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Development of multipurpose sunscreen for the sensitive areas of the face and design of the manufacturing process

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El mismo sol funde la cera y seca la arcilla.

Clemente de Alejandría.

Este trabajo es un reflejo de años de estudio, experiencias y retos, vividos y superados gracias al apoyo de amigos y familiares.

Por eso quiero agradecer en primer lugar a mi familia, porque gracias a ellos soy la mujer que soy hoy y me han dado la oportunidad de crecer, formarme en lo que más me gusta e impulsarme a ser una persona trabajadora y resiliente independientemente de las circunstancias. A mis amigos, por estar en los mejores y peores momentos, porque durante estos años, sabiéndolo o no, han sido un pilar fundamental para seguir y lograr llegar hasta aquí.

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SUMMARY

The limited availability of sunscreens for the sensitive areas of the face led to the development of sunscreens for eye contour (eye cream sunscreen) and lips (lip sunscreen), followed by the design of their manufacturing process. It was encouraged by the growth of the sun protection market, due to the increasing awareness of risks related to sun exposure, which are of special importance in the eye contour and lips, as these are areas with less protection capability.

For this reason, the market trends were identified through market analysis and bibliographic search, allowing the identification of consumer needs, which resulted in the development of broad-spectrum sunscreens with sun protection factor 50 that moisturize and soothe the skin, providing an enhancing effect that enables layering with makeup, and, in the case of the lip sunscreen, giving a nude color that lasts a minimum of 2 hours; additionally, environmentally friendly packaging were designed, with refillable containers made of bamboo, recycled plastic, and aluminium.

According to these needs, the quality factors and their performance indices were defined, whereby the eye cream sunscreen would be a pseudoplastic oil-in-water nanoemulsion with low eye-stinging ability, and the lip sunscreen would be a water-in-oil emulsion-based suspension with thixotropic behaviour, solid-like at room temperature, with a pleasant taste and smell.

UV filters, humectants, and emollients were chosen as active ingredients to meet the quality factors, they were specified in terms of concentration and characteristics of each, and subsequently, their manufacturing processes were designed by selecting equipment and establishing batches of 150 kg of each product, with 2 batches per year for the eye cream sunscreen and 4 batches for the lip sunscreen.

Keywords: Sunscreen, product development, manufacturing process, lips, eye contour.

RESUMEN

La disponibilidad limitada de protectores solares para áreas sensibles de la cara llevó al desarrollo de protectores solares para el contorno de ojos (protector de ojos) y para los labios (protector de labios), seguido del diseño del proceso de fabricación. Esto fue incentivado por el crecimiento del mercado de protección solar, debido a un aumento en la concienciación de los peligros relacionados con la exposición al sol, lo cual es de especial importancia en el contorno de ojos y en los labios, ya que son zonas con menor capacidad de protección.

Por esta razón, se determinaron las tendencias de mercado a través de búsquedas bibliográficas y un análisis de mercado, permitiendo identificar las necesidades de los consumidores, lo que resultó en el desarrollo de protectores solares de amplio espectro con factor de protección 50 que hidratan y suavizan la piel, dando un efecto de realce que permita la aplicación de maquillaje, y en el caso del protector de labios, dando un color natural que dure mínimo 2 horas; además se diseñaron envases ecológicos reutilizables, hechos de bambú, plástico reciclado y aluminio.

De acuerdo a las tendencias se definieron factores e índices de calidad, según los cuales el protector de ojos sería una nanoemulsión pseudoplástica aceite en agua, con baja capacidad de irritar los ojos, y el protector de labios sería una suspensión con base de emulsión agua en aceite, con comportamiento tixotrópico y sólido a temperatura ambiente, y un sabor y olor agradable.

Los activos que se escogieron para cumplir los factores de calidad fueron filtros UV, humectantes y emolientes; las concentraciones y características de cada uno se especificaron y, posteriormente, se diseñó el proceso de fabricación, seleccionando los equipos y estableciendo lotes de 150 kg de cada producto, con 2 lotes al año para el protector de ojos y 4 lotes para el protector de labios

SUSTAINABLE DEVELOPMENT GOALS

The United Nations set 17 sustainable development goals (SDGs) to address the following 5 areas (5 Ps) by 2030: people, planet, prosperity, peace, and partnership.

The chemical industry is of great importance in meeting the SDGs. Specifically, the development and manufacturing of the products developed in this work could mainly meet 2 areas:

- People: The application of sunscreen prevents skin conditions and diseases and reduces the prevalence and recurrence of some diseases, consequently improving the users' good health and well-being (SDG-3). In particular, it addresses target 3.4, which consists of reducing premature mortality from non-communicable diseases, one of which is cancer.
- Planet: The use of refillable packaging reduces waste generation by reusing the same packaging several times and, thereby, reducing the production of new packaging; in addition to the usage of recycled plastic in the packaging (target 12.5).

  Moreover, the sustainable management and efficient use of natural resources (target 12.2) is supported by the use of bamboo, which, in addition to being biodegradable, is easily renewable, due to its fast growth, and also consumes less water than trees to live.

  Additionally, the campaigns carried out to promote the product must inform people about the environmental advantages of using refillable packaging with the materials used, raising awareness about the consequences of single-use plastic (target 12.8).

  The past 3 targets ensure sustainable consumption and production patterns (SDG 12).

1. INTRODUCTION

Ultraviolet radiation (UVR) is present in everyone's life, primarily due to sunlight, and although UVR improves health by stimulating vitamin D production, and treating chronic diseases like psoriasis and eczema, prolonged exposure can cause skin damage.

The damage that can cause sun exposure includes sunburn, skin cancer, photosensitive reactions; actinic keratosis, which are precancerous rough and scaly growths; and photoaging, which is related to wrinkles, irregular pigmentation, and roughness of the skin (1).

Sunscreen products are used to protect the skin from UVR by absorbing, scattering, or reflecting ultraviolet (UV) rays. Its use is mainly associated with the summer season, although in recent years, due to awareness campaigns, people are more prone to use sun protection daily (2).

Studies have shown that people rarely apply sunscreen on the eye contour and the lips (3), areas that are particularly important to protect due to their reduced natural protection.

Nowadays some products on the market are sold specifically for these areas, but consumers are looking for improvements that made them more wearable by providing an enhancing finish to the skin, improving its health and appearance while protecting it from UVR.

Consequently, this work will develop sunscreens that fulfill the above characteristics to cover the usually unprotected eye contour and lips. It is expected that the design of products that are compatible with everyday life will encourage people to protect the skin of these sensitive areas.

Throughout this work, the market trends will be evaluated through a bibliographic search of patents, articles, books, legislation, and reports, along with the analysis of the products available in the market, with the objective of establishing quality factors that differentiate the products to be developed, and subsequently, to be able to formulate the products and design their manufacturing process, optimizing them through the integration of both processes.

2. OBJECTIVES

The main objective of this project is to develop multipurpose sunscreens for sensitive areas of the face, specifically for lips and eye contour, and subsequently, to design their manufacturing process.

To achieve the main objective, it has been specified the following sub-objectives:

- Conceptualize both products according to people's needs, through market analysis based on bibliographic search.
- Define the product quality factors and indexes, to reach the differentiating factor of each product.
- To formulate the products by selecting ingredients that allow the achievement of the defined factors and compliance with the related European regulations.
- Design the manufacturing process and select the necessary equipment for the process.

3. PRODUCT CONCEPTUALIZATION

3.1. MARKET TRENDS

Consumer buying behaviour has changed over time, nowadays most people buy skincare according to recommendations on social media. Furthermore, when consumers buy online, they invest more time researching and buying products with specific characteristics (4). Specifically, the demand for skin nourishing and protecting products is rising due to increasing awareness of skin disorders and skin damage (5).

People are looking for cruelty-free or vegan products (5) which at the same time cover the ‘clean beauty’ standards (4), this means that ingredients cannot be ‘harmful’ or ‘toxic’ or they have to be ‘chemical free’, but as we know every ingredient that a product has will be a chemical, so when people talk about sunscreen with these characteristics they mean inorganic sunscreen actives and they are called ‘natural’ or ‘organic’ (6).

In terms of packaging, consumers will look for quality, a container that allows using the entire product, and eco-friendly materials (5, 7).

The global skincare market is forecast to continue to grow (5, 7), just like the sun protection market, although this one depends on the season because some people up until now associate sun protection with summer (6). Nevertheless, campaigns about the harmful effects of sun exposure are improving the sun protection market.

Currently, people want a multi-functional product with a light and non-greasy finish and an easy application that aligns with the flexible lifestyle of these days and age (6, 7).

3.1.1. Market analysis

A few sun protection products in Europe are marketed specifically for eyes and lips. With the purpose of creating a product that fulfills customers’ requirements, the key ingredients, and consumer ratings of some products have been evaluated (see Appendix 1).

Since Spain is in an area that can reach a very high UV index, with an intensity of UV radiation up to 9 (8), which means sun protection is needed (9), the criteria to choose these products was based on the recommendation of dermatologists, who advocate using a broad-spectrum sunscreen with high sun protection factor (SPF) daily, minimum an SPF 30 (10).

To better understand the terms *broad-spectrum* and *SPF*, they will be defined as:

A *broad-spectrum* sunscreen protects against UVB and UVA radiation, UVB rays are called sunburn rays and are the main responsible for causing skin cancer, they have a wavelength between 290 nm and 320 nm and represent about 5 % of solar radiation reaching our skin, while UVA represents 95 %. UVA has longer wavelengths, therefore, penetrates deeper into the skin causing early photoaging and enhancing skin cancer. UVA divides into UVA-I, which is between 340 nm and 400 nm, and UVA-II is in the range 320 nm – 340 nm (11,12).

The *SPF* is determined by ISO 24444:2019 and represents the ratio of the minimum UV energy necessary to produce an erythema (sunburn) on protected skin, to the energy required on unprotected skin (13).

Consequently, every product evaluated is a broad-spectrum sunscreen, with a minimum SPF of 30, and its ingredients and the main characteristics that people are looking for are presented below.

3.1.1.1. Eye cream sunscreen

Regarding sunscreen for the eye area, in theory, every sunscreen on the market could be used around the eyes, the problem is that with some of them, the user can have a stinging or burning sensation, moreover, it can layer badly with makeup or look and feel unpleasant by itself.

To achieve people's wants, the active ingredients included are emollients, which soothe the skin; humectants, which bring water to the skin; and UV filters.

The most used ingredients in eye cream sunscreens, according to their function, are:

- *UV Filters*

UV filters can be classified as organic (chemical) and inorganic (physical) according to their composition. It is a common belief that organic filters are worse for skin and eyes since they are considered to be more irritating and even toxic because of their synthetic or 'chemical' nature, added to their action mechanism (14, 15); they act by absorption, but so do the inorganic filters, although the term ‘physical’ is due to the belief that inorganic filters work by reflecting light, this phenomenon, along with scattering, is the least responsible for light protection, particularly due to the particle size used nowadays to minimize the white finish that larger particles caused (16).

Therefore both, organic and inorganic filters protect primarily by absorption, and whereas there are organic filters that are irritating, there are others that are not, this fact will be taken into account when selecting the filters to be included in the eye cream sunscreen.

The most used organic filters are:

Ethylhexyl Methoxycinnamate / Octinoxate is primarily a UVB filter (17), used due to its many benefits, it is little to non-irritating nor photosensitizing, and it is hypoallergenic (18).

Ethylhexyl Salicylate / Octisalate is used as a complementary ingredient to increase UVB protection (19), stabilize other sunscreen actives, neutralize free radicals, and add emollient properties to the formula (20).

Butyl Methoxydibenzoylmethane / Avobenzone absorbs UVA radiation (21) and is hypoallergenic (19). Avobenzone is photo-unstable therefore it must be formulated with photo stabilizers, specific emollients, and/or antioxidants (21, 19)

Octocrylene is a broad-spectrum filter, mainly absorbing UVB and UVA-II (22). Octocrylene is photostable and adds emollient and water-resistant properties (23), but it can be an allergen (19).

Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine is a highly effective broad-spectrum filter (UVB, UVA-II, and UVA-I) (24). It is photostable and can be a stabilizer to other sunscreen actives (19, 24).

And the inorganic filters most commonly seen in sunscreens are:

Titanium dioxide is a broad-spectrum filter that protects mainly against UVB. It has the risk of free radical formation in the presence of light, coating is used to reduce this risk (25, 26).

Zinc oxide is a broad-spectrum filter that protects predominantly against UVA radiation (26). ZnO is nonreactive but may be unstable under irradiation (25).

- *Emollients*

C12-15 Alkyl Benzoate is a highly polar and low-viscosity liquid that improves dispersion (27), it also has solvent properties and provides a silky and non-oily finish to the final product (28), it does not cause skin nor eye irritation (29).

Dimethicone is a hypoallergenic silicone, that provides water-resistant properties while allowing transepidermal water loss, it also adds a non-oily finish to the formula (30) and improves spreading and absorption (31), dimethicone decreases skin irritation (32), although it can cause eye irritation (33).

Butylene glycol acts as a humectant, solvent, emollient, and stabilizer, furthermore, it has antimicrobial properties, nonetheless, it can be an irritant to eyes and skin (34).

