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FORMULATION AND SPF EVALUATION OF PHYSICAL SUNSCREEN CONTAINING TITANIUM DIOXIDE AND ZINC OXIDE

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Abstract – *Sunscreen is a product that protects the skin from the undesirable effects of the sun, and the active ingredients of physical sunscreen are the group that is often prioritized for use. Research is needed to formulate and evaluate the SPF index of physical sunscreens containing titanium dioxide and zinc oxide with the desire to develop a safe sunscreen product that provides high sunscreen effectiveness and meets consumer tastes. The cream is prepared through surveys evaluating the emulsification capacity of emulsifying excipients, oil-phase excipients, and the ratio of titanium dioxide and zinc oxide. The optimal cream formulation was selected after assessing organoleptic sensation, physicochemical stability, pH, skin irritability, microbial limits, heavy metal limits, and SPF rating according to COLIPA guidelines. The results showed that the initial study successfully prepared a physical sunscreen containing 1% Span 80, 0.5% tween 80, 6% cetyl alcohol, 3% stearic acid, 9% titanium dioxide, and 1% zinc oxide. The resulting cream was smooth and homogeneous, had a pH of 6, did not cause irritation on rabbit skin, and had an SPF value of 26.1, creating a premise for the next studies.*

Keywords: SPF, sun protection factor, sunscreen, titanium dioxide, zinc oxide.

I. INTRODUCTION

Skin health is currently a concern for almost everyone, and the protection of the skin against the effects of the sun (UV rays – Ultraviolet) is being researched. Recently, cosmetic products and pharmaceuticals with the addition of sunscreen active ingredients on the market have been increasingly developed. In particular, active ingredients in physical sunscreen, including titanium dioxide and zinc oxide, are often preferred due to their advantages, such as being impermeable to the skin, non-irritating, effective immediately after application, and having a prolonged duration of action [1]. Titanium dioxide has the ability to prevent UVB better, while zinc oxide has a wider UV absorption curve in both UVA and UVB. Therefore, when coordinated together in the formula, titanium dioxide and zinc oxide provide sunscreen on the wavelength strip [1, 2].

Various methods were used to evaluate the protective effect of the skin against the effects of UV rays. However, SPF (sun protection factor) is one of the most important and widely used indicators [3]. Therefore, this research proceeded to formulate and evaluate the SPF of sunscreens with titanium dioxide combinations (TiO_2) and zinc oxide (ZnO) to create a composition with high sun protection that is safe for the skin and has potential for application to the market.

II. RESEARCH OVERVIEW

Titanium dioxide and zinc oxide are active ingredients in physical sunscreen. Physical sunscreens work by reflecting or scattering UV rays. The properties of this group are benign, less irritating, and less susceptible to changes when exposed to direct sunlight, so they can protect the skin under the influence of the environment for a long time. With high applicability in preventing the effects of ultraviolet rays on the skin, Tran Thi Hai Yen et al. [4] prepared cream by the direct emulsification method, then combined TiO_2 into the cream by the dispersion method. As a result, the sunscreen cream containing 5% TiO_2 had a smooth texture, with a medium UV protection

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effect with SPF 20^{+}. In 2021, Jayati et al. [5] researched a sunscreen with a combination of 7% ZnO, 4% TiO_2, and 8% virgin coconut oil (VCO) as antioxidants. This research showed that the finished cream has good physicochemical properties, is stable during storage life, and achieves the best SPF value. In 2023, Duong Thi Bich et al. [6] successfully prepared a natural sunscreen composed of 2% TiO_2, 6% ZnO, 20% shea butter, 6% almond oil, and 9% beeswax with SPF 50.6.

Following these prior studies, this paper was developed to further explore making cosmetic sunscreen with high sun protection using common and easy-to-find excipients. The project's purpose is to create safe, environmentally friendly sunscreen products that would be suitable for many users.

III. RESEARCH METHODS

A. Materials, location, and time

Materials: TiO_2, ZnO, cetyl alcohol, stearic acid, vaseline, sodium lauryl sulfate (SLS), tween 80 and span 80, sunflower oil, glycerin, isopropyl myristate, triethanolamine, sodium benzoate and carbomer 940 meet cosmetic manufacturing standards.

Location and time: The experiment was conducted at the Research Laboratory, Pharmacy Department, School of Medicine and Pharmacy, Tra Vinh University, Vietnam from May 2023 to March 2024.

