SYNTHESIS OF SUNSCREEN WITH ZnO/TiO_2 NANOPARTICLES FOR BROADBAND UV BLOCKING

SUNSCREEN INEQUITY: EXAMINING SOCIAL AND REGULATORY BARRIERS IN SUNSCREEN ACCESSIBILITY FOR PEOPLE WITH DARKER SKIN

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On my honor as a University student, I have neither given nor received unauthorized aid on this assignment as defined by the Honor Guidelines for Thesis-Related Assignments.

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Introduction

The United States regulates sunscreen as a drug by the Food and Drug Administration (FDA), rather than as a cosmetic (Faguy, n.d.) like many other countries. This delays the U.S. sunscreen market, as new products require rigorous testing and approval. For example, over 30 ultraviolet-absorbing ingredients are approved worldwide, but in the U.S., only 17 have approval (Addae & Weiss, 2024). Metal-oxides, such as zinc oxide and titanium dioxide, are two examples of active ingredients approved by the FDA. A major issue with metal-oxide mineral sunscreens is the white cast they often leave, especially on darker skin. This can discourage people of color from wearing sunscreen (Fadulu, 2018), increasing their risk of skin cancer.

I propose developing a mineral-based sunscreen using nanoparticles that eliminate the cause of white casts, allowing people with darker complexions to wear sunscreen easily. This process involves various social, technical, and economic implications that can be shaped by new technologies, impacting the user interactions surrounding mineral-based sunscreens. I will draw on the STS framework of user configuration to investigate how the development and use of sunscreen resulted in diverse racial impacts, influenced by differing perceptions of risk associated with skin exposure. Specifically, I will examine how technical and social factors, like U.S. sunscreen regulation and the misconception that people of color do not need sunscreen, have affected marginalized groups' access to adequate skin protection. I will conduct this research by analyzing how technology is constrained by its design within user configuration, and how sunscreen specifically has been designed for decades without darker complexions in mind.

Because the challenge of developing an accessible sunscreen is sociotechnical in nature, it requires attending to both its technical and social aspects to accomplish successfully. In what follows, I set out two related research proposals: a technical project proposal for developing a mineral-based nanoparticle sunscreen and an STS project proposal for examining the historical lack of accessible sunscreen and skin protection education for people of color.

Technical Project Proposal

In 2020, the global sunscreen market was valued at 10.7 billion USD, this market is expected to grow at 4.0% each year from 2021-2028 (Grand View Research). Sunscreen has transformed from a tedious beach day ritual to an everyday personal cosmetic. The greater popularity of sunscreen as part of people's skincare routine raises a need for sunscreen formulation to reach a wider commercial audience. Zinc oxide (ZnO) and titanium dioxide (TiO_2) are common active ingredients used to absorb, reflect, and refract UV rays. They are used in many sunscreen formulations to avoid skin irritation and allergic reactions that chemical sunscreen ingredients can cause.

Some compounds in chemical sunscreen have been found to harm coral. In response, oxybenzone and octinoxate have been banned in places such as Hawaii and the U.S. Virgin Islands due to the coral-bleaching effects they have (Miller et al, 2021). However, zinc oxide and titanium dioxide are considered reef-safe, largely due to their low solubility in water. This also means they last longer on the skin, contributing to their overall desirability (American Chemical Society).

As of 2021, zinc oxide and titanium dioxide are the only active ingredients Generally Recognized As Safe (GRAS) by the U.S. Food and Drug Administration (FDA). Other mineral and chemical ingredients have insufficient data to be considered as GRAS. However, mineral-active ingredients have the downside of leaving a white cast on the user’s skin, discouraging people from regular usage. Nanoparticles are particles that are invisible to the human eye and show promise to minimize or eliminate the white cast that mineral sunscreens can cause. Therefore, this capstone project aims to model a synthesis process for broad-spectrum sunscreen from direct precipitation of zinc oxide and titanium dioxide nanoparticles.