- *Humectant*

Glycerin / **Glycerol** is an alcohol soluble in water, that improves hydration and skin barrier recovery. It is non-irritating to the eyes and skin (35).

Sodium Hyaluronate is a salt of hyaluronic acid, which has an excellent capacity to retain water, therefore improving skin hydration and skin repair. Sodium hyaluronate is non-irritant to the eyes and it is not known to cause skin irritation (36).

3.1.1.2. Lip sunscreen

On the other hand, regarding sunscreen for the lips, they are usually sold in gloss or balm form, and people look for a product that hydrates and moisturize the lips, looks good, is easy to reapply, and mainly, does not taste or smell bad.

The most common key ingredients of the lip products evaluated are:

- *UV Filters*

The most used UV filters are octisalate, avobenzone, octocrylene, and ethylhexyl triazone, the first three filters have been defined before.

Ethylhexyl / Octyl Triazone is mainly a UVB filter, oil soluble, and usually photostable (37), it is not a skin irritant or sensitizing, and it is also not toxic in case of ingestion (38).

- *Emollients*

Butyrospermum Parkii (Shea) Butter is used due to its soothing, occlusive, antioxidant, and viscosity-increasing properties, moreover, it can increase UV protection (39). It does not irritate or sensitize the skin and is safe to ingest. (40).

Ricinus Communis (Castor) Seed Oil is used for its skin soothing, occlusive, perfuming, and stabilizing properties, it is safe to ingest according to the FDA, but it can be a skin irritant and cause allergy (41).

Beeswax is secreted by bees, alternatively, it can be synthetically produced. It has multiple properties, such as antioxidant, antimicrobial, anti-inflammatory, occlusive, humectant, and emollient properties, additionally, it increases the firmness, adhesiveness, elasticity, and plasticity of the formula. It is non-irritant, hypoallergenic, and safe to ingest (42).

Octyldodecanol is a fatty alcohol used as a surfactant (43), fragrance (44), vehicle, emollient, and dispersant, furthermore, it increases the viscosity and stability of the formula. It is safe to use in cosmetics (45).

3.2. PRODUCT FUNCTIONALITY

The functionality of both products will be defined according to the market trends and the people’s needs previously analyzed, therefore they will be multifunctional products, which protect from UV rays, improve skin health, and has an enhancing finish.

Additionally, the intended customers must be identified to specify the finish and other functionalities. Based on the reviews of the products, and the studies made about sun protection usage tendencies in Spain (2, 46), the primary consumers of both products are women who are between 18 and 50 years old, consequently, as the usage of makeup is usually associated with women, the products must layer well with makeup.

On the other hand, for a better understanding of the relation between skin health and UV rays, the skin barrier function must be understood. The skin barrier is responsible for protecting the body from external aggressors and regulating the internal water content. It is affected by some actives, UV radiation, environmental factors, like temperature and humidity, and so on.

Specifically, the skin barrier function of the eyelids and lips is weak (47), and it is worsened by UV rays because it causes oxidative stress and inflammation (48), consequently, the skin must be protected from UV exposure.

Besides these points, every zone has its characteristics, and for that reason, its own needs to be covered by the product's functionalities, which are going to be presented following.

3.2.1. Eye cream sunscreen

The skin around the eyes shows the first visible signs of ageing due to its continuous movement and structure. It is the thinnest skin of the body, in this area the thicknesses of the epidermis and dermis, the top two layers of skin, are about 0.05 mm and 0.30 mm respectively (49), while, for example, in the forehead are 1.25 mm and 0.13 mm (50), because of this fact, the periocular zone is more sensitive to external factors. Moreover, around 5 % to 10 % of skin cancer develops in the eyelids (51). Therefore, to prevent skin cancer and premature skin ageing, sun protection will be the main function of this product, presenting a high SPF of 50.

In addition, to improve the skin's health and appearance, the skin must be hydrated, and moisturized. In cosmetics, hydration consists of providing water using a humectant, while moisturization lies in locking the water into the skin, which is accomplished by emollient ingredients. Taking into consideration that these qualities are different and the necessity of each one generally depends on the skin type; both will be included as major functions.

In order to obtain an optimal makeup finish, skin must be hydrated, and moisturized, whilst cannot be oily. In other words, the product will be a makeup primer that prepares the skin smoothing it, creating a canvas that allows an even application of a tinted product, but at the same time, can be worn well on its own, since sunscreen must be used every day and not all consumers wear makeup daily; by the same reason the product will not have any color added.

3.2.2. Lip sunscreen

The lip skin is characterized by higher transepidermal water loss and lower hydration than the skin of the rest of the face, coupled with the fact that skin water content is correlated with chapped lips (52), results in hydration and moisturization being two of the main functions of the lip sunscreen to improve skin health and appearance, and this can be achieved through the addition of humectants and emollients to the formula.

By reason of the lips having little melanin (53), which is the natural protection of the skin from UV radiation, and poor skin barrier function, photoprotection of the lips is an essential product function. Furthermore, in this area, UV exposure is related to the risk of lip cancer, the prevalence of actinic cheilitis lesions, the recurrence of herpes labialis (54), and the development of vertical lip lines (smoker lines), hence, the lip sunscreen will have an SPF 50.

Due to the continuous movement and contact with fluids, the lip product should be long-lasting and comfortable, for these two functions to coexist there must be a balance, where long-lasting means that the product stays on a minimum of 2 hours, and comfortable means that it maintains the lips moisture and elastic even after most of the product is gone. To achieve both functions at the same time, a lip balm is the best choice.

Because sunscreen must be reapplied every two hours and lip products wear out when eating or drinking, it needs to wear out evenly and be easy to reapply. Likewise, it must extend evenly to ensure total coverage with UV protection, to improve pre or post-lipstick application, and to make lips look good when it is on its own. To enhance the finish on the lips, the product will have a subtle nude color, allowing it to blend with other colors and look natural when worn alone.

3.3. PRODUCT PACKAGING

When shopping in physical stores, the packaging is part of the first impression of potential buyers, therefore it must stand out to attract them and encourage them to buy the product.

Nowadays there are thousands of products available at every visit to the store, and the color is the most striking feature to differentiate the brand from competitors (55). Every color conveys different sensations and meanings, for instance, white express cleanliness and purity, green is related to nature and gives confidence, along with the idea of being good to health, orange transmits the feeling of the brightness of the sun and has an exciting effect (56), and blue is associated with moisturizing and soothing properties (57). Consequently, to associate both products with the sun and their moisturizing properties, the packaging will have orange and blue colors.

Depending on the material, the packaging of lip products varies (see Appendix 1), sometimes, when if made of glass or plastic, is transparent, at other times it is of the color of the product and, occasionally it is not related to the color of the product but to the characteristic color of the brand, the collection, or the packaging material.

According to the market analysis, eco-friendly materials are on the rise, and using them allows the brands to meet the three R's; reduce, reuse, and recycle. To fulfill the 'green' or eco-friendly standards there are cosmetics companies that are using recycled plastic, glass, paper, metal, and bamboo, among others (58); in addition to this, brands are creating refillable packaging and reducing the quantity of material used, which means not including extra protection as boxes and protectives plastics if not needed. However, people look for quality packaging, to this end, the material chosen must be resistant enough to look good and remain undamaged during transportation, storage, and use of the product.

Furthermore, regarding materials, it should be considered that one of the main functions of packaging in cosmetics is to keep the product chemically stable, in consequence, chemical compatibility must be taken into account to ensure the required shelf life of the product.

Additionally, the type and shape of the packaging influence the perception of the customer (55). Therefore, to meet the needs of the market trends, consisting of an eco-friendly quality product, refillable packaging have been selected. Regarding the lip sunscreen, it is chosen a cylindrical stick, with a bamboo outer casing and an aluminium inner mechanism, giving the message of quality and sustainable products; likewise, to keep the same line, in the case of the eye cream sunscreen, by reason of being a cream, the best packaging would be a collapsible tube made of recycled plastic formed by rLDPE (recycled low-density polyethylene), and rHDPE (recycled high-density polyethylene), additionally, the inner layer would be virgin PE (polyethylene) (59), and the tube cap would be made of bamboo.

The packaging cap is another essential part to consider owing to the function of protecting the product from contaminants and keeping the product inside so that it is not wasted, besides satisfying this need, it is also considered the ease of use and durability, taking into account that it will be used frequently for a long time because it is refillable, therefrom both products will have a screw cap.

Another point to evaluate is the ease of use and transportation, where size assumes greater importance. Respecting transportation, the smaller the product, the less environmental impact, and the lower cost. On the other hand, since the intended use of both products is daily, with a constant application every 2 hours, the packaging should be small, more specifically, of a volume that can fit in a purse or a pocket, and in this way fits in with today's lifestyle.

The eye cream sunscreen volume is defined based on the typical volume of the eye creams on the market, which is 15 mL; alternatively, the lip sunscreen size is selected by the packaging's external height and diameter, which are 7 cm and 2 cm respectively, these measures made the product easy to carry, and capable of contain 4 g of product.

Finally, the labelling must be defined according to Article 6 of Directive 76/768/EEC (60). The product must contain, visible and legible, the following information:

- Name and address of the responsible person.
- Nominal content, except in the case of packaging containing less than 5 g o 5 mL.
- Date of minimum durability, this date is not mandatory if the minimum durability is more than 30 months, in this case, it should be indicated the period after opening (PAO) for which the product is safe to use.
- Precautions to be observed in use (on an enclosed tag if it is impossible to fit on the packaging).
- Batch number or reference for identifying the product (only on the packaging if the product is too small).
- Function of the product, unless it is clear from its presentation.
- List of ingredients, in descending order of weight. Except for ingredients in a concentration of less than 1%, they can be listed in any order after those of more than 1%. The list can be only on the packaging or on an enclosed tag if it cannot fit on the packaging.

  It must be added the word 'nano' in brackets after nanomaterials.

  If the product is marketed in several color shades, colorants may be listed adding the words 'may contain' or the symbol '+/-', and the 'Colour Index' nomenclature shall be used, where applicable.

Regarding sunscreen, according to the Commission Recommendation 2006/647/EC (61), should be added warnings like 'Do not stay long in the sun, even while using a sunscreen product', 'Keep babies and young children out of direct sunlight', and 'Over-exposure to the sun is a serious health threat'.

It also may include instructions for use, such as ‘Apply the sunscreen product before exposure’, ‘Re-apply frequently to maintain protection, especially after perspiring, swimming or towelling’, and an indication of the quantity needed to achieve the effectiveness claimed.

The label, for the efficacy of UV protection, if the product is under a measured sun protection factor (SPF) between 50.0 and 59.9, should indicate an SPF of 50, and the words ‘High protection’, and it should add the letters ‘UVA’ in a circle to display the UVA protection if the content level is a minimum of 1/3 of the SPF (62).

To sum up the packaging decisions and requirements, a packaging model of both products have been made, the eye cream sunscreen is shown in Figure 3.1 and the lip sunscreen is presented in Figure 3.2.

Figure 3.1. Packaging model of the eye cream sunscreen, made of recycled plastic and bamboo. Own design on a blank tube of (63).

Figure 3.2. Packaging model of the lip sunscreen, made of aluminium and bamboo. Own design on a blank lipstick packaging of (64).

3.4. PRODUCT CONCEPTUALIZATION SUMMARY

Product conceptualization has been based on current market trends, which are focused on environmental and animal-friendly products, including ingredients and packaging materials, along with a growing demand for skin care products that protect and improve skin health.

The conceptualization of both products has been condensed in Table 3.1.

Table 3.1. Summary of the conceptualization of the products to develop.

<table>
<tr><th>Parameter</th><th>Eye cream sunscreen</th><th>Lip sunscreen</th></tr>
<tr><td>Intended costumer</td><td colspan="2">Women between 18-50 years old</td></tr>
<tr><td rowspan="3">Function</td><td colspan="2">Sun Protection Factor: 50
Moisturization
Improve makeup application</td></tr>
<tr><td>Smoothing</td><td>Coloring (Nude)
Long-lasting (2 h)</td></tr>
<tr><td colspan="2"></td></tr>
<tr><td rowspan="3">Packaging</td><td>Collapsible tube with a screw cap</td><td>Cylindrical stick with a screw cap</td></tr>
<tr><td>Recycled plastic + Bamboo</td><td>Aluminium + Bamboo</td></tr>
<tr><td colspan="2">Refillable
Ease of use and transport
Chemically compatible</td></tr>
<tr><td>Labelling</td><td colspan="2">Blue + Orange
Printed: SPF 50 + UVA in a circle, name and address of the responsible person, nominal content, minimum durability date, period after opening, precaution, batch number or reference, function, list of ingredients, warnings, instruction for use</td></tr>
<tr><td>Size</td><td>15 mL</td><td>4 g</td></tr>
</table>

4. IDENTIFICATION OF PRODUCT QUALITY FACTORS

To guarantee customer satisfaction, the desired product performance has to be identified, for this reason, quality factors will be defined by further detailing product functionality, and by adding other relevant features, done this, they will be evaluated by performance indices. Some examples are shown in Table 4.1, considering that the lip sunscreen is a composite, and the eye sunscreen is a cream.

Table 4.1. Indices for typical chemical-based consumer product quality factors, based on information from (65).