B. Methods

Preparation of physical sunscreens containing titanium dioxide and zinc oxide

- Cream preparation process

With the water phase, carbomer 940 was weighed and stirred quickly into room-temperature water. Then, the solution was allowed to swell completely for 30 minutes to create gel A. Water-soluble ingredients (glycerin, sodium benzoate) were dissolved in pure water and then mixed into gel A with isopropyl myristate before being stirred to create mixture B. TiO_2 was finely ground and then sifted through a 125 μm sieve. Titanium dioxide was dispersed into mixture B according to the principle of homogeneity of mixture C, heating mixture C to 65–70^{o}C.

In the oil phase, oil excipients (stearic acid, cetyl alcohol, and vaseline) were weighed and melted. The mixture was stirred to become homogeneous. The emulsifier (SLS, span 80, and tween 80) and finely ground ZnO were later added. Then the mixture was sifted through a 125 μm sieve and dispersed into the oil phase according to the principle of homogeneity. The oil phase was heated to 60–65^{o}C.

The water and oil phases were coordinated with appropriate equipment under the right conditions, stored at room temperature for 24 hours, and then evaluated.

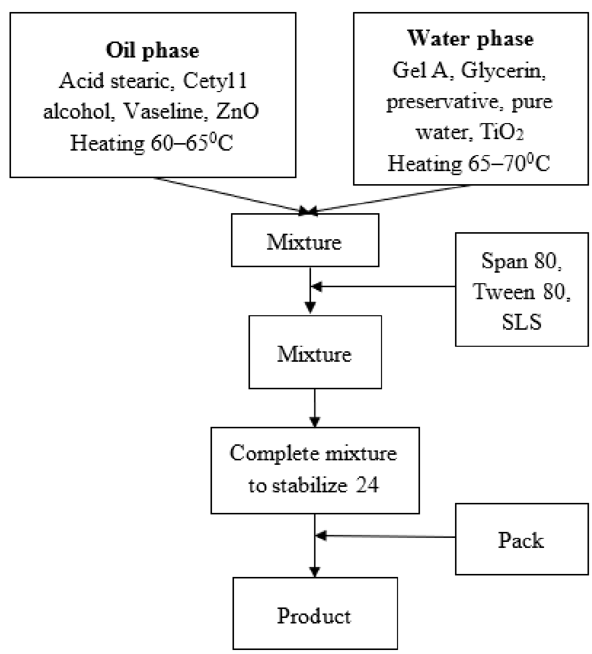

Fig. 1: The process of preparing sunscreen formulas that contain titanium dioxide and zinc oxide

- Survey and formulation to optimize cream properties

The cream was formulated with ingredients including water phase, oil phase, and emulsifiers.

To adjust the cream's texture, oil-based excipients (stearic acid, cetyl alcohol, vaseline) and emulsifying excipients (SLS, span 80, tween 80) were investigated at different rates of use.

- Survey of the ratio of titanium dioxide and zinc oxide

Titanium dioxide and zinc oxide were added to the composition with average usage rates of 10%, then transmitted spectrophotometry was performed to evaluate the SPF and select the formula with the highest SPF.

Evaluation of some quality indicators of physical sunscreens containing titanium dioxide and zinc oxide

Sensory: According to Appendix 1.12 Vietnamese Pharmacopoeia V [7], the cream sample achieves the sensory when the uniform cream is opaque white, smooth, and very few or without air bubbles, when applied to the skin, it can create a smooth thin film, not too white.

Physicochemical structure stability of the emulsion [4]: 3.0 g of cream was put into a 15 ml centrifuge tube with a centrifugal rate of 5000 rpm, time 60 minutes. The survey was evaluated successfully when the sample after 60 minutes of centrifugation did not separate layers and had few air bubbles.

Evaluate the pH of the product [8]: The pH of the cream was measured by a pH meter (Edge Hi2002) at room temperature (25 ± 2^oC). The pH requirement of the cream was from 5–7 to ensure skin irritation.

Determination of SPF [9, 10]: Based on COLIPA in vitro SPF testing method guidelines 2011 (Comité de Liason des Associations et Européenes de Industrie et de la Parfumerie – European Association of Cosmetics, Toiletries and Fragrances) and ISO 24443:2021. Sunscreen product is spread evenly on the cuvette by weight with a density of approximately 1.3 mg/cm^2. Transmission spectrophotometer scans were conducted in the wavelength range from 290 nm to 400 nm on the Jasco V-630 spectrophotometer. The blank sample a cuvette without cream. SPF indicators were calculated by the formula (1).

$$\text{SPF} = \frac{\sum_{290}^{400} S\lambda.E\lambda.d\lambda}{\sum_{290}^{400} S\lambda.E\lambda.T\lambda.d\lambda} \qquad (1)$$

Skin irritation assessment: The cream was applied to the swabs. The swabs were fixed at the experimental sites, observed and record erythematous nodules and edema at 4, 24, 48, and 72-hour markers. Erythema and edema were scored according to the guidance document issued by the Ministry of Health of Vietnam on Decision No. 3113/1999/QD-BYT dated October 11, 1999 'Promulgate standards limiting bacteria, mold in cosmetics and skin irritation test methods' [11]. The cream sample was concluded without irritation when the average score is from 0–0.5.

Heavy metal limits: To evaluate the safety of the product, the cream samples were checked to limit heavy metals including lead content (Pb), arsenic content (As), and mercury (Hg) with similar standard levels Application (Pb $\leq$ 20 ppm, As $\leq$ 5 ppm and Hg $\leq$ 1 ppm are found in the product) according to regulations for cosmetics issued by the Ministry of Health of Vietnam through cosmetic management regulations [12].

Microbiology limits [12]: The product was tested to limit bacterial contamination with the criteria of the total number of microorganisms counted $\leq$ 1000 cfu/g; *Pseudomonas aeruginosas*, *Staphylococcus aureus*, and *Candida albicans* should not be contained in 0.1 g or 0.1 ml of product.

IV. RESULTS AND DISCUSSION

A. Formulation of physical sunscreens containing titanium dioxide and zinc oxide

The orientation formula is formulated from the combination of excipients (% KL/KL) conventionally excipient system A is presented in Table 1.

From the foundation orientation formula in Table 1 (conventional is system A), a survey was conducted to investigate the use of emulsification excipients (span 80, SLS, and tween 80), the ratio of excipients for cream texture modification

Table 1: Formulation of cream ingredient orientation

Excipients group	Name	Usage rate (%)
Excipients mixed with oil	Cetyl alcohol	X
	Stearic acid	X
	Vaseline	X
	Sunflower oil	18
Emulsifiers	Span 80	X
	Sodium lauryl sulfate (SLS)	X
	Tween 80	X
Sunscreen	Titanium dioxide	X
	Zinc oxide	X
Excipients mixed with water	Carbomer 940	0,1
	Glycerin	5
Preservative excipients, pH aids	Sodium benzoate	0,1
	Triethanolamine	1
	Isopropyl myristate	5
Distilled water	Distilled water	100

**Note: The 'X' sign is present the excipients to be surveyed in the formula*

(cetyl alcohol, stearic acid, and vaseline), and the ratio of sunscreen (titanium dioxide and zinc oxide).

Emulsification excipients survey

Table 2: Survey results with emulsified excipients sodium lauryl sulfate (SLS), tween 80 and span 80 at 0.5%–1%

	Sa 1	Sa 2	Sa 3	Sa 4	Sa 5	Sa 6	Sa 7
Excipient system A	+	+	+	+	+	+	+
SLS	**0.5**	**1**	**0.5**	**1**	**0.5**	- -	- -
Span 80	**0.5**	**0.5**	**1**	- -	- -	**1**	**0.5**
Tween 80	**0.5**	- -	- -	**0.5**	**1**	**0.5**	**1**
Evaluate	 Samples 1, 2, 3, 4, and 7 have liquid creamy substances with lots of air bubbles. Two samples 5 and 6 have a thick, smooth cream texture with few air bubbles.						

**Note: the '+' sign is present in the formula, the '–' sign is not present in the formula, Sa: Sample*

The results in Table 2 show that the creamy textures of samples 5 and 6 were soft and smooth, creating a stable emulsion without layer separation.

Emulsified excipients are a vital ingredient that is added to the formulation to ensure stability in the emulsion structure and the cream that is formed. SLS, span 80, and tween 80 are the most popular options on the market. Survey results of these emulsified excipients at various concentrations show that two pairs of ratios: 0.5% SLS combined with 1% tween 80 and 1% span 80 combined with 0.5% tween, help the cream's dense, soft, smooth, and homogenous composition create a stable oil/water emulsion structure. Surveys also show that emulsified excipients need to be combined in appropriate proportions to create emulsions, improve physical appearance, improve adherence to the skin, provide comfort while using, and prevent irritation.

