to block more UVA rays (2), while titanium dioxide blocks more UVB rays (3). Therefore, C has more absorbance activity In the 290nm to 320nm region than the other formulas, while B has more activity In the 320nm to 400nm region (1). This is all tied together with their calculated critical wavelengths: A = 371.03nm, B = 374.89nm, and C = 370.74nm.*
(2&3) courtesy of Dr. Ken Dembny



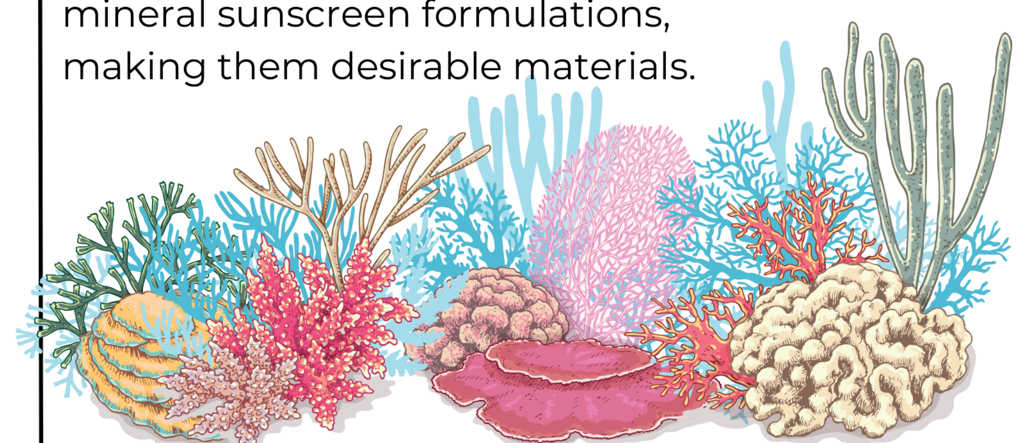
Images 4-8. *Mineral sunscreens are also known as physical sunscreens because they sit on top of the skin to create a barrier on the skin's surface that reflects and scatters UV rays to prevent damage and sunburn. There is a big comparison between the plain substrate (4) or lotion with no SPF (5) against the 3 on-market mineral sunscreens. Formula B had more zinc oxide (7), while Formula C had more titanium dioxide (8).*



Images 9-13. *With the prototypes, it is easy to see the differences in ratios of zinc oxide and titanium dioxide, since the latter is more reflective under this UV light (11,12). The prototypes with more zinc oxide did not reflect as much and also absorbed Into the substrate more easily (10,13).*

SUSTAINABILITY

There is a large push to incorporate mineral sunscreen into the market due to environmental concerns. For example, Hawaii banned the chemical sunscreens oxybenzone and octinoxate in 2021 due to their perceived role in harming/bleaching coral reefs. Many other countries are sure to move toward passing laws to protect the ocean. Currently, the FDA has approved zinc oxide and titanium dioxide for mineral sunscreen formulations, making them desirable materials.



CONCLUSION

Testing has shown that UVA/UVB rays are part of the same continuous electromagnetic spectrum, so it is imperative to include both zinc oxide and titanium dioxide in mineral sunscreen formulations to best protect against the whole spectrum of harmful rays. A higher critical wavelength means more protection against UV rays, especially UVA. Therefore, the FDA directs that formulas must be broad spectrum with a critical wavelength of at least 370nm, and have an SPF of 15 or more.

Recommended steps for further exploration would include calculating the UV protection factor, SPF, and critical wavelengths of the lab-made prototypes to evaluate efficacy. Focusing on aesthetics of the formulation process will be crucial, such as adding emulsifiers which will improve viscosity and cohesion. Overall, more research is needed to determine if zinc oxide and titanium dioxide have potential to completely replace chemical sunscreens.

REFERENCES

(1) A.C. Green, Regular Application of Sunscreen Can Prevent Skin Cancer, *J. Cosmet. Sci.* 71, 191-196 (2020)

(2) R.M. Sayre, N. Kollias, R.L. Roberts, A. Baqer and I. Sadiq, Physical sunscreens, *J. Soc. Cosmet. Chem.*, 41, 103-109 (1990).

(3) E. Tuddenham, "*In Vitro* Method for the Determination of the UVA Protection Factor and 'Critical Wavelength' Values of Sunscreen Products" COLIPA - The European Cosmetics Association *In vitro* UV Protection Method Task Force Guideline, 2009.

(4) J. Brito, "Formulating with Zinc Oxide," Society of Cosmetic Chemists 73rd Annual Scientific Meeting and Technology Showcase, 2019.

(5) C. Seidell, and M. Perkins, "Building a High SPF Sunscreen Formulation with Inorganic Filters," Society of Cosmetic Chemists 75th Annual Scientific Meeting and Showcase, 2021.

(6) N.A. Shaath, Impact of Sunscreen Regulations in the United States on Suncare Development, *J. Cosmet. Sci.*, 71, 227-231 (2020).

(7) U.S. Department of Health and Human Services, Food and Drug Administration, Center for Drug Evaluation and Research (CDER), "Labeling and Effectiveness Testing: Sunscreen Drug Products for Over-The-Counter Human Use — Small Entity Compliance Guide," Guidance for Industry, 2012.

(8) M. Pelizzo, E. Zattra, P. Nicolosi, A. Peserico, D. Garoli and M. Alaibac, "In Vitro Evaluation of Sunscreens: An Update for the Clinicians," *International Scholarly Research Notices*, vol. 2012, Article ID 352135, 4 pages, 2012.

(9) Skin Cancer Foundation, www.skincancer.org/riskfactors/sunburn

(10) Dr. Ken Dembny, https://drdembny.com/critical-wavelength-and-broad-spectrum-uv-protection/