Quality factor	Delivery system		Performance index
	Composite	Cream	
Sensorial quality factors			
Visual appearance: transparent, opaque, pearlescent, color	✓	✓	Arbitrary indices based on panelist evaluation
Smell: fragrant, odorless, stinky	✓	✓	
Taste: Sweet, sour, bitter	✓	✓	
Sense upon application: smooth, oily, sticky		✓	
Physicochemical quality factors			
Product stability (resistance against creaming)		✓	Shelf life
Ability to change phase upon application	✓	✓	Melting point, glass transition temperature
Mechanical quality factors			
Resistance to failure	✓		Tensile strength
Resistance to indentation (hardness)	✓		Hardness numbers
Ease of failure by fracture (toughness)	✓		Fracture energy
Elasticity	✓		Young's modulus
Rheological quality factors			
Ease of spreading when rubbed onto a surface, applied by brush, or shaken		✓	Viscosity at application shear rate
Ability to flow under gravity		✓	Yield value
Ability to provide even coating when applied on a surface		✓	Minimum thickness at which even coating is observed

According to the previous table, quality factors will be divided into sensorial, physiochemical, mechanical, and rheological, to which functional factors will be added, and those to be applied to each product are defined below.

4.1. SENSORIAL QUALITY FACTORS

Sensorial quality factors are directly related to the customer experience because they consist of the sensations that users have when applying the product, which, being skincare products, must be pleasant in all senses to stand out in the market.

4.1.1. Eye cream sunscreen

One of the eye cream sunscreen functions is to improve makeup application and looks well when worn alone, therefore the **visual appearance** once the product is applied to the skin should be transparent to allow the skin to be seen through it, and simultaneously, to improve the appearance, the product should have a subtle pearlescence, so the eye contour will look brighter and healthier because of the light reflection. These factors will be evaluated by panelists.

Furthermore, to improve the finish when it is applied, according to market trends the **sense upon application** should not be sticky or oily and, considering that the eye contour skin is particularly delicate, it must be smooth. These factors are related to rheological factors therefore they will be evaluated by panelists and with the indices defined in the rheological section.

Besides sense upon application, the **sense after application** also should be evaluated since the smoothing and moisturization of the skin are product functions, the stickiness in this stage should also be evaluated to ensure comfort while using it. They will be determined by panelist evaluation once the product is absorbed.

In terms of **smell,** there is no limitation, other than not to cause eye irritation; for this reason, the product will not have any added fragrance.

The index to evaluate these factors consist of panelist evaluations applying an assessment scale. For this method, it will be used Table 4.2, which presents a scale where 0 equals none, and 9 is high intensity. The scale shows a target area (white), which represents the optimal numbers to obtain, a borderline area (light blue), which is acceptable but cautions that this factor needs to be improved, and an unacceptable zone (dark blue), where the product does not fulfill the guidelines.

Table 4.2. Assessment scale of eye cream sunscreen sensorial quality factors with the target (white), borderline (light blue), and unacceptable (dark blue) areas.

Quality factor	Assessment scale									
Visual appearance										
(Once the product is extended on the skin)										
Transparency	0	1	2	3	4	5	6	7	8	9
Pearlescence	0	1	2	3	4	5	6	7	8	9
Sense upon application										
Stickiness	0	1	2	3	4	5	6	7	8	9
Oiliness	0	1	2	3	4	5	6	7	8	9
Smoothness	0	1	2	3	4	5	6	7	8	9
Sense after application (of the skin)										
Stickiness	0	1	2	3	4	5	6	7	8	9
Moisture	0	1	2	3	4	5	6	7	8	9
Smoothness	0	1	2	3	4	5	6	7	8	9

4.1.2. Lip sunscreen

In the case of lip sunscreen, regarding **visual appearance**, the product will be relatively opaque with a color nude and certain pearlescence. The opacity, pearlescence, and even coating will be evaluated by the assessment scale in Table 4.3, with a scale where 0 = none and 9 = high intensity.

Concerning nude colors, not all colors enhance every skin tone, which is why a selection process was carried out to achieve the best tone (see Appendix 2). This color tone must be consistent because is a function of the product, it will be used a spectrophotometer with a color tolerance system that consists in giving a reference color (Figure 4.1), which will be compared with the sample by quantifying the visual difference through the ΔE, from 0 to 100, given by the spectrophotometer (66), the acceptable ΔE value is set in less than 1, which means that the difference in colors is not perceptible by human eyes (67).

Figure 4.1. Lip sunscreen color reference: Pantone 21-3-2 CP.

The **sense upon and after application** should be the same: smooth, for an enjoyable application and finish, not oily or sticky, to improve durability and meet market trends, and, in addition, after the application must leave the skin moisturized. These factors will be evaluated by panelists using Table 4.3.

One of the main requisites of lip sunscreen users is a pleasant **taste** and **smell**. For its proximity to the nose, if a fragrance is added, is more noticed, and even though the product is not meant to be eaten it is possible that part of it goes into the mouth when eating, drinking, or licking, therefore the taste of the product should be considered. But when it comes to tastes and smells everyone has different preferences, consequently the product will have just enough fragrance and flavoring to cover the bad taste of sunscreen actives and the smell of the base. In this case, the numbers in Table 4.3, with respect to aroma and flavor, are equivalent to the following hedonic scale: 0 = extremely unpleasant, 1 = moderate unpleasant, 2 = unpleasant, 3 = slightly unpleasant, 4 = neutral, 5 = slightly pleasant, 6 = pleasant, 7 = moderate pleasant, 8 = extremely pleasant (based on 68).

Table 4.3. Assessment scale lip sunscreen sensorial quality factors with the target (white), borderline (light blue), and unacceptable (dark blue) areas.

Quality factor	Assessment scale									
Visual appearance										
(Once the product is extended on the skin)										
Opacity	0	1	2	3	4	5	6	7	8	9
Pearlescence	0	1	2	3	4	5	6	7	8	9
Evenness	0	1	2	3	4	5	6	7	8	9
Sense upon application										
Stickiness	0	1	2	3	4	5	6	7	8	9
Oiliness	0	1	2	3	4	5	6	7	8	9
Smoothness	0	1	2	3	4	5	6	7	8	9
Sense after application										
Stickiness	0	1	2	3	4	5	6	7	8	9
Oiliness	0	1	2	3	4	5	6	7	8	9
Moisture	0	1	2	3	4	5	6	7	8	9
Smoothness	0	1	2	3	4	5	6	7	8	9
Pleasantness										
Taste	0	1	2	3	4	5	6	7	8	
Smell	0	1	2	3	4	5	6	7	8	

4.2. RHEOLOGICAL QUALITY FACTORS

Rheology is the study that encompasses the interrelation among force, deformation, and time of matter that has the ability to flow (69). It deals with the behavior of viscoelastic materials, which lies between the behavior of solids (elastic) and that of fluids (viscous).

Fluids can be classified depending on their viscosity behavior, viscosity being defined as the resistance to flow, which represents the ratio of shear stress to shear rate. Fluid classification is as follows:

- Newtonians, that obey Newton's law where viscosity is independent of shear rate.
- Non-Newtonians, whose viscosity is not constant and, therefore, is dependent on the shear rate.

In turn, non-newtonian fluids are classified as:

- Pseudoplastic or shear thinning: its viscosity decreases when the shear rate increases.
- Dilatant or shear thickening: when the shear rate increases, its viscosity rises.
- Bingham plastic: it acts like a Newtonian fluid once a minimum stress is applied, this force that is required to flow is the yield shear stress.
- Thixotropic: it has time-dependent shear thinning properties, which means that when the shear rate increases, viscosity decreases, but takes some time to return to its initial state.

In the case of the eye cream sunscreen, it must be easily poured out of the packaging but cannot run off by itself, and regarding the application, it must spread easily without dripping on the skin. For these characteristics to be met, the product should be a pseudoplastic fluid.

The lip sunscreen, on the other hand, must be thixotropic because it should remain solid while on the packaging, but when rubbed on the lips it must be smooth to ensure a comfortable, even, and easy application, and this texture has to last a certain time to modify the final look, and finally, it should return to almost its initial viscosity, which means it has to be almost solid to stay on the lips with minimal transference.

Once the desired behavior of each product has been chosen, rheological quality factors will be defined considering the following typical shear rates of applications: (10^1 - 10^3) s^{-1} for extrusion from a tube, (10^2 - 10^4) s^{-1} for topical application, and (2.10^3 - 10^4) s^{-1} for lipstick application (70).

4.2.1. Eye cream sunscreen

To evaluate the **ease of spreading**, viscosity must be measured. The ideal viscosity when the product is applied (approximate shear rate: 500 s^{-1}) is about 0.025 Pa.s (70), and around 0.628 Pa.s at low shear rates (10 s^{-1}) (71).

In order to avoid dripping, the product should have a yield point greater than 20 Pa, which will prevent it from **flowing under gravity** (70).

The usage of a rotational rheometer will give the shear profiles needed to evaluate these factors.

Additionally, it has been said previously that **even coating** is essential to achieve optimal sun protection, therefore the minimum thickness at which even coating is observed should match a product application of 2 $mg.cm^{-2}$, which is the quantity used for testing the SPF (61).

4.2.2. Lip sunscreen

The **thixotropic behavior** of lip products can be determined by applying a three-step shear rate test, the test should be made at 32 °C and 25 °C, which are the average lip and room temperatures (72). It should be obtained a profile similar to the one shown in Figure 4.2.

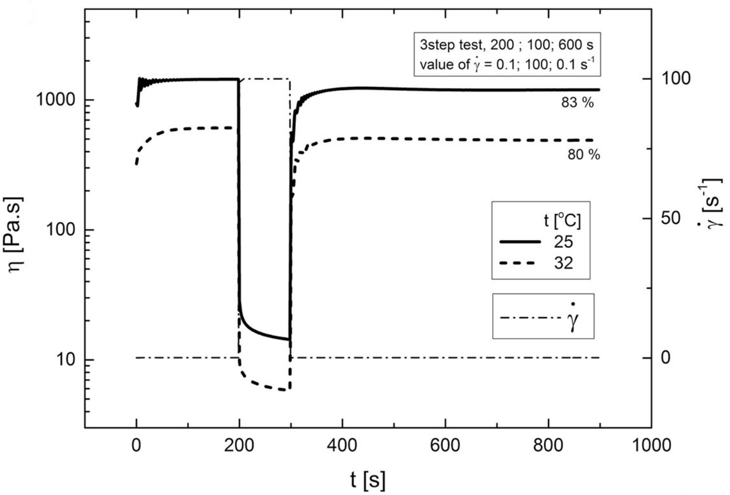


Figure 4.2. Thixotropy three-step test results of a lanolin product (72).

Through an oscillation test, **viscoelastic parameters** can be obtained, like the elastic/storage modulus (G'), which indicates the product solid behavior, the viscous/loss modulus (G'') which indicates the liquid behavior, and the yield point, which indicates the change from solid to liquid-like behavior. At room temperature the lip sunscreen is expected to have a solid-like behavior (G' > G'') to ensure that it keeps its shape while the consumer is not applying it.

Finally, to test for **adhesion** and **ease of spreading**, a 'squeeze and tack' test can be used. Spreadability is measured by the maximum force applied to a sample between parallel plates until a given thickness is achieved, and the adhesion, which is related to the stickiness of the product, is evaluated by the tension required to separate the upper plate and calculated by the area under the force-time curve obtained (72).

All the previous tests will be made with a rotational rheometer.

4.3. PHYSICOCHEMICAL QUALITY FACTORS

To determine the physicochemical quality factors, the type of system must be specified. Emulsions are dispersed systems composed of two immiscible liquids, depending on these, they can be classified as oil-in-water (O/W), water-in-oil (W/O), and oil-in-oil (O/O); where the first one is the dispersed phase and the second one is the continuous phase or the medium where is dispersed (73). Suspensions or dispersions, on the other hand, consist of solid particles dispersed in a medium (74).

Because of its characteristics, the eye cream sunscreen should be an O/W emulsion, to reduce its oiliness, which is one of the market trends, and to improve layering with makeup, since liquid makeup available on the market is usually water-based.

In turn, the lip sunscreen will be an emulsion-based suspension, where the pigments are dispersed in a W/O emulsion, which will allow to include ingredients that improve moisturization (75), a main function of the product.

Once the system has been specified, the physicochemical quality factors will be described.

To evaluate the **product stability**, because dispersed systems are not in equilibrium, destabilization mechanisms that may occur in the system will be briefly explained: Particles can bind to each other without losing identity, this is called *Flocculation*; in turn, when two droplets bind to each other losing their identities it is *Coalescence*; and when there is no particle-to-particle contact, but small particles dissolve in the continuous phase and then make a larger particle in the dispersed phase grow it is called *Ostwald ripening*; that said *Sedimentation/Creaming* is the most common instability on emulsions (76) and occurs when two phases separate due to the difference in their densities.

Shelf life is the performance index of product stability and is defined as the period during which the product will maintain its specifications without significant changes, which means a 5% change from the initial concentrations of actives or any failure to meet the acceptance criteria the parameters evaluated, consequently, it consists of measuring the parameters that may change, by performing accelerated and real-time/long-term stability testing (77).