Survey of excipients for cream texture modification

After surveying the ratio of excipients to adjust the cream's texture according to the required emulsifier ratio, as illustrated in Table 3 and Table 4, it was observed that sample 21 has a thick, smooth cream texture that is comfortable on the skin without causing a greasy sensation. Moreover, its emulsion structure is durable and does not cause layers to separate.

For the cream to have a soft, smooth texture, adhere well to the skin, and not be greasy or interfere with the skin's physiological processes, the physical adjustment excipients were investigated at different concentrations to find out the appropriate concentration ratio to meet the established requirements. Survey results show that when cetyl alcohol is not present in the formula, the cream samples ranged from liquid to thick. Cream samples with a high percentage of stearic acid often create a lot of air bubbles, and samples with a high percentage of vaseline also do not give the cream a satisfactory consistency. Furthermore, due to the presence of vaseline in the formulation, cream samples often have a greasy feeling and are difficult to apply to the skin, almost without creating an emulsion structure. Nonetheless, by mixing cetyl alcohol and stearic

Table 3: Survey results with stearic acid, vaseline, and cetyl alcohol rate 3%–6% when combined with SLS 0.5% and tween 80 at 1%

	Sa 8	**Sa 9**	**Sa 10**	**Sa 11**	**Sa 12**	**Sa 13**	**Sa 14**	**Sa 15**	**Sa 16**	**Sa 17**
Excipient system A	+	+	+	+	+	+	+	+	+	+
SLS	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Tween 80	1	1	1	1	1	1	1	1	1	1
Cetyl alcohol	**3**	**4.5**	**3**	**6**	**4.5**	**3**	**6**	- -	- -	- -
Stearic acid	**3**	**4.5**	**6**	**3**	- -	- -	- -	**4.5**	**3**	**6**
Vaseline	**3**	- -	- -	- -	**4.5**	**6**	**3**	**4.5**	**6**	**3**
Evaluate										
	The texture of samples 8, 11, 12, and 17 were slightly dense with a smooth creamy consistency and had few air bubbles. Despite this, samples 8, 11, and 12 display an oily layer on the surface. The texture of samples 9, 10, 12, and 14 were thick and smooth creams, with minimal air bubbles. However, there is an oily layer on the surface of samples 9, 10, and 12. Sample 13 was slightly dense with a smooth creamy consistency and had few air bubbles. Upon application to the skin, particles that do not dissolve can be sensed. The texture of samples 15 and 16 were fluid and smooth, with a lot of air bubbles present.									

**Note: the '+' sign is present in the formula, the '–' sign is not present in the formula, Sa: Sample*

Table 4: Survey results with stearic acid, vaseline, and cetyl alcohol at 3%–6% when combined with span 80 1% and tween 80 at 0.5%

	Sa 18	**Sa 19**	**Sa 20**	**Sa 21**	**Sa 22**	**Sa 23**	**Sa 24**	**Sa 25**	**Sa 26**	**Sa 27**
Excipient system A	+	+	+	+	+	+	+	+	+	+
Span 80	1	1	1	1	1	1	1	1	1	1
Tween 80	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Cetyl alcohol	**3**	**4.5**	**3**	**6**	**4.5**	**3**	**6**	- -	- -	- -
Stearic acid	**3**	**4.5**	**6**	**3**	- -	- -	- -	**4.5**	**3**	**6**
Vaseline	**3**	- -	- -	- -	**4.5**	**6**	**3**	**4.5**	**6**	**3**
Evaluate										
	The texture of samples 18, 20, 21, 22, and 24 have a thick and smooth cream texture with few air bubbles. The texture of samples 19 and 20 have a thick, spongy cream texture with lots of air bubbles. Sample 23 has a thick, spongy cream texture with lots of air bubbles, and when applied, it feels greasy. The texture of samples 25 and 27 has a thick, smooth cream texture with few air bubbles. Sample 26 was fluid and smooth with few air bubbles.									

**Note: the '+' sign is present in the formula, the '–' sign is not present in the formula, Sa: Sample* acid with emulsified excipients in the correct quantities (Sample 21), a stable and pleasant-to-use cream with a thick, smooth texture and few air bubbles was produced.

Investigate the ratio of titanium dioxide and zinc oxide

The results of simultaneously investigating the ratio of titanium dioxide and zinc oxide and evaluating SPF are presented in Table 5.

Table 5: Survey results of titanium dioxide and zinc oxide at 1%–9% and SPF assessment results

	Sa 28	Sa 29	Sa 30	Sa 31	Sa 32
Excipient system A	+	+	+	+	+
Span 80	1	1	1	1	1
Tween 80	0,5	0,5	0,5	0,5	0,5
Cetyl alcohol	6	6	6	6	6
Stearic acid	3	3	3	3	3
Titanium dioxide	**1**	**9**	**3**	**7**	**5**
Zinc oxide	**9**	**1**	7	**3**	**5**
SPF	**21.8**	**26.1**	**14.2**	**14.8**	**9.3**
Evaluate	The samples surveyed had a thick, smooth cream texture, few air bubbles, and no layer separation after centrifugation				

**Note: the '+' sign is present in the formula, the '–' sign is not present in the formula, Sa: Sample*

The results of the survey indicate the ratio of titanium dioxide and zinc oxide shows that with different concentration ratios, the cream has a smooth, stable texture and does not cause a greasy feeling on the skin or the presence of non-dissolvable particles that collect on the skin after application. At the same time, after conducting an SPF evaluation, the emulsion structure of sample 29 is both beautiful and sustainable, achieving the highest sun protection ability.

B. Evaluation of some quality indicators of physical sunscreens containing titanium dioxide and zinc oxide

After formulating the optimum formula, the researchers evaluated some testing quality indicators and presented the results in Table 6. The 29 cream sample's evaluation results meet sensory requirements: the cream is opaque white, smooth,

Table 6: The results of evaluating some quality indicators for prepared cream

Targets	Sensory	Physico-chemical structure stability of the emulsion	pH	SPF	Irritation test	Heavy Metal Limits	Microbiology limits
Result	The cream is milky white, thick, smooth, with few air bubbles	No phase separation, less air bubbles	6	26.1	No irritation	Reached	Reached

**Note: the '+' sign is present in the formula, the '–' sign is not present in the formula, Sa: Sample*

has a uniform texture and very few or no air bubbles. When applied to the skin, it can create a smooth, thin texture that is not overly white. The cream meets the requirements of the emulsion physicochemical structure stability criteria, creating a stable emulsion structure without layer separation after centrifugation for 5000 rounds for 60 minutes. Moreover, the cream does not irritate when testing irritation to rabbit skin, and a pH of 6 is consistent with the physiological pH of the skin and does not change the resistance of sunscreen active ingredients to UV rays. The product has been tested for bacterial and heavy metal contamination limits by the Analysis and Testing Center of Tra Vinh University.

Evaluating SPF using the in vitro SPF method is safe for humans and produces fast and low-cost results. As a result, after measuring the absorption spectrum and calculating according to the SPF calculation formula, the cream has an SPF value greater than 20 (SPF 26.1). According to the European Commission's guidelines 2006/647/EC classifying the protective effect of sunscreen products, sunscreen products with an SPF between 15 and 29.9 provide medium protection [13]. This shows that sunscreens containing 9% titanium dioxide and 1% zinc oxide have medium sun protection ability.

Through surveying and evaluating the construction of a physical sunscreen formula containing 9% titanium dioxide and 1% zinc oxide, it has been shown that the research has successfully applied the skin protection effect against UV rays of titanium dioxide and zinc oxide as well as evaluated the SPF index of the prepared cream. Compared with the research of Tran Thi Hai Yen et al. [4] in 2019, combining titanium dioxide with zinc oxide gives better sun protection effectiveness than using titanium dioxide alone. At the same time, the ratio of 9% titanium oxide and 1% zinc gives a lower sun protection index than the study by Duong Thi Bich et al. [6], with 2% titanium dioxide and 6% zinc oxide. Due to limited experimental conditions, the project has not been able to develop a formula with a high SPF index as expected. However, the evaluation surveys have created a premise for further research.

V. CONCLUSION

The survey formulations are designed to find the most optimal formula with high sun protection ability to protect the skin against the harmful effects of UV rays while meeting physical requirements, and providing comfort during use.

Research has developed the optimal formula and manufacturing process for physical sunscreen containing 9% titanium dioxide and 1% zinc oxide. The product meets the basic quality criteria of cosmetics, does not cause skin irritation, and has medium sun protection. It is necessary to research and test other excipients to improve the SPF and evaluate the water resistance of the product, enhancing the potential for widespread product application in the market.

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