Mineral Nanoparticle Synthesis

Zinc oxide reflects both UVA (320-400 nm) and UVB (280-320 nm) rays of ultraviolet light away from one's skin. This is important because ultraviolet radiation can damage the DNA in skin cells and pose a significant cancer risk. Although ZnO nanoparticles do not scatter visible light, the particles remain able to reflect and scatter UV light.

The ZnO needed for our sunscreen will be synthesized through direct precipitation. The advantages of the direct precipitation method are the small range of particle sizes it produces, cheap raw materials, and the ability to be done in a continuous operation. Common precipitation precursors are zinc sulfate and zinc nitrate (Ghorbani et al. 2015). Zinc nitrate will be used in our process because it is significantly cheaper. Using zinc nitrate as the precursor, it is combined with a hydroxide such as NaOH, KOH, or LiOH. A precipitation reaction occurs when these precursors are mixed, yielding $Zn(OH)_2$. This is then filtered, washed with distilled water and alcohol, and then calcined in an oven at high temperatures over several hours. The $Zn(OH)_2$ decomposes into ZnO on the nanoparticle scale (Wang et al, 2010).

$$Zn(NO_3)_2 + 2XOH \rightarrow Zn(OH)_2 + 2XNO_3$$

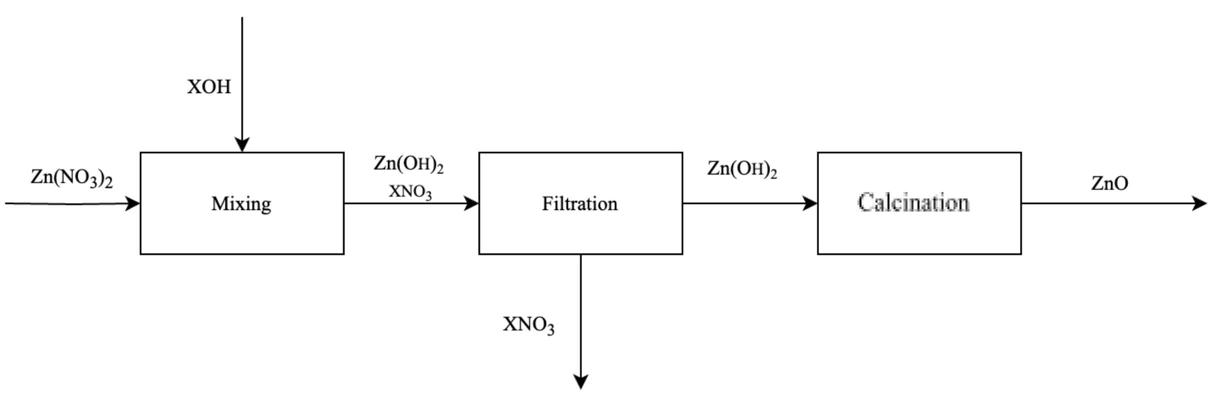

Figure 1: Process flow diagram of direct precipitation of ZnO from $Zn(NO_3)_2$.

TiO_2 will be synthesized similarly to ZnO using titanium (IV) isopropoxide and distilled water as a precursor. This produces a white precipitate of TiO_2 and $(CH_3)_2CHOH$, aka rubbing alcohol, which can be purified by distillation and sold for profit. The properties of our TiO_2 product can be controlled by the amount of water, reaction conditions, and the presence of additives to obtain our desired particle size and composition. The white precipitate of titanium dioxide is filtered out and dried into a powder. The remaining reactants may be recycled within the reaction.

$$Ti(OCH(CH_3)_2)_4 + 2H_2O \rightarrow TiO_2 + 4(CH_3)_2CHOH$$

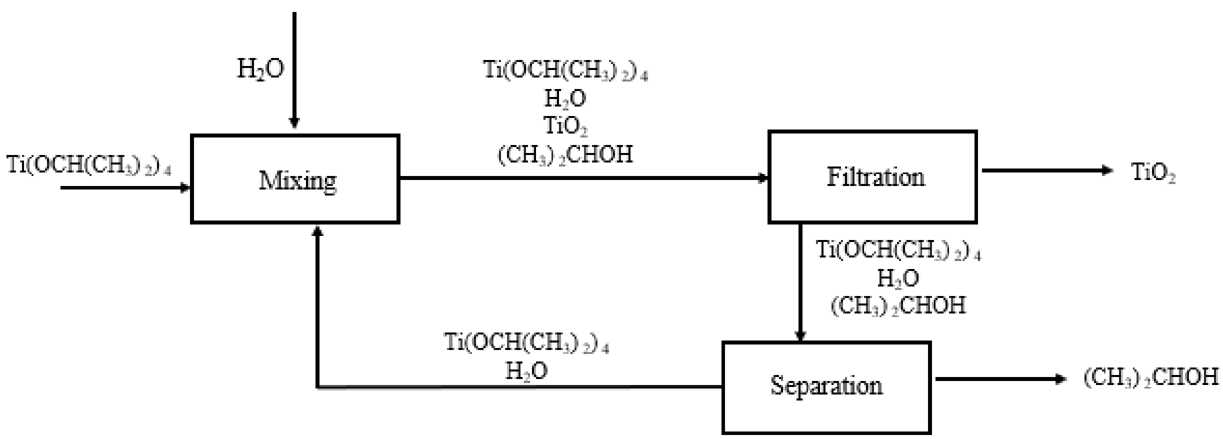

Figure 2: Process flow diagram of direct precipitation of TiO_2 from $Ti(OCH(CH_3)_2)$.

Triglyceride Synthesis

Sunscreens contain various inactive ingredients that act as emollients, dispersing agents, and antioxidants. One compound that serves these functions is caprylic/capric triglyceride. Caprylic triglyceride is a mixed triester formed from palm or coconut oils and glycerin (Mungali et al., 2021). For this process, palm oil is the best choice for making the product as affordable as possible. Palm oil is significantly cheaper, coming in at roughly \$688 per MT versus \$1,159 per

MT of coconut oil (Bamber et al., 2016). The synthesis of caprylic triglyceride begins with steam hydrolysis, followed by esterification, which forms an ester from an acid and alcohol. Steam hydrolysis is used to separate the caprylic and capric fatty acids from glycerol in palm oil. This process is run at high temperatures and pressures, roughly 250 C and 50 bar respectively (Nitbani et al., 2020). Once this separation has been completed, the caprylic acid and glycerol are reacted via esterification to produce the caprylic/capric triglycerides. The conditions for this process are conducted at a high temperature and pressure, with a catalyst (Liu et al., 2021). After, final purification is done to deodorize the product. One of the components of caprylic triglyceride that enhances its attractiveness as an additive is caprylic acid. Caprylic acid adds benefits such as increased shelf life, homogeneous dispersion of active ingredients, moisture, and free radical protection. The increased shelf life is a result of the stability of the component, which is incredibly resistant to oxidation (Mungali et al., 2021). This classifies caprylic acid as an antioxidant, which could protect the skin from damaging free radicals from the sun, and free radicals from the breakdown of the zinc oxide. Also, as an emollient, caprylic acid protects the moisture barrier of the skin and is recommended for sensitive skin (Mungali et al., 2021). Finally, capric acid allows other ingredients in the product to remain suspended and prevent any separation.

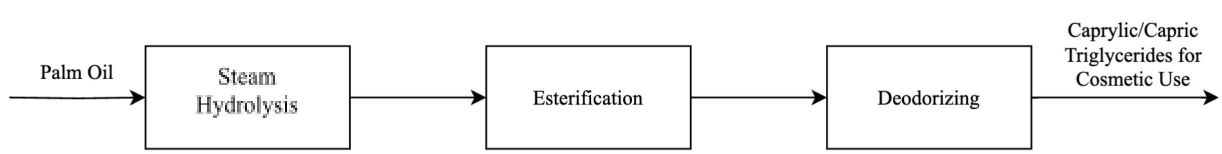

Figure 3: Process flow diagram of caprylic/capric triglyceride production.

Importance

ZnO and TiO_2 are both white and are effective at reflecting light. As a result, mineral sunscreens can often leave a white cast, the white residue on the skin after sunscreen application. As a result, people feel less inclined to use sunscreen to avoid a pale or ashy appearance, especially for those with darker skin tones. However, this can be avoided through the use of metal oxide nanoparticles (Addae & Weiss, 2024). ZnO and TiO_2 particles should be smaller than 50 nm for them to not be visible to the human eye. However, TiO_2 also has a skin permeation threshold of 45 nanometers meaning it is important to precisely control its size (Filon et al., 2015). Because of this, nanoparticles can reduce the white cast from mineral sunscreens currently on the market.

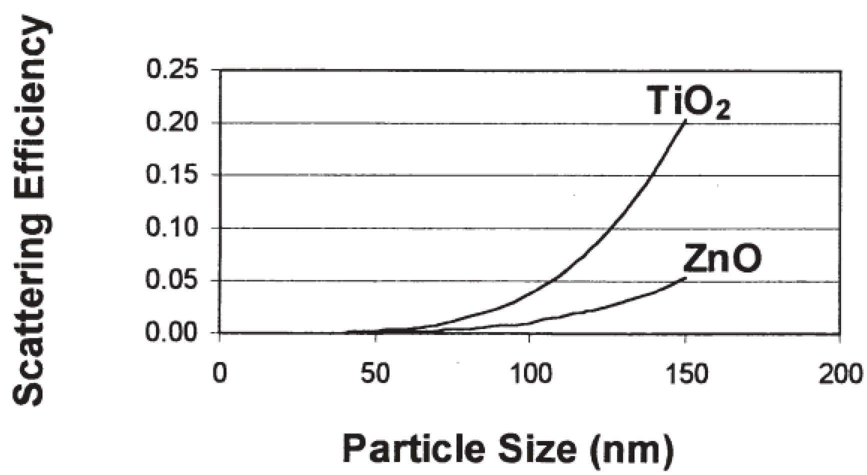

Figure 4: Scattering efficiency in comparison to nanoparticle size (Pinnell et al., 2000).

The sunscreen that will be produced is planned to be hypoallergenic and fragrance-free. Mineral sunscreens are regarded to be better for those with sensitive skin since they lack some compounds in chemical sunscreens that can be irritants. Another source of irritation can come from the use of fragrances. In a 2019 study, it was found that fragrances are the most common allergen in high SPF sunscreens found in the United States (Keyes, 2019). By making the product with ingredients that cause minimal allergic reactions, it allows anyone to use the sunscreen without discomfort. The selected ingredients are also known to be non-comedogenic, or non-pore-clogging, allowing the sunscreen to be used by those who are acne-prone.

There are a handful of sunscreens on the market that utilize mineral nanoparticles. Some of the most popular are Murad's City Skin Age Defense Broad Spectrum SPF 50 | PA++++ and La Roche Posay's Anthelios Mineral Zinc Oxide Sunscreen SPF 50. Both of these products are being sold for more than twenty dollars per fluid ounce compared to the roughly three dollars per fluid ounce of regular mineral sunscreen; which poses an issue with the affordability of this type of product (La Roche Posay, Murad Skincare). This is, in part, due to the more complex and expensive development of these novel sunscreens, but it also significantly hinders their accessibility and marketability to a wider market. Minimizing the cost of this product through optimization of its synthesis is necessary to increase the accessibility of this product such that the average consumer can afford a visually pleasing and non-comedogenic sun-blocking product.

Execution

This work will be completed by modeling the synthesis process of zinc oxide, titanium dioxide, and triglyceride to optimize variables such as flow rates, temperature, and reaction rate. Modeling the processes themselves will be performed using Aspen Plus Version 14 with raw material thermodynamic data obtained from NIST Thermodata Engine (TDE) (Aspentech: Knowledge base, 2017). Additionally, both safety and cost analyses will be performed to assess the viability of this product on the market. This design work will be done over two semesters with a detailed deliverable in the spring of 2025.

STS Project Proposal

The FDA has been regulating sunscreen since 1978 (Drissi et al., 2021), with two categorical ingredients, inorganic and organic absorbers of ultraviolet radiation. Organic ingredients are commonly seen in chemical sunscreens, but these are not suitable for everyone, especially those with sensitive skin, prone to reactions. Otherwise, inorganic, or mineral-based ingredients, like zinc oxide and titanium dioxide, have been around since the 1940s (Muinos, 2014). These ingredients are known for being hypoallergenic, and suitable for all skin types, but come at one devastating downfall, a stark white cast, one of which is incredibly noticeable on dark complexions. Not only did this make mineral sunscreens unattractive to people of color, but it was a common belief for the past several decades that people of color do not need to wear sunscreen, which is an incredibly misleading danger.

According to a study conducted by Rebecca Fliorent, Alicia Podwojniak, Lianne Adolphe, and Katharine Milani in 2023, black people on average reported using sunscreen significantly less than other ethnic groups of lighter complexion. Not only this, but black people reported receiving less information on average from their primary care physician about the risks of melanoma, as well as significantly fewer skin checks for abnormalities related to sun exposure. This is one of the leading factors that causes melanoma to be much more dangerous, resulting in a significantly lower survival rate for people of color than white people. Although white people are more likely to have sun damage and ultimately skin cancer, it is often caught in the later stages for people of color, making it much more high risk. Additional studies have determined that although people of color with melanoma are at a much higher risk, they are less concerned than other groups about melanoma, and are often unlikely to notice malignant developments on the skin (Fliorent et al., 2023). Overall, the lack of accessible noncomedogenic sunscreens on the market, the target audience for sunscreen, the inequality of knowledge regarding melanoma between racial groups, and the perpetuated ideology of sunscreen being unnecessary for darker complexions have all contributed to the lack of sunscreen wearers who are people of color.

Focusing on these specific interactions and how they work as a network offers a deeper understanding of why sunscreen is inaccessible to people of color. Inaccessibility in this context does not represent the availability of sunscreens on the market, but rather the availability of sunscreens that work for their complexion, product affordability, and knowledge regarding the importance of skin protection. For these reasons, I argue that implicit racial bias, effectiveness over aesthetics, consumer ignorance and habits, and cost, taken together, have perpetuated the lack of people of color adapting sunscreen into their daily routines.

The framework I will use to assess the use of sunscreen by people of color will be user configuration (Oudshoorn & Pinch, 2003). Within user configuration, technology is constrained by its design, determining its accessibility. The design choice determines whether or not actors can interact with the technology via its intended setting. The key is to assess the configured user as intended by the engineers and governing bodies and how this may have overlooked other actors affected by the technological design. Additionally, I will use Christina Lindsay's (2003) approach to assess how social groups configured the user identity by implicit racial biases, and how this technical project serves the reflexive user with an accessible product.

Conclusion

My technical design project will provide a new sunscreen safe for sensitive skin while using nanoparticles to eliminate white cast. The sunscreen will be accessible to people with darker complexions, removing the burden of an undesirable appearance that most mineral-based sunscreens have. My STS research will offer an in-depth analysis of what social factors have historically influenced the lack of sunscreen adoption by marginalized groups, placing them at higher risk for skin cancer. By understanding how various factors, like social misconceptions, inadequate knowledge, racial biases, and sunscreen regulation have limited sunscreen acceptance for people of color, I will apply these insights to provide a more inclusive product. Together, I will address the sociotechnical inadequacies of making effective and accessible sunscreen, providing a practical solution with product design, and highlighting the importance of user configuration on inclusive product development and education to improve sun protection for everyone.

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