For *long-term stability testing*, the conditions selected are 25 ± 2 ºC and 60 ± 5% RH (relative humidity), since Spain is in the Climatic Zone II (characteristic climatic conditions: 22 ºC and 52% RH) (78), and the tests will be at months: 0, 3, 6, 9, 12, 18, 24, 30 and 36, since the products are expected to have a shelf life of 3 years. Because the shelf life is greater than 30 months, the PAO must be indicated, therefore the products will be formulated and tested to have a PAO of 1 year.

Accelerated stability testing is performed as a preliminary step to estimate the shelf life without having to wait for the actual shelf lifetime. To increase the rate of chemical degradation or physical changes, it is performed at (40 ± 2) ºC and (75 ± 5) % RH, for 6 months, with the following frequency: (0, 1, 2, 3, 4 and 6) months (78).

Photostability is another important factor for both products, due to the fact that, as it was stated in the market analysis section, some of the most used UV filters are photo-unstable, despite this, some studies have evaluated the best way to improve the photostability of every UV filter, the combination of them, and the sunscreen formula (79), furthermore, the products will not only be formulated to ensure photostability but the packaging selected is opaque therefore the product is not usually exposed to light.

The *LUMiFuge* will be used to find the best composition for each product according to its stability, it works by evaluating the light transmission in function of the time elapsed and the position in the vial used, and allows to determine shelf life, sedimentation, creaming, aggregation, flocculation, and polydispersity – which is the difference in particle sizes that favors sedimentation and Oswald ripening – in a maximum of 24 hours, due to the accelerated physical changes caused by centrifugation of the sample (80).

The parameters and other factors to be evaluated that are specific to each product are described below.

4.3.1. Eye cream sunscreen

For the eye cream sunscreen stability test the sensorial and rheological quality factors have to be fulfilled, and homogeneity (lack of creaming), pH, and color changes must be evaluated.

The color of the product and the pH are given by the ingredients selected in the next section. Moreover, the color of emulsions may depend on their type, sunscreens can be formulated as macro and nanoemulsions, the main difference between the two is the size particle, while macroemulsion particles are about 200 nm which gives the emulsion a milky white color, and nanoemulsions particles measure between 10 and 200 nm which make them translucent and bluish, additionally, nanoemulsions are more stable, although macroemulsion solar protection is slightly higher (81), consequently, to have a more translucent and stable product, the eye cream sunscreen will be a nanoemulsion.

4.3.2. Lip sunscreen

In the case of the lip sunscreen stability test, sensorial and rheological quality factors also must be met, additionally, the oxidation of some ingredients such as oils can make the product smell and taste bad (82), for this reason, and as another way to test stability, oxidation will be evaluated through differential scanning calorimetry (DSC), which measure the heat released by exothermic reactions that happen during oxidation (83).

The **ability to change phase upon application** is partially evaluated with the rheological performance indices, but it is also important to ensure that the product maintains its shape at room temperature, and considering that it is sun protection, is expected to be used in places where temperatures can reach up to 47.6 ºC (84), hence the melting point shall be set between 60.0 ºC and 75.0 ºC, in order to have a security margin of about 10 ºC from the maximum and to comply with the standard values (85). The melting point will be estimated through the capillary method.

4.4. MECHANICAL QUALITY FACTORS

Mechanical factors play an important role in the application of lip products. To test the **breaking point** of the stick, a cantilever test will be performed with a texture analyzer, this test measures the force applied with a hemispherical edged blade on the lip sunscreen stick (Figure 4.3), the test mimics the bending movement and force applied when using the product.

Figure 4.3. Cantilever test setup to perform the test on lipstick (86).

In addition to the breaking point, which will be a parameter of quality and consistency through the batches, the cantilever test allows obtaining the hardness of the product from the maximum force applied (87), and, with the sensorial quality factors the ideal hardness can be determined.

4.5. FUNCTIONAL QUALITY FACTORS

Regarding functional quality factors, those functions that have been covered with other quality factors will not be repeated here.

Firstly, the official test to determine the **sun protection factor** (SPF) is regulated by the ISO 24444:2019. The SPF test method is an in vivo test made with a solar simulator (xenon arc lamp or equivalent), that relates the individual minimal erythemal dose for skin without any protection (MED_{iu}) to the individual minimal erythemal dose for a skin section cover with 2

$mg.cm^{-2}$ of the sunscreen under test (MED_{ip}). The individual sun protection factor (SPFi) is determined with Equation 4.1 (12).

$$SPF_I = \frac{MED_{ip}}{MED_{iu}} \quad (4.1)$$

The MED is the lowest erythemal effective radiant exposure (H_{er}), calculated by Equation 4.2, that produces the first erythema (reddening of the skin) with defined borders from 16 h to 24 h after UV exposure (12).

$$H_{er} = \int_t^{\cdot} E_{er}(t)\, dt \quad (4.2)$$

Where E_{er} is the erythemal effective irradiance, which is calculated with the Equation 4.3 that integrates the spectral irradiance E(λ) multiplied by the erythema action spectrum $s_{er}(\lambda)$, which represents the ability of UV radiation to produce erythema, at each wavelength λ in the range of UVB and radiation (12).

$$E_{er} = \int_{290}^{400} E(\lambda)\, s_{er}(\lambda)\, d\lambda \quad (4.3)$$

The subjects that are part of the test panel shall have an individual typology angle (ITAº) greater than 28º, this value reflects the skin tone measured by a spectrophotometer or a skin colorimeter. Moreover, for the test to be valid, it must have between 10 and 20 valid SPFi results, and the total UVA I and UVA II irradiated shall be ≥ 60% and ≥ 20 % of the total UV irradiance, respectively (12).

Secondly, the **UVA protection factor** (UVA-PF) will be tested following the ISO 24442:2022, this regulation follows the same method as described above, but rather than measuring the MED, it measures the minimal persistent pigment darkening dose (MPPDD), which is the 'lowest UVA dose that produces the first persistent pigment darkening response, observed between 2 h and 24 h after the end of the UVA exposure' (88).

Thirdly, to evaluate eye-stinging ability, duration, and improvement in makeup application, a variety of tests will be performed by a minimum of 10 volunteers. The three tests will be evaluated after applying 2 $mg.cm^{-2}$ of product to the intended area, the quantity applied should be weighed by difference with an analytical balance.

The **eye-stinging ability** of the eye cream sunscreen will be determined by the average of the subjects' rating, the volunteers will rate the eye-stinging sensation according to the scale: 0 = absent, 1 = faint, 2 = mild, 3 = moderate, and 4 = intense. The acceptable result is set at 1.5, and the target result is 0.7 or less. Furthermore, the eye cream sunscreen will be applied on just one eye, and, in the other eye, an eye ointment will be used as a control, the result will be evaluated considering the eye-stinging ratio of the product to the eye ointment (89).

The **durability** of the lip sunscreen is related to adhesion, but to test the actual time that the product stays on the lips and the sun protection remaining after 2 h, which is the period of reapplication, it will be used a facial analyzer machine (JANUS or equivalent).

A photograph will be taken with UV light without any product and another one with the specified quantity of lip sunscreen, the time of application will be set as the baseline, and after the application, a photograph will be taken every 30 min. The volunteers cannot eat, kiss, or rub their lips during the time of the test.

UVB absorption is correlated with SPF following Equation 4.4 (90), therefore, the UV absorption of a sunscreen with SPF 50 is 98.0%. Considering this, with the 5 images of the test, a grey scale from 0 to 98 will be made to measure the UV Absorption, where 0 is the color of the skin without any product and 98 is the color with the product on the baseline. The test will be satisfactory if the average of the absorption results after 2 hours of application is 96.7 %, which is the equivalent absorption of an SPF 30, the minimum recommended (10).

$$Absorption = 100 - \frac{100}{SPF} \qquad (4.4)$$

Appendix 3 shows an example of the test images and the calculations to evaluate the product.

Finally, to test the **improvement in makeup application** a comparative test will be performed. Regarding the eye cream sunscreen, a water-based concealer will be used on both eye contours, the difference will be that one side will be only prepared with skincare the volunteer normally uses, and the other will also have the eye cream sunscreen underneath the concealer. In the case of lip sunscreen, a lipstick or a gloss will be applied, and the lip sunscreen will be used only on one side of the mouth.

The volunteers will rate the finish just after application and 2 h after, when re-application is supposed to be made, and, depending on the volunteers' skin type, makeup will change in one way or another. The rating system consists in comparing the finish with and without the product, following the scale: 0 = much worse, 1 = worse, 2 = same, 3 = better, and 4 = much better, where if the average result is 2 or more is acceptable, and it is preferable for the result to be greater than 3.

4.6. QUALITY FACTORS SUMMARY

Although the quality factors have been divided, some of them are included in more than one section, besides this, the quality factors of the eye cream sunscreen and the lip sunscreen that have been defined in this section are summarized in Table 4.4 according to the section in which the correspondent performance index is made.

Table 4.4. Quality factors summary of the products to be developed.

Quality factor	Eye cream sunscreen	Lip sunscreen
Sensorial	Transparent, pearlescent	Opaque, pearlescent, Pantone 21-3-2 CP
	Without fragrance added	Pleasant taste and smell
	Sense upon application: Smooth, not sticky, and not oily	
	Sense after application: Moisturized, smooth, and not sticky	Sense after application: Moisturized, smooth, not oily, and not sticky
Rheological	Pseudoplastic	Thixotropic
	Ease of spreading	
	Even coating	
	Does not flow under gravity	Adhesive
	Ease of pouring out of the packaging	Solid-like behavior at room temperature
Physicochemical	Product stability: Photostable, Shelf life: 3 years, PAO: 1 year.	
	O/W nanoemulsion	W/O emulsion-based suspension
		Phase change: Melting point: (60 - 75) ºC
Mechanical		Breaking point
		Hardness
Functional	Sun Protection Factor: 50	
	Improvement in makeup application	
	Low eye stinging	Duration of color and sun protection: 2 h

5. PRODUCT FORMULATION

Once the products have been conceptualized and the quality criteria have been set, both products can be formulated by selecting ingredients that fulfill the established characteristics. The selection of ingredients and their concentrations will be based on the market analysis done, along with patents and articles with similar criteria.

The ingredients of each product will be divided as follows: *Actives*, which are substances that perform the main functions of the product; *vehicles*, which are the carrier system of the active components; and *additives*, which have a specific function that is not the main ones.

Although both products have some functions that are the same, therefore some ingredients may overlap, due to the difference in use and form, the formulation developed below will be different for each product.

5.1. EYE CREAM SUNSCREEN INGREDIENTS

The selection of the ingredients of the eye cream sunscreen is focused not only on fulfilling the main functions of the product but also on reducing the probability of eye stinging. Due to this fact, the eye-stinging effect of each ingredient should be taken into consideration.

The *vehicle* of the product will be the most used component (see Appendix 1), **water**, and its quantity will depend on the rest of the ingredients that will be selected below.

5.1.1. Active ingredients

- *UV filters*

Regarding sun protection, the product should be a broad-spectrum sunscreen, consequently, must have a minimum critical wavelength of 370 nm, which is 'the wavelength for which the section under the integrated optical density curve is equal to 90 % of the integrated section between 290 nm to 400 nm (61).

To verify that the formulation chosen complies with the minimum critical wavelength, UVA-PF/SPF ratio, and SPF, the BASF sunscreen simulator has been used (91).

Based on the patent of Karpov et al., US 2009/009887 A1 (89), to have a low eye-stinging sunscreen, it should include at least one organic and one inorganic active ingredient, preferably including 15 % zinc oxide (ZnO), 7.5 % octinoxate, and 5 % octisalate, by weight. These specifications were taken as a starting point for the iterations made in the BASF sunscreen simulator, after which different mixtures of the most used UV filters were evaluated (see Appendix 4) until the quality criteria were reached.

The final selection of UV filters ingredients and their quantities, by weight, is the following:

-Organic actives: 7.0 % **ethylhexyl methoxycinnamate** (octinoxate – Uvinul® MC 80), 4.5 % **ethylhexyl salicylate** (octisalate), and 5.5 % **bis-ethylhexyloxyohenol methoxyphenyl triazine aq** (Tinosorb® S Lite Aqua).

-Inorganic active: 14.0 % **zinc oxide (nano)** (Z-Cote®).

According to the simulator, this formulation will have an SPF 54.5, consequently, the product would fit into the category of High protection with SPF 50. Additionally, the product will accomplish a UVA-PF of 1/3 SPF (UVA-PF: 18.3) and can be classified as broad-spectrum sunscreen because the critical wavelength is 379 nm. Figure 5.1 shows the absorption curve of the product in which the absorption of each UV range can be seen.

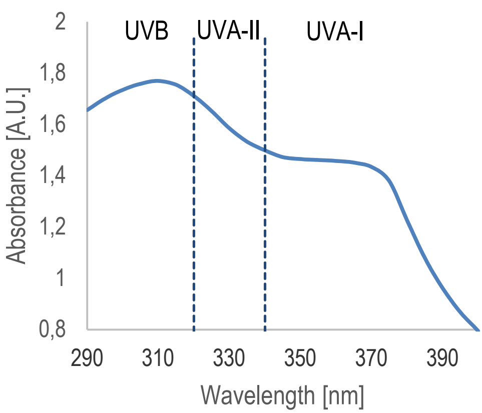


Figure 5.1. Eye cream sunscreen UV absorption spectra. Based on data from (91).

- *Emollients*

Although octisalate provides emollient properties, more emollients should be added to achieve the expected moisturizing effect.

Firstly, the **C12-15 Alkyl benzoate** is selected among the most used emollients because of the stated benefits, but mainly for not causing eye irritation. Based on the patent of Karpov et al. the chosen concentration is 5.0% (89).

Additionally, jojoba oil and squalane will be added as emollients, they do not leave a greasy feeling on the skin, and both are sebum-like oils, which means that are similar to the natural skin oil, and not eye-irritating (92, 93).

Jojoba oil is actually a liquid wax ester with antioxidant, anti-inflammatory, soothing and moisturizing properties (94), moreover, it improves skin elasticity and restores skin shine (95). For skin care product is more used in the concentration range (1.0 – 5.0) % and for eye makeup products the range is (0.1 – 1.0) %, therefore, as the eye cream sunscreen is a mixture of both, the concentration selected is 1% (96).

Conversely**, squalane** is part of sebum and has antioxidant, hydrating, moisturizing, and soothing properties (97). Squalane is mainly extracted from sharks, but because the products must be vegan to meet market trends, Phytosqualan, which is a vegan alternative obtained from olives (98), is selected. It was chosen a quantity of 5 %, which is the average of the most used concentrations (93).

- *Humectants*

Finally, to add hydration to the skin, glycerin and sodium hyaluronate, the humectants presented in the market trends section, are added to the formulation.

Based on market analysis, the concentration of **glycerin** is set at 5 %, as is commonly used, because around this concentration the hydrating benefit is achieved without making the product sticky (99).

Sodium hyaluronate obtained from bacterial fermentation is going to be used at concentrations of 0.5 %, which represent the average in skincare and makeup (100). Depending on the size, the ingredient will have different effects, the bigger the molecule the least penetration into the skin, therefore low molecular weight (20 kDa – 300 kDa) will be used, to achieve long-lasting hydrating and anti-aging effects (101).

5.1.2. Additives

- *Preservatives*

Preservatives allow to achieve the established shelf life by reducing the risk of microbial contamination (102).

The most used preservatives in the products evaluated on the market analysis are ethylhexylglycerin and phenoxyethanol. The ethylhexylglycerin could be irritating to the eyes (103), which is why is discarded for this product; the **phenoxyethanol**, on the other hand, is regulated by the European Union with a maximum concentration of 1.0 %, and at this concentration, the ingredient is not a skin or eye irritant (104), therefore is going to be included at 0.5 %, the usual quantity for skincare products (105)

Additionally, although is not its main function, the C12-15 alkyl benzoate can act as a preservative (106).

- *Thickeners*

The components added to increase the viscosity or change the rheological properties of the product can be solids or thickeners (107).

In this case, **xanthan gum** was chosen because it does not irritate eyes or skin (108) and gives a pseudoplastic behavior (107), a characteristic required for the eye cream sunscreen. A quantity of 0.3 % by weight is used, a concentration that could be modified if necessary to meet the quality criteria.

- *Surfactants*

Emulsions are stabilized by surfactants, which are molecules with a hydrophilic head and a hydrophobic tail, that have the ability to adsorb at interfaces and the capacity for self-aggregation in different structures.

The surfactant is selected based on the suggestions of Karpov et al. (89), and the HLB (hydrophilic-lipophilic balance) number, which represents the affinity of the surfactant on a scale from 0 to 20, where the higher the number the more hydrophilic or water affine. To be used in O/W emulsions the HLB of the surfactant should be between 8 and 18 (109)

Equation 5.1 is used to estimate the HLB number required (HLB_{req}) to select the best surfactant, it consists of adding the HLB of each element in the oil phase (HLB_i) multiplied by its mass fraction (z_i) (110).

$$HLB_{req} = \sum z_i \cdot HLB_i \quad (5.1)$$

The HLB numbers of each component are 6, for jojoba oil (111); 13 for C12-15 Alkyl benzoate (112); and 12 for squalene (113), which results in a HLB_{req} 11.9.

Based on the above-mentioned, it is chosen 4 % of **polyethylene glycol 400 mono-oleate** (PEG-400 or PEG8-MO), which is a no-ionic liquid emulsifier with an HLB number of 12 (114), that does not irritate the eyes and lips (115).

- *Buffer*

A product with a pH in the range 6.0 – 7.6 is less irritating to the eyes, because it is the pH range of natural lacrimal fluids (116), therefore a buffer, which is an ingredient that adjusts or stabilizes the product pH (117), is going to be added to ensure that the product is within this range.

A buffer included in the products analyzed is sodium citrate, its use in non-irritating eye products is suggested by the patent US 9,067,083 B2 (116) and is typically used between 0.02 % and 2.00 % (117). It can have a pH from 7.5 to 9.0 at room temperature (118), consequently, the required quantity will be added at the end of the formulation to match the mentioned pH range 6.0 – 7.6.

5.2. LIP SUNSCREEN INGREDIENTS

The ingredients will be chosen considering the quality criteria of the lip sunscreen, with a particular focus on avoiding an unpleasant taste.

5.2.1. Active ingredients

- *UV filters*

For lip sunscreens, the concern with selecting organic UV filters is that they give a bad taste to the product, whereas adding inorganic UV filters may result in a whitish finish and thicken the formula.

Considering the above, in addition to the market analysis, only organic UV filters will be used. And to eliminate the bad taste, a taste-masking ingredient will be added, which is a method that was proven in patent US 9,399,008 B2 (119)

As with the eye cream sunscreen, iterations were made in the BASF simulator until established criteria were met (see Appendix 4), resulting in the following composition: 6.5 % **ethylhexyl salicylate** (octisalate), 5.0 % **bis-ethylhexyloxyphenol methoxyphenyl triazine** (Tinosorb® S), 4.0 % **butyl methoxydibenzoylmethane** (avobenzone), 4.5 % **ethylhexyl triazone**, and 6.5 % **octocrylene.**

The UV filters chosen are those most used according to the market analysis, with the addition of Tinosorb® S to improve the UVA-PF and SPF while reducing the total concentration of UV filters.

With the chosen mixture, according to the BASF sunscreen simulator, an SPF 51.1, a UVA-PF 17.3, and a critical wavelength of 373 nm are achieved, values that allow the product to fit in the high protection category with SPF 50, and to be classified as a broad-spectrum sunscreen. The absorption curve of this mixture is shown in Figure 5.2, where it can be seen the product absorption of each UV light.

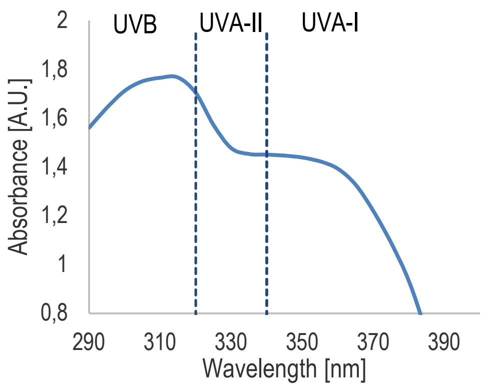


Figure 5.2. Lip sunscreen UV absorption spectra. Based on data from (91).

- *Emollients*

Among the most used emollients, the **synthetic beeswax** is chosen first, as it is multifunctional, acting as an emollient and at the same time as the base or vehicle of the product. The quantity of beeswax shall be determined in the section 'vehicles' to ensure that the mixture of waxes achieves the required hardness and melting point.

The **sorbeth-2-hexaoleate,** is an ester that besides having emollient properties**,** should be included to act as the taste-masking ingredient by forming a complex with the UV filters, to be effective at taste-masking it must be included in a minimum ratio of ester to UV-filters of 0.60 : 1.00 by weight (119), more preferably 0.85 : 1.00, therefore it is going to be included at the maximum quantity possible, which is 16.4 % of the product (0.62 : 1.00), at this concentration is not a skin irritant.

The **shea butter** will be added in a concentration of 10 % in order to obtain all the benefits stated in the market analysis section (39).

The **octyldodecanol** is chosen because it can act as emollient and as surfactant, and at the same time improve the smell of the product and the pigment dispersion, it is more used for lipstick in the range of (5 – 10) % (45), the quantity will be selected according with the other surfactants to be added, taking into account that the HLB of the octyldodecanol is 5.9 (120)

Castor oil is used in lip products from 15 % to 81 % (41), consequently, the quantity selected to be able to include the rest of the ingredients is 15 %.

To increase the moisture provided by the product, **jojoba oil** will be added, it is usually used in lip products in the range of (0.1 – 1.0) % (121), and according to the patent US 9,399,008 B2, moisturizing oils are added to lip balms in concentrations starting at about 1.0% (119), therefore the quantity selected is 1.0%.

- *Humectants*

To improve hydration, **aloe vera** (aloe barbadensis leaf juice) will be added. It is a water-soluble ingredient that improves skin elasticity and has antiseptic, antibacterial, antifungal, and antioxidant properties (122). The selected concentration is 0.50 % of freeze-dried aloe vera extract, which increases the water content of the skin with each application (123).

5.2.2. Additives

- *Preservatives*

It is chosen to include **phenoxyethanol** at 0.1%, which is the average concentration used in lipsticks (104).

Currently, **Tocopherol** (α-Tocopherol acetate) is commonly used in lip products as a form of vitamin E to prevent oxidation, with a maximum concentration of 2 %, additionally, it reduces transepidermal water loss, adds photoprotective effects (124) and improves the photostability of avobenzone (125). Tocopherol will be added at 0.5 % based on the patent US 9,399,008 B2 (119).

- *Pigments*

To achieve the color of the product (Figure 4.1), some pigments must be added, the pigments necessary for this product, that are allow by the European Commission are: **CI 42090, CI 15850, CI 77491, CI 77492, CI 77891**, whose colors are represented in Figure 5.3.

Figure 5.3. Pigments colors to be used in the lip sunscreen.

Pigments will be added representing 4 % by weight in total to achieve the required color with a slight translucency (126), where the pigment mixture consist of 16 % CI 42090, 8 % CI 15850, 33 % CI 77491, 13 % CI 77492, and 30 % CI 77891. These quantities are estimated using the RGB (red, green, blue) color model with Microsoft Publisher (see Appendix 5) and may vary due to the color of the base, which depends on the natural color of the waxes and oils.

- *Surfactants*

Since the HLB number of the octyldodecanol is at the upper limit of the HLB range for W/O emulsifiers, which goes from 3 to 6 (109), another emulsifier will be added to modified it, the calculation of the HLB of a mixture (HLB_{mix}) is made following Equation 5.2, where HLB_i is the HLB number of the surfactant i, and X_i represents its mass fraction in the mixture (110).

$$HLB_{mix} = \sum X_i \cdot HLB_i \quad (5.2)$$

The concentration of octyldodecanol will remain at its minimum typical use, 5 %, in order to change the HLB of the mixture with as minimal quantity of other surfactants as possible, because at low concentrations of the aqueous phase, the minimum diameter of droplets is accomplished with less than 5 % of surfactant (127), which lower the possibility of coalescence and sedimentation, and consequently, improve stability.

Adding 1 % of **monoolein** (glyceryl oleate), which is a non-irritant co-surfactant widely used in lip products (128) with an HLB number of 3.8 (127), results in an HLB_{mix} = 5.5, which is within the range of W/O emulsifiers. The final ratio of octyldodecanol and monoolein will be determined through the analysis of stability with the LUMiFuge.

5.2.3. Vehicles

Distilled water and **glycerol** are added as vehicles of the aqueous phase at 5 %, which is a concentration that allows a smoother application (127). The addition of glycerol in a 50 : 50 ratio to water is chosen to improve hydration.

The vehicles of the continuous phase are waxes. Due to the fact that the melting point of the product depends mainly on the melting point of the waxes (127), the resulting melting point of the mixture of waxes should be between 60 ºC and 75 ºC, according to the quality criteria, and the softening point should be about 32 ºC, which is the lip temperature.

The most used waxes are microcrystalline wax (cera microcristallina) and beeswax, their melting point range are 56 ºC - 78 ºC (127) and 60 ºC - 67 (129), respectively. Although they are within the range, carnauba wax (Copernicia cerifera cera) is normally added to harden the product (127, 85), it has a melting point between 81 ºC and 86 ºC (130).

To have the required properties the composition of waxes will be as follows: 5 % **carnauba wax**, 7 % **microcrystalline wax**, and 3 % **beeswax** (127).

5.3. PRODUCT FORMULATION SUMMARY

Table 5.1 and Table 5.2 show the ingredients of the eye cream sunscreen and the lip sunscreen with their INCI (international nomenclature of cosmetic ingredients) name, their concentration by weight, and their function.

Table 5.1. Eye cream sunscreen formula summary.

Ingredient	Quantity (wt %)	Function
Aqua (Water)	47.7	Vehicle
Zinc Oxide (nano)	14.0	UV-filter
Ethylhexyl Methoxycinnamate	7.0	UV-filter
Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine	5.5	UV-filter
Glycerin	5.0	Humectant
C12-15 Alkyl Benzoate	5.0	Emollient and preservative
Squalane	5.0	Emollient, humectant, and antioxidant
Ethylhexyl Salicylate	4.5	UV-filter and emollient
PEG-400	4.0	Surfactant
Simmondsia Chinensis Seed Oil	1.0	Emollient and antioxidant
Sodium hyaluronate	0.5	Humectant
Phenoxyethanol	0.5	Preservative
Xanthan gum	0.3	Thickener
Sodium citrate	q.s	Buffer

(a) q.s: ‘quantum sufficit’ or ‘sufficient quantity’ indicates that the amount added would be the necessary to achieve the required pH.

Table 5.2. Lip sunscreen formula summary.

Ingredient	Quantity (wt %)	Function
Sorbeth-2-Hexaoleate	16.40	Taste-masker and emollient
Ricinus Communis Seed Oil	15.00	Emollient and fragance
Butyrospermum Parkii Butter	10.00	Emollient, thickener, and antioxidant
Cera Microcristallina / Microcrystalline Wax	7.00	Vehicle and emollient
Ethylhexyl Salicylate	6.50	UV-filter and emollient
Octocrylene	6.50	UV-filter and emollient
Octyldodecanol	5.00	Emollient, surfactant and fragance
Copernicia Cerifera Cera	5.00	Vehicle and emollient
Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine	5.00	UV-filter
Ethylhexyl triazone	4.50	UV-filter
Butyl methoxybenzoylmethane	4.00	UV-filter
Synthetic beeswax	3.00	Emollient, vehicle, humectant, and antioxidant
Aqua (Water)	2.50	Vehicle
Glycerin	2.50	Vehicle and humectant
CI 77491	1.32	Colorant
CI 77891	1.20	Colorant
Simmondsia Chinensis (Jojoba) Seed Oil	1.00	Emollient and antioxidant
Glyceryl Oleate	1.00	Surfactant
CI 42090	0.64	Colorant
CI 77492	0.52	Colorant
Aloe Barbadensis Leaf Juice	0.50	Humectant and antioxidant
Tocopherol	0.50	Antioxidant
CI 15850	0.32	Colorant
Phenoxyetanol	0.10	Preservative

6. PRELIMINARY DESIGN OF THE MANUFACTURING PROCESS

To design the manufacturing process of the products characterized above, it is necessary to define the operation mode and the annual production, afterwards, according to Wibowo et al. (70), a process flow diagram should be drawn up, followed by the equipment selection and the designation of the order of addition of ingredients.

6.1. ANNUAL PRODUCTION

The cosmetic industry works by campaigns, regarding the sun care industry, nowadays awareness campaigns are launched all year long to encourage people to use sunscreen every day and not only in summer. This fact affects the sales of sunscreen products according to the season, and therefore the annual production.

The manufacturing process can be batch, in which a series of operations is carried out in a determined time to obtain a specific production, or continuous, where all the operations run at the same time and the production is undefined.

Since the facilities of the cosmetic industry are used to produce multiple products with relatively small batches, they commonly operate with batch processes. The heuristic that said that annual productions of over 500 000 kg are more efficient if done in continuous processes to confirm the operation mode will be used to confirm the selection of this operation mode (132).

It is known that the annual production of a lip care product may be about 150 000 units (133), and that sunscreens sales of one product can reach 189 600 units per year (134), since the eye cream sunscreen is a more targeted product and is likely to reach a smaller market, at least the first year of launch, product sales are estimated to be 10 %, or 20 000 units rounded up. These numbers are set as the annual production of the lip sunscreen and the eye cream sunscreen, respectively.

Considering that the average density of creams is 1 000 kg/m^3, due to their water content, and that each eye cream sunscreen has 15 mL, the annual production of eye cream sunscreen will be 300 kg. Meanwhile, as the lip sunscreen has 4 g of product, the annual production will be 600 kg. Both productions are below 500 000 kg, therefore the best operation mode is the most used in the industry, the batch process.

As it was said, in the pharmacy and cosmetic industry multiple products are made, therefore the batches of lip and eye cream sunscreen will be interspersed with the production of other products. This fact allows doing a few batches of each product without having inactive times, which leads to the decision to make 2 batches of the eye cream sunscreen per year, to be sold in 2 campaigns, one for the summertime and another one for winter, when people use more sun protection due to light reflection on the snow, particularly in winter sports; with respect to the lip sunscreen, 4 batches will be made, one batch every 3 months, since it is a product that is more likely to be used on a daily basis, and therefore, more requested, these will be varied, the first batches will manufacture the whole product, with the bamboo casing, and thereafter, depending on demand, will alternate between the manufacture of refill-only products and whole products.

6.2. MANUFACTURING PROCESS

The manufacturing process of each product is different; therefore, their processes and the estimated time of each operation will be described as follows.

6.2.1. Eye cream sunscreen

The phases of creams are usually premixed separately, as well as the insoluble ingredients (70), which in this case is only the zinc oxide, that does not need a pre-treatment because the raw material is bought with the required particle size, so it can be directly included in the heated dispersed phase (135).

Once the dispersed phase and the continuous phase have been premixed, they are heated, then the dispersed phase is added to the continuous phase, and mixed, subsequently, the emulsion is homogenized, and cooled, the temperature-sensitive ingredients are added, and the pH is adjusted (135), finally, the product is filled in its packaging. The flow chart that describes the previous operations is presented in Figure 6.1.

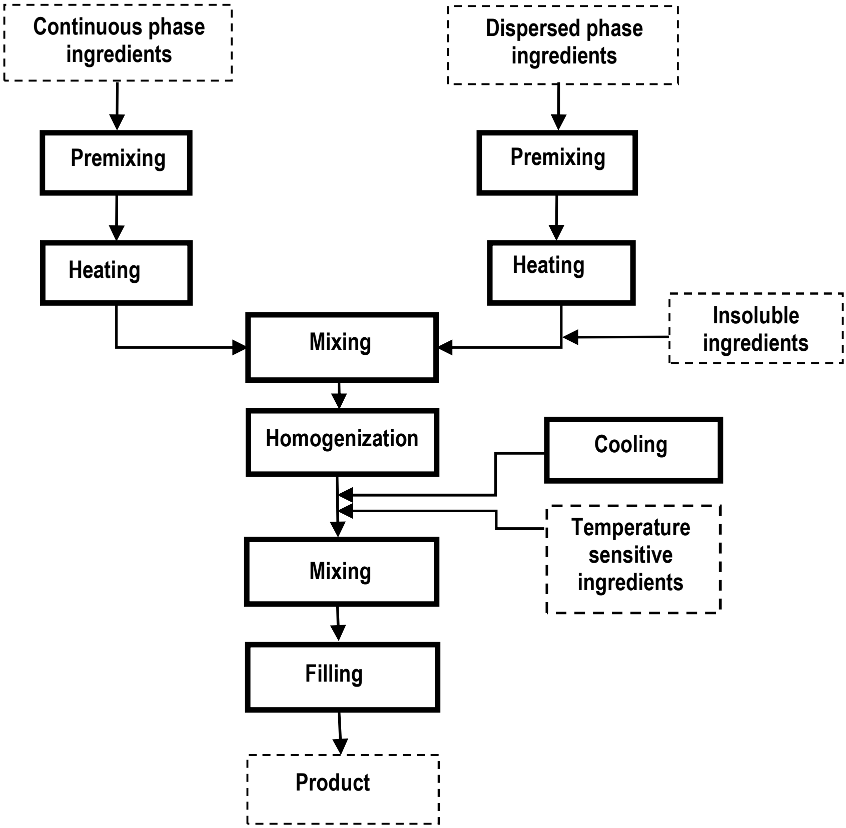


Figure 6.1. Flow chart of the eye cream sunscreen manufacturing process.

Following Table 6.1 shows the ingredients according to their phase, which is necessary to further detail the operations by specifying the order of addition.

Table 6.1. Classifications of ingredients according to their phase.

Continuous phase	Discontinuous phase	Insoluble
Water	Ethylhexyl Methoxycinnamate	Zinc Oxide (nano)
Glycerin	C12-15 Alkyl Benzoate	
Phenoxyethanol	Squalane	**Temperature sensitive**
Xanthan gum	Ethylhexyl Salicylate	Sodium hyaluronate
Bis-Ethylhexyloxyphenol	PEG-400	Sodium citrate
Methoxyphenyl Triazine (Tinosorb)	Simmondsia Chinensis Seed Oil	

The ingredients of the discontinuous phase are added sequentially, mixed, and heated to 80 ºC, once the mixture is heated (about 30 minutes later) the zinc oxide should be added slowly while the discontinuous phase is stirred at high speed for 30 minutes (135).

For the continuous phase, xanthan gum is slowly dispersed into glycerin (136) and mixed for 20 minutes or until a homogeneous solution is obtained (solution A), additionally, the water is mixed with the phenoxyethanol, and the Tinosorb, and heated to 80 ºC (solution B), which could take around 30 minutes, then the solution A is added to the heated solution B and mixed for about 20 minutes (135).

During the mixing operation, the discontinuous phase is added slowly in droplets to the continuous phase while stirring and maintaining 80 ºC for 30 minutes to form a pre-emulsion (135).

Next, homogenization is carried out to reduce the size of the droplets (70), the chosen method is cavitation, which, by the difference in pressure, the vapour bubbles (cavities) formed in the emulsion collapse suddenly and induce shock waves and liquid jets that disrupt and break droplets (137).

Based on patent EP 1 468 672 B1 (138), a nanoemulsion can be obtained by cavitation if 2 to 10 successive passages of the pre-emulsion are performed at a pressure between 400 bar and 700 bar, although the optimum number of passages and pressure will be decided based on stability analysis, the minimum of both ranges are set as a starting point, therefore 2 passages at 25 ºC and 400 bar will be made to form the emulsion, additionally, the temperature should be lowered back to 25 ºC between the passages.

Once the emulsion is homogenized and at room temperature, the sodium hyaluronate is sprinkled over the mixture and stirred for 45 minutes at a rotational speed of 1 600 rpm to achieve an even distribution of the ingredient and, at the same time, avoid molecular weight modification due to mechanical or thermal influences (139).

Afterwards, the pH is measured, and sodium citrate is added while mixing until the emulsion is in the required pH range, which is between 6.0 and 7.6, this could take about 10 minutes.

Finally, 15 mL of emulsion are filled into the packaging to obtain 10 000 units of eye cream sunscreens.

6.2.2. Lip sunscreen

The lip sunscreen manufacturing process operations are shown in Figure 6.2, where different solutions are premixed according to the division presented in Table 6.2.

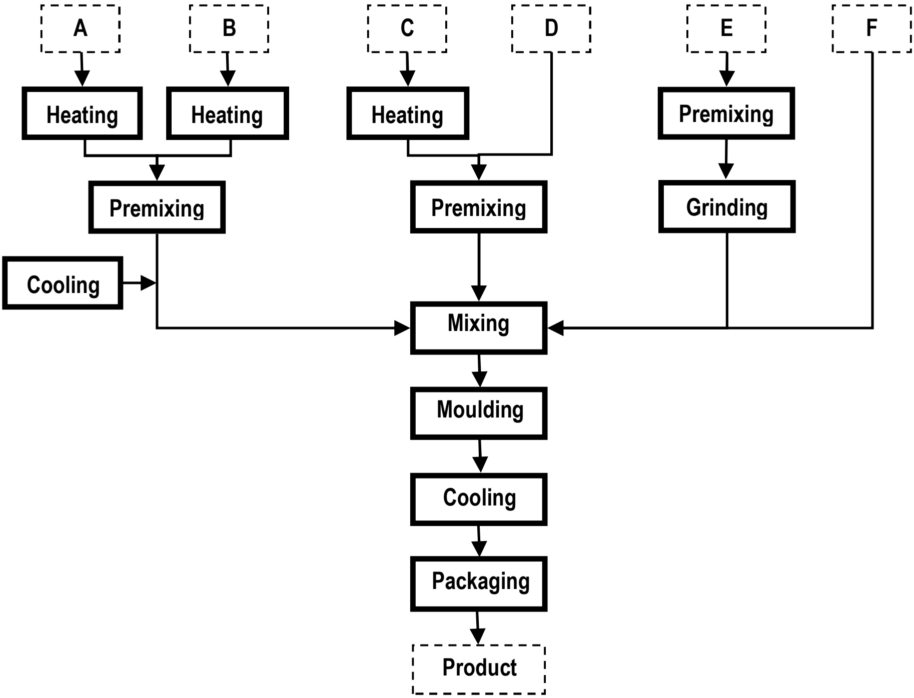


Figure 6.2. Flow chart of the lip sunscreen manufacturing process.

Table 6.2. Classifications of the lip sunscreen ingredients according to their addition.

A	B	D	E	F
Shea Butter	Water	Octisalate	Castor oil	Phenoxyetanol
Microcrystalline wax	Glycerin	Octocrylene	CI 77491	
Octyldodecanol	Aloe vera	Tinosorb S	CI 77891	
Carnauba wax		Ethylhexyl triazone	Jojoba Oil	
Beeswax	**C**	Avobenzone	CI 42090	
Tocopherol	Sorbeth-2-		CI 77492	
Glyceryl Oleate	Hexaoleate		CI 15850	
	(spider ester)			

The ingredients A are heated to 90 ºC and mixed for 40 minutes or until the mixture is molten, at the same time, the aqueous phase (B) is mixed and heated to 90 ºC, which could take about 30 minutes, then the mixture B is dispersed into the mixture A while stirring for 5 minutes at 10 000 rpm (127). Before the mixing operation the premixture should be cooled to 75 ºC (119).

According to patent US 9,399,008 B2 (119) the spider ester (C) should be heated to 55 ºC, and ingredients D should be added while stirring for 30 minutes and maintaining a temperature of 55 ºC to form the complex.

The ingredients E are mixed for about 45 minutes or until forming a paste, which is then ground 3 times to avoid a grainy feel by dispersing and reducing the diameter of the pigment particles (140).

The premixtures and the phenoxyethanol (F) are stirred at 75 ºC for about 2 hours. Once homogenized, the mixture is dispensed into a mold by filling and cooling during 20 minutes at a rate of 2.4 ºC/min to crystallize the continuous phase (127), obtaining small crystals that result in a smoother product (85).

Once solidified, the lip sunscreens are transferred to the aluminium mechanism; if the batch is made to sell the units only as spare parts, a cap will be added to protect the product; otherwise, if the batch is made to be sold as a complete product, the inner mechanism is assembled into the bamboo casing.

6.3. EQUIPMENT SELECTION

Although the manufacturing process of each product is different, the objective is to optimize the capital investment by using the same equipment when it is possible. For this reason, the equipment chosen will be presented below according to the operation they perform.

- *Mixing*

The batches of both products are 150 kg, which is equivalent to 150 L, consequently, the capacity required for the mixing operations is the same, therefore, in order to have a margin to add the necessary quantity for adjustments, the equipment selected for both products should be an industrial mixer with a capacity of 200 L.

The **Bachmix Compact** (Figure 6.3), from the supplier Bachiller, is the equipment chosen for mixing (141), the selection was based on the fact that it allows making products with high viscosity, which is useful for the lip sunscreen production, and fine emulsions, which is a requisite of both products.

Figure 6.3. Industrial mixer Bachmix Compact (141).

As can be observed in Figure 6.3, the Bachmix Compact has a coaxial agitator, with inner and outer impellers that can be independently controlled to operate in counter-rotation, co-rotation, or single rotation, each one at different speeds, which allows the reduction of the power consumption and improve the mixing performance by achieving a more uniform mixing throughout the entire vessel (142), additionally, it has scrapers that prevent product built-up on the walls and bottom of the vessel.

Furthermore, it has a high shear rotor-stator system (141), that allows for achieving a homogeneous mixture and particle size reduction by mechanically shearing the product. Additionally, the solid and liquid ingredients can be added through the integrated inlet improving the mixing efficiency.

Finally, the selected Bachmix Compact has a working capacity from 40 L to 200 L, and operating temperatures up to 200 ºC (141), which provides flexibility for the different operating conditions of the variety of products to be manufactured. Furthermore, it is thermally insulated and has a jacket for heating or cooling, which will use low-pressure steam for heating both products, and water for cooling; in this case, cooling water will be used for the lip sunscreen and chilled water for the eye cream sunscreen.

The **Bachmix Compact** of **200 L** will be used for the following operations: mixing of both products, premixing of the continuous phase of the eye cream sunscreen, and premixing of the ingredients A with the ingredients B of the lip sunscreen.

A **Bachlab** of **100 L** will be used for the premixing of the discontinuous phase of the eye cream sunscreen, and the premixing of the ingredients C and D of the lip sunscreen. The Bachlab selected has a working capacity from 20 L to 100 L, and a working temperature between 20 ºC and 100 ºC, the rest of the characteristics are the same as those mentioned for the Bachmix Compact.

An overhead stirrer from IKA will be used to mix solids in liquids in smaller quantities, the **MINISTAR 80 digital** (Figure 6.4) can stir up to 50 L with a maximum viscosity of 60 000 cP, and a maximum speed of 500 rpm (143). It will be used with an IKA's **R 1382 Propeller stirrer** (Figure 6.4), which is 316L stainless steel 3-bladed agitator that can mix fluids with a viscosity of up to 10 000 cP, at a mixing speed of over 800 rpm, and is designed to create an axial flow that with an up and bottom flow pattern improves mixing by preventing the particles from setting on the bottom of the vessel (144, 145).

Figure 6.4. IKA stirrer equipment. Left: MINISTAR 80 digital (143). Right: R 1382 propeller stirrer (145).

The MINISTAR 80 and the R 1382 stirrer will be used to premix the ingredients B and E of the lip sunscreen, and disperse the xanthan gum in glycerin for the eye cream sunscreen, they will be stirred in 316L stainless steel **mixing vessels** with a capacity of **10 L**, **35 L**, and **8 L** respectively, which follows the optimum proportions where the liquid level is equal to the vessel diameter (see Appendix 6 for calculations) (146).

- *Homogenization*

Cavitation is achieved with high-pressure homogenizers, which can increase the temperature up to 20 ºC at the working conditions of the eye cream sunscreen manufacturing process, due to the compression of the product passing through a narrow valve at a high flow rate that results in cavitation, impact, and turbulence (147).

An external heat exchanger can be added to prevent the heating of the product or can be included in the equipment, which is the case of the high-pressure homogenizer selected, an **AH22-100** from ATS (148).

The AH22-100 homogenizer (Figure 6.5) can process up to 500 L/h at a maximum pressure of 1500 bar, achieving after one cycle a particle size below 100 nm in more than 95 % of the emulsion (148). Consequently, the homogenization could be performed in about 40 minutes, according to the previously mentioned parameters.

Figure 6.5. AH22-100 high-pressure homogenizer (148).

- *Grinding*

The equipment selected for grinding is the **EXAKT 120S Plus three roll mill** (Figure 6.6) made of aluminium oxide, that can process up to 27.5 L/h and allows to achieve a particle size down to 5 µm. Consequently, the process would take approximately 3 hours.

This equipment has three parallel rolls that rotate in opposite directions at different speeds, consequently, when the product is fed into the gap between the fist and the second roll, it is dispersed longitudinally on the center roll and transported to the gap between the second and third roll, where the product is dispersed and homogenized to the required particle size due to the crushing and high shearing produced when passing through a narrow gap at the different rolls speeds, finally, the scrapper removes the finished product from the third roll (149).

Three roll mills are found in different materials such as steels and ceramics, the aluminium oxide was chosen to avoid contamination with heavy metals and to improve durability because its hardness (150).

Figure 6.6. EXAKT 120S Plus three roll mill (149).

- *Filling*

The **HX-009 automatic tube filling and sealing machine** (Figure 6.7), from the manufacturer SZHX Machine, can process up to 28 pieces per minute (151), which means that for a batch of 10 000 units of eye cream sunscreen, the machine would fill the tubes with 15 mL of product, seal them with coding, and trim the ends in about 6 hours.

Figure 6.7. HX-009 automatic tube filling and sealing machine (151).

The HX-009 machine is ideal for multiproduct plants because it can seal plastic and aluminium laminated tubes, with a tube diameter between 13 mm and 50 mm, and a tube height between 50 mm and 250 mm, as well as a filling range between 6 mL and 500 mL. Additionally, it is made of AISI 304 (stainless steel), which made it corrosion resistant, and of AISI 316 in the area in contact with the product, which improves corrosion resistance to acidic, alkaline, and chloride media (151).

- *Moulding / Cooling / Packaging*

The Cosmatic's **lipstick moulding machine SM 3000** (Figure 6.8) is chosen for the final operation of the lip sunscreen manufacturing process.

The SM 3000 is equipped with a melting tank of 120 L, from where the liquid product will be filled into silicone molds heated by infrared radiation, which reduces the probability of solid layers forming in the middle of the stick that would increase the risk of breakage during use. Additionally, it has a cooling system to solidify the product, with a minimum temperature of -20 ºC, after this zone, a mechanical system demolds the product, transferring it to the inner mechanism, and finally, an auto-loader system places the bases and caps of the products (152).

Considering that the machine processes up to 3 200 units per hour, and that one batch of the lip sunscreen contains 37 000 units, it would take approximately 12 hours to mold, cool and pack the entire batch.

Figure 6.8. Lipstick moulding machine SM 3000 (152).

6.4. MANUFACTURING PROCESS SUMMARY

To summarize the preliminary design of the manufacturing process, the manufacturing order guidelines for the eye cream sunscreen are presented in Table 6.3, and in Table 6.4 for the lip sunscreen; additionally, a process flow diagram was made for each product (Figure 6.9 and Figure 6.10).

Table 6.3. Eye cream sunscreen manufacturing guidelines.

	MANUFACTURING	**Compounded by:**
a	Add the discontinuous phase ingredients to the Bachlab (R-1), stir, and heat to 80 ºC.	
b	Add the zinc oxide slowly to the heated mixture and stir at high speed for 30 minutes.	
c	In an 8 L mixing vessel (M-1), disperse slowly the xanthan gum in the glycerin, while stirring with a MINISTAR 80 digital and a R1382 Propeller stirrer for 20 minutes or until homogeneous.	
d	In the Bachmix Compact (R-2), stir and heat to 80 ºC the water, phenoxyethanol and tinosorb. Then add the solution from step c and stir for 20 minutes.	
e	Add slowly the discontinuous phase in the R-2, while stirring for 30 minutes, maintaining the mixer at 80 ºC. Then, cool the pre-emulsion to 25 ºC.	
f	Homogenize the pre-emulsion in the AH22-100 homogenizer (HG-1), performing 2 passages at 400 bar, and 25 ºC.	
g	Add the emulsion to the R-2, and sprinkle the sodium hyaluronate, while stirring for 45 minutes at 1 600 rpm.	
h	Measure the pH and write it below. pH : ________ Add sodium citrate if needed and stir until achieving a pH in the following range: 6.0 - 7.6	
i	Load the tubes and the emulsion in the HX-009 tube filling and sealing machine (F-1) and configure it to fill 15 mL of product in each tube.	

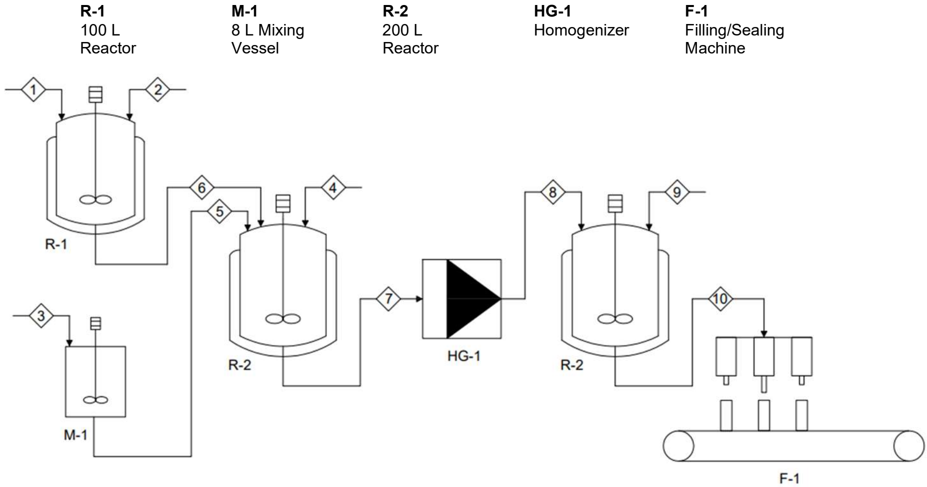
Table 6.4. Lip sunscreen manufacturing guidelines.

	MANUFACTURING	Compounded by:
a	Add the ingredients A to the Bachmix Compact (R-2), heat to 90 ºC, and stir for 40 minutes or until the mixture is molten.	
b	Put a 10 L mixing vessel (M-2) in a water bath, add the ingredients B, heat to 90 ºC, and stir with a MINISTAR 80 digital and a R1382 Propeller until the aloe vera is dissolved and the mixture is homogeneous.	
c	Add the mixture from step b to the R-2 and stir at 10 000 rpm for 5 minutes. Then cool to 75 ºC.	
d	In the Bachlab (R-1), heat the ingredient C to 55 ºC. Then add the ingredients D while stirring for 30 minutes, maintaining the mixture at 55 ºC.	
e	In a 35 L mixing vessel (M-3) stir the ingredients E with a MINISTAR 80 digital and a R1382 Propeller for 45 minutes or until forming a paste.	
f	Ground 3 times the paste of ingredients E with the 120S Plus three roll mill (G-1).	
g	Add the ingredient F and the premixtures of steps d and f to the R-2. Stir for 2 hours at 75 ºC.	
h	Transfer the mixture to the lipstick moulding machine SM 300 (F-2) and pack 37 000 units.	

According to the estimated times and considering that the premixtures can be done at the same time, the whole manufacturing process of the eye cream sunscreen would take about 10 hours, while the lip sunscreen manufacturing process would take approximately 17 hours.

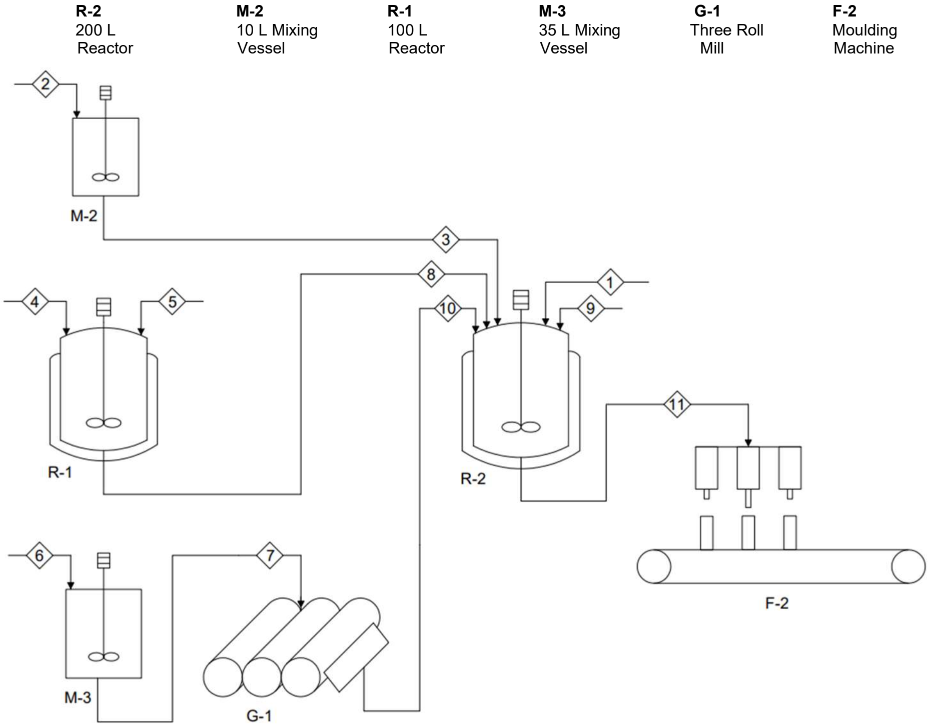
Below Figure 6.9 and Figure 6.10 show the diagrams for the manufacturing process of the eye cream sunscreen and the lip sunscreen, respectively.

The streams in the process flow diagrams are numbered according to the order of addition, furthermore, their mass composition is defined for a batch of 150.00 kg, and the equipment is identified as specified in Table 6.3 and Table 6.4.



Stream	1	2	3	4	5	6	7	8	9	10
Mass [kg]										
Water	0.00	0.00	0.00	71.55	0.00	0.00	71.55	71.55	0.00	71.55
Zinc oxide	0.00	21.00	0.00	0.00	0.00	21.00	21.00	21.00	0.00	21.00
Octinoxate	10.50	0.00	0.00	0.00	0.00	10.50	10.50	10.50	0.00	10.50
Tinosorb® S Lite aq	0.00	0.00	0.00	8.25	0.00	0.00	8.25	8.25	0.00	8.25
Glycerin	0.00	0.00	7.50	0.00	7.50	0.00	7.50	7.50	0.00	7.50
C12-15 Alkyl benzoate	7.50	0.00	0.00	0.00	0.00	7.50	7.50	7.50	0.00	7.50
Squalane	7.50	0.00	0.00	0.00	0.00	7.50	7.50	7.50	0.00	7.50
Octisalate	6.75	0.00	0.00	0.00	0.00	6.75	6.75	6.75	0.00	6.75
PEG-400	6.00	0.00	0.00	0.00	0.00	6.00	6.00	6.00	0.00	6.00
Jojoba oil	1.50	0.00	0.00	0.00	0.00	1.50	1.50	1.50	0.00	1.50
Sodium hyaluronate	0.00	0.00	0.00	0.00	0.00	0.00	0.75	0.75	0.00	0.75
Phenoxyethanol	0.00	0.00	0.00	0.75	0.00	0.00	0.75	0.75	0.00	0.75
Xanthan gum	0.00	0.00	0.45	0.00	0.45	0.00	0.45	0.45	0.00	0.45
Sodium citrate	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	q.s	q.s
Total	**39.75**	**21.00**	**7.95**	**80.55**	**0.95**	**60.75**	**150.00**	**150.00**	**-**	**-**

Figure 6.9. Eye cream sunscreen process flow diagram.



Stream	1	2	3	4	5	6	7	8	9	10	11
Mass [kg]											
Sorbeth Hexaoleate	0.00	0.00	0.00	24.60	0.00	0.00	0.00	24.60	0.00	0.00	24.60
Castor oil	0.00	0.00	0.00	0.00	0.00	15.00	15.00	0.00	0.00	15.00	15.00
Shea butter	22.50	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	22.50
Microcrystalline wax	10.50	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	10.50
Octisalate	0.00	0.00	0.00	0.00	9.75	0.00	0.00	9.75	0.00	0.00	9.75
Octocrylene	0.00	0.00	0.00	0.00	9.75	0.00	0.00	9.75	0.00	0.00	9.75
Octyldodecanol	7.50	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	7.50
Carnauba wax	7.50	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	7.50
Tinosorb® S	0.00	0.00	0.00	0.00	7.50	0.00	0.00	7.50	0.00	0.00	7.50
Ethylhexyl triazone	0.00	0.00	0.00	0.00	6.75	0.00	0.00	6.75	0.00	0.00	6.75
Avobenzone	0.00	0.00	0.00	0.00	6.00	0.00	0.00	6.00	0.00	0.00	6.00
Beeswax	4.50	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	4.50
Water	0.00	3.75	3.75	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3.75
Glycerin	0.00	3.75	3.75	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3.75
CI 77491	0.00	0.00	0.00	0.00	0.00	1.98	1.98	0.00	0.00	1.98	1.98
CI 77891	0.00	0.00	0.00	0.00	0.00	1.80	1.80	0.00	0.00	1.80	1.80
Jojoba oil	0.00	0.00	0.00	0.00	0.00	1.50	1.50	0.00	0.00	1.50	1.50
Glyceryl oleate	1.50	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.50

(Continues)

(Continued)

Stream	1	2	3	4	5	6	7	8	9	10	11
CI 42090	0.00	0.00	0.00	0.00	0.00	0.96	0.96	0.00	0.00	0.96	0.96
CI 77891	0.00	0.00	0.00	0.00	0.00	0.78	0.78	0.00	0.00	0.78	0.78
Aloe vera	0.00	0.75	0.75	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.75
Tocopherol	0.75	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.75
CI 15850	0.00	0.00	0.00	0.00	0.00	0.48	0.48	0.00	0.00	0.48	0.48
Phenoxyetanol	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.15	0.00	0.15
Total	**54.75**	**8.25**	**8.25**	**24.60**	**39.75**	**22.50**	**22.50**	**64.35**	**0.15**	**22.50**	**150.00**

Figure 6.10. Lip sunscreen process flow diagram.

7. Conclusions

The development of multipurpose sunscreens for the eye contour and the lips has been carried out based on a bibliographic search through patents, regulations, books, and articles, along with a market analysis of the products available on the market and the consumers' opinions.

It was found that consumers are looking for a product that moisturizes, soothes the skin, offers sun protection, and is also versatile, in the sense that it looks good on its own or with makeup. Additionally, it was identified that the intended consumers are women between 18 and 50 years old, in Spain, which led to establish that both products offer broad-spectrum protection with SPF 50; and that the best packaging would be refillable, in the case of the eye cream sunscreen, would be a 15 mL collapsible tube of recycled plastic (rLDPE, and rHDPE) with a bamboo screw cap, and in the case of the lip sunscreen would be a cylindrical stick with a screw cap made of bamboo, with an aluminium inner mechanism with a capacity of 4 g of product.

Based on this, quality factors and their performance indices were defined to make both products stand out, establishing that they should satisfy the consumers' needs analyzed, and have a shelf life of 3 years, with a PAO of 1 year. Specifically, the eye cream sunscreen would be a transparent and pearlescent, fragrance-free, O/W nanoemulsion with a pseudoplastic behavior and a yield point of 20 Pa, with ingredients that ensure the product's low eye stinging ability; on the other hand, the lip sunscreen would be a W/O emulsion-based suspension, long lasting, opaque, pearlescent, and color Pantone 21-3-2 CP, with a pleasant taste and smell, presenting a thixotropic behavior with a melting point between 60 ºC and 75 ºC and a softening point around 32 ºC.

In order to meet the quality factors, the ingredients of both products were selected based on European regulations and the concentrations typically used for each product. The active ingredients of both products are UV filters, humectants, and emollients; and in the case of the lip sunscreen, a taste-masking ingredient was also included to ensure a pleasant taste.

Finally, the manufacturing process of each product was designed to operate in batches of 150 kg. For the eye cream sunscreen, 2 batches per year will be produced and for the lip sunscreen, 4 batches per year, which may vary according to demand. Regarding the equipment, industrials vessels were selected to be used in the mixing operations of both processes, but due to the difference in the manufacturing process, a homogenizer and a filling/sealing machine were chosen for the eye cream sunscreen, while a three-roll mill and a moulding machine were selected for the lip sunscreen.

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ACRONYMS

HLB: Hydrophilic-Lipophilic Balance.

MED: Minimal Erythemal Dose.

MPPDD: Minimal Persistent Pigment Darkening Dose.

O/O: Oil-in-Oil.

O/W: Oil-in-Water.

PAO: Period After Opening.

PE: Polyethylene.

RH: Relative Humidity.

rHDPE: Recycled High-Density Polyethylene.

rLDPE: Recycled Low-Density Polyethylene.

SPF: Sun Protection Factor.

UVA-PF: UVA Protection Factor.

UVR: Ultraviolet adiation.

UV: Ultraviolet.

W/O: Water-in-Oil.

APPENDICES

APPENDIX 1: MARKET SEARCH

Table 1. Key ingredients and rating of sunscreens market for the eye contour.

Product	SPF	Rating		Key ingredients	
Advanced day eye protect MEDIK8 (153)	30	Absorption	4	UV Filter	Ethyelxyl Methoxycinnamate, Diethylamino Hydroxybenzoyl Hexyl Benzoate, Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine.
		Moisture	5	Emollient	C12-15 Alkyl Benzoate, Dimethicone, Coconut Alkanes, Cetearyl Alcohol, Coco-Caprylate/Caprate, Hydroxypropyl Bispalmitamide MEA.
		Spreadability	3		
		No irritant	3	Vehicle	Water, Butylene Glycol.
		Makeup layering	4	Humectant	Glycerin, Sodium Hyaluronate, Lactic Acid, Butylene Glycol, Ectoin, Saccharide Isomerate, Isosorbide Dicaprylate
CC Eye cream ERBORIAN (154)	25	Absorption	3	UV Filter	Ethylhexyl Methoxycinnamate, Zinc Oxide [Nano], Titanium Dioxide [Nano], Ethylhexyl Salicylate
		Moisture	3	Emollient	Cyclomethicone, C12-15 Alkyl Benzoate, Dimethicone, Aluminum Hydroxide, Methicone, Palmitic Acid, Stearic Acid, Silica Dimethyl Silylate
		Spreadability	4		
		No irritant	4	Vehicle	Aqua/Water, Dipropylene Glycol, Methyl Trimethicone, Butylene Glycol
		Makeup layering	4	Humectant	Glycerin, Butylene Glycol, Centella Asiatica Extract, Acetyl Tetrapeptide-5
Foto Ultra Age Repair Fusion Water ISDIN (155, 156)	50	Absorption	4	UV Filter	Ethylhexyl Methoxycinnamate, Butyl Methoxydibenzoylmethane, Ethylhexyl Triazone, Titanium Dioxide
		Moisture	5	Emollient	Dimethicone, Lecithin, Pentapeptide-34 Trifluoroacetate
		Spreadability	5		
		No irritant	3	Vehicle	Aqua (Water), Butylene Glycol, Propylene Glycol, Propanediol

		Makeup layering	4	Humectant	Butylene Glycol, Propylene Glycol, Glycerin, Propanediol, Sodium Hyaluronate
Bright-Eyed 100% Mineral Eye Cream SUPER-GOOP! (157)	40	Absorption	3	UV Filter	Zinc Oxide, Titanium Dioxide
		Moisture	2	Emollient	Caprylic/Capric Triglyceride, Glyceryl Stearate Citrate, Cetyl Esters, Cetearyl Alcohol, Olive Oil Polyglyceryl-6 Esters, Caprylyl Glycol
		Spreadability	3		
		No irritant	4	Vehicle	Water, Propanediol, Butyloctyl Salicylate, 1,2-Hexanediol
		Makeup layering	2	Humectant	Glycerin, Propanediol, Glyceryl Glucoside, Caprylyl Glycol
Physical Eye UV Defense SKIN-CEUTICALS (158)	50	Absorption	3	UV Filter	Titanium Dioxide, Zinc Oxide
		Moisture	3	Emollient	Dimethicone, C12-15 Alkyl Benzoate, Triexylhexanoin, Hydrogenated Jojoba Oil.
		Spreadability	3		
		No irritant	4	Vehicle	Isohexadecane
		Makeup layering	2	Humectant	________________

(a) Consumer rating system: 1: Terrible 2: Bad 3: Correct 4: Good 5: Excellent.

Table 2. Key ingredients and rating of lip sunscreens on the market.

Product	SPF	Rating		Key ingredients	
Resist Anti-aