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

BEYOND THE BURN: ANALYSIS OF NEUTRAGENA'S SUNSCREEN REFORMULATION

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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

Ultraviolet (UV) radiation is a major contributor to harmful effects from sun exposure, including sunburn, DNA damage in skin cells, and an increased risk of skin cancer. Developing effective sun protection that reflects or absorbs UV radiation is essential for mitigating these health risks. While many sunscreens are available today, there is an ongoing need for improvement, particularly in expanding UV protection and incorporating technologies that enhance efficacy.

One promising approach uses zinc oxide (ZnO) and titanium dioxide (TiO_2) nanoparticles, which provide broad-spectrum UV protection while remaining clear on the skin and reducing allergenic potential. My team and I aim to develop a scalable, factory-level process for synthesizing ZnO/TiO_2 nanoparticle sunscreens that address common concerns: minimizing the white cast typical of mineral sunscreens, reducing irritation associated with chemical sunscreens, and improving the cost-effectiveness of nanoparticle-based formulas.

To understand the factors driving sunscreen reformulation and redesign, such as Neutrogena's 2020 reformulation, I will apply the Science and Technology Studies (STS) framework of the Social Construction of Technology (SCOT). By examining how social groups and stakeholder concerns shaped Neutrogena's sunscreen product design, we can better address the factors influencing reformulation. Focusing solely on safety and environmental impacts, while overlooking stakeholder needs, risks ignoring the root causes of dissatisfaction with product design and the reasons behind their redesign.

Because the challenge of sunscreen usage 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 ZnO/TiO_2 nanoparticle sunscreen and an STS project proposal for examining the effect of relevant stakeholders' concerns in the reformulation of Neutrogena's sunscreens.

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, 2024). 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.

Chemical sunscreens containing compounds such as oxybenzone and octinoxate have been banned in places such as Hawaii and the U.S. Virgin Islands due to their harmful coral-bleaching effects (Miller et al., 2021). In contrast, zinc oxide and titanium dioxide are considered reef-safe, largely due to their low solubility in water. This also means that they last longer on the skin which contributes to their overall consumer desirability (American Chemical Society, 2024).

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 so small they are invisible to the human eye and show promise to minimize or eliminate the white cast 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 has the ability to reflect both UVA (320-400 nm) and UVB (280-320 nm) rays of ultraviolet light away from one's skin. This is important because UV radiation can damage the DNA in skin cells and pose a significant cancer risk. Although ZnO nanoparticles do not scatter visible light, the particles still are able to reflect and scatter UV light. The ZnO needed for our sunscreen will be synthesized through direct precipitation. Advantages of the direct precipitation method is 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 to purchase. 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 $Zn(OH)_2$ is dehydrated in the oven and is then recrystallized to produce ZnO on the nanoparticle scale (Wang et al., 2010).

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

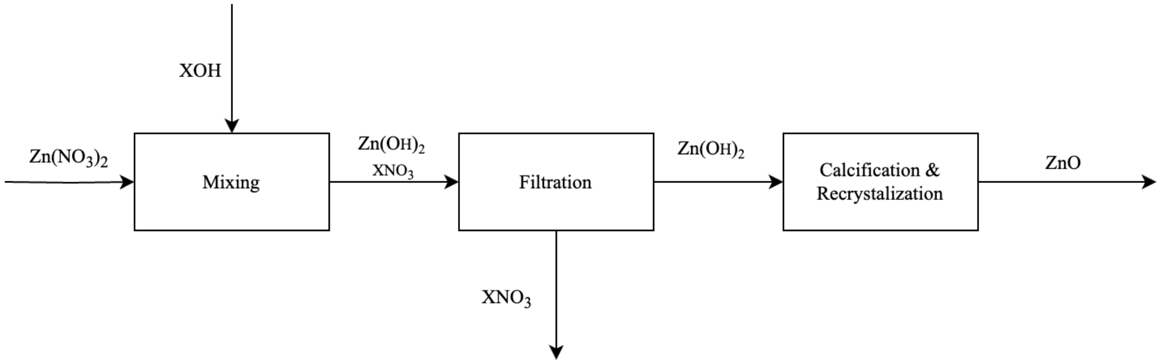

Figure 1: Process flow diagram of direct precipitation of ZnO from $Zn(NO_3)_2$.

TiO_2 will be synthesized in a similar manner as ZnO using titanium (IV) isopropoxide with isopropyl alcohol and distilled water as a precursor. This produces a white precipitate of TiO_2 and $(CH_3)_2CHOH$, also known as rubbing alcohol, which can be separated and sold for profit. The properties of our TiO_2 product can be controlled by the amount of water, reaction conditions, and presence of additives to obtain our desired particle size and composition. Magnesium oxide is a common substance used to neutralize this reaction and yield TiO_2 in the desired crystal structures (Li et al., 2008). The white precipitate is filtered out and dried into a powder.

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

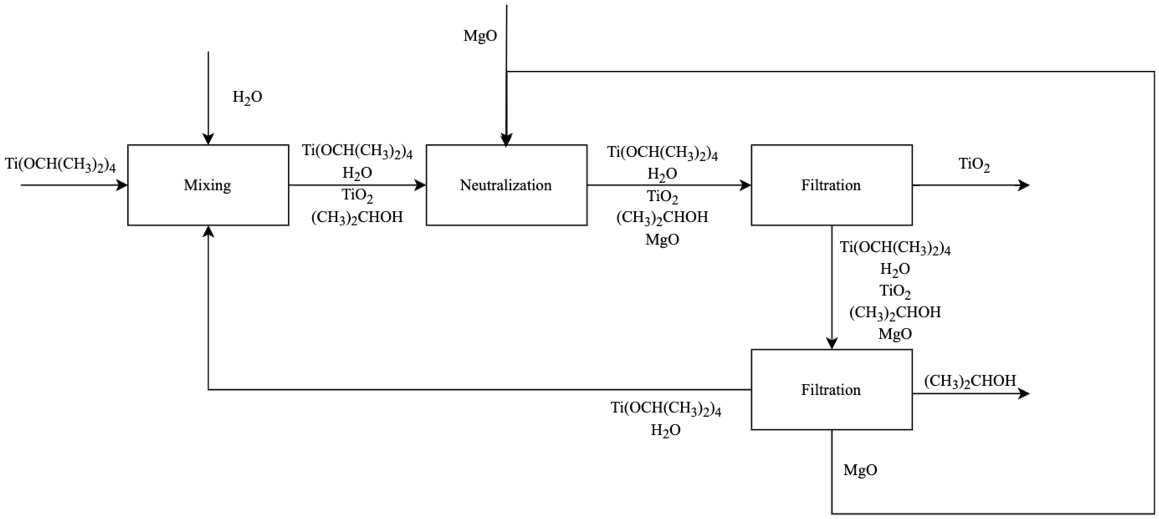

Figure 2: Process flow diagram of direct precipitation of TiO_2 from $Ti(OCH(CH_3)_2)$.

Triglyceride Synthesis

Sunscreens contain various inactive ingredients that act as emollients, dispersing agents, and antioxidants. Emollients are essential in sunscreen formulations, providing a moisturizing base that binds other ingredients together and helps them spread evenly across the skin. 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 saponification, followed by esterification. Saponification uses steam hydrolysis 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 enhance 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.

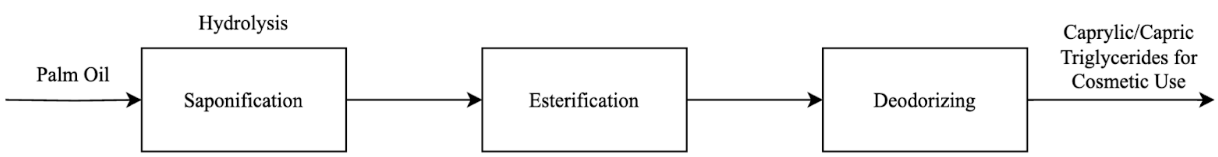

Figure 3: Process flow diagram of caprylic/capric triglyceride production.

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 smaller than 50 nm are not visible to the human eye. Because of this, nanoparticles can reduce the white cast from mineral sunscreens currently on the market. 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).

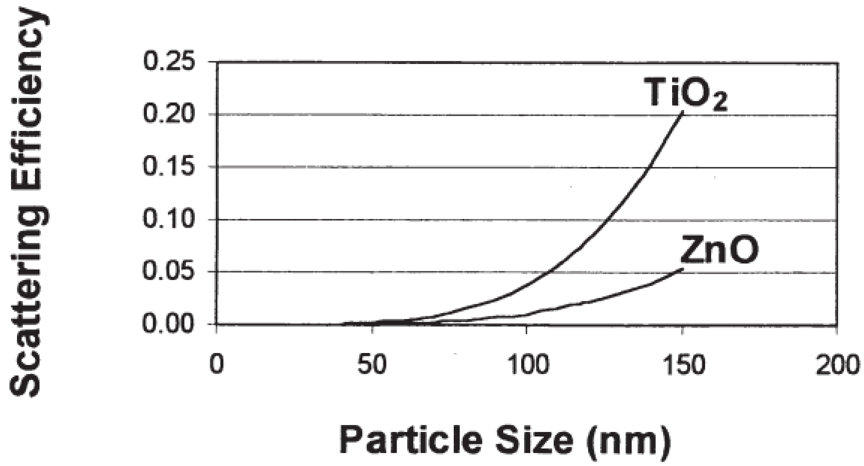

Figure 4: Scattering efficiency in comparison to nanoparticle size (Pinnell et al., 2000).

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, 2024; Murad Skincare, 2024). This is, in part, due to the more complex and expensive development of these novel sunscreens, but it also significantly hinders its accessibility and marketability towards 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 the course of two semesters with a detailed deliverable in the spring of 2025.

STS Project Proposal

Sunscreen is a proven and essential tool for reducing the risk of skin cancer, including melanoma, and mitigating other chronic health conditions. Since the 1970s, the FDA has regulated sunscreen; however, some approved ingredients may pose risks to human health (Michele, 2024). For instance, a 2019 study examined chemical UV filters like oxybenzone and found they contribute to coral bleaching and are present in fish populations – raising several environmental concerns (Schneider & Lim, 2019). Moreover, oxybenzone has been shown to penetrate the skin and has been linked to hormone disruption (Amarelo, 2023).

In 2023, *Time* Magazine published an article titled "How Sunscreen Became Controversial," highlighting ingredient concerns as a major factor driving sunscreen reformulation (Ducharme, 2023). Before 2020, Neutrogena used oxybenzone - a highly effective UV filter – as an ingredient in all of its chemical sunscreens. While the FDA continues to approve oxybenzone and other chemical UV blockers as safe for use, advocacy groups like the Environmental Working Group have strongly opposed their use, citing environmental damage and health risks.

Government action further amplified this shift. In 2018, Hawaii announced a ban on sunscreens containing oxybenzone, effective in 2021, effectively eliminating a key market for companies like Neutrogena (Amarelo, 2023). In her *Time* article, Jamie Ducharme argues that such incidents, compounded by media and social media discussions, have fueled public skepticism and distrust of sunscreen safety (Ducharme, 2023).

As a result of these pressures, Neutrogena reformulated their sunscreens, including removing oxybenzone as an active ingredient in 2020 (*The Lowdown on Sun Protection & Sunscreen Ingredients | Neutrogena®*, n.d.). This reflects broader market trends: only 13% of non-mineral sunscreens currently contain oxybenzone, compared to nearly 50% in 2021 (Amarelo, 2023). Authors such as Ducharme attribute Neutrogena's sunscreen reformulation to how advocacy, consumer demand, and government regulation have collectively driven a decline in the use of controversial ingredients.

While concerns about ingredients significantly shape public sentiment, focusing solely on this factor oversimplifies the broader range of social influences driving demands for sunscreen reformulation, as seen in the case of Neutrogena. Discussions often fail to account for stakeholder priorities, such as the aesthetic appeal and comfort of sunscreen on the skin, which play a crucial role in consumer preferences. Additionally, many analyses overlook the interconnected social, technical, and economic factors that dictate who uses sunscreen and why. The societal influence of specific stakeholder groups, and the extent to which their needs are prioritized in sunscreen design and formulation, further complicates the issue. These dynamics ultimately determine which products are developed, marketed, and embraced by the public, highlighting the multifaceted nature of sunscreen reformulation.

To understand why Neutrogena's sunscreens were changed and redesigned, we must consider how product design can better reflect the values of a range of social groups and how current shortcomings contribute to dissatisfaction and mistrust. Notably, several underrepresented groups play a leading role in driving the demand for the reformulation of sunscreen, raising issues around ingredient safety, environmental impact, and inclusivity in product design. These groups advocate for sunscreens that align more closely with their personal values and specific needs, which often go unmet by mainstream products. I intend to apply the Science, Technology, and Society (STS) framework of the Social Construction of Technology (SCOT) to examine how the perspectives of relevant social groups shaped the design of Neutrogena's sunscreen and continue to shape the design of sunscreens across the market. SCOT argues that the design of technology emerges from the priorities and influences of the social groups who use it (Pinch & Bijker, 1984). Current sunscreen products frequently fail to address the needs of all intended users, disrupting the balance of each social group's desires. This imbalance highlights the growing demand for redesigns that better accommodate diverse perspectives and priorities.

By drawing on SCOT, I aim to demonstrate how the lack of representation among certain stakeholder groups contributes to a design that fails to align with a broader equilibrium of social needs. To support this analysis, I will examine consumer reviews, surveys, and news articles, which capture diverse user perspectives and reveal points of dissatisfaction. Through this approach, I will illustrate how the exclusion of underrepresented social groups from the sunscreen development process reinforces a cycle of mistrust and decline in use, despite the well-documented health benefits that sunscreen provides. Understanding this dynamic is essential for developing sunscreens that not only provide effective UV protection but also align with the values and needs of a diverse population.

Conclusion

In summary, a ZnO/TiO_2 nanoparticle sunscreen aims to deliver efficient UV protection that is aesthetically pleasing, non-comedogenic, and affordable. Achieving this balance requires simulation techniques to optimize synthesis processes while ensuring cost-effectiveness. This project also addresses the social factors contributing to the reformulation of Neutrogena's sunscreens in 2020, applying the Social Construction of Technology (SCOT) framework. SCOT offers insights into how influential social groups shape product perception and use, guiding a design that considers all stakeholders and enhances the sunscreen's appeal and usability across diverse user needs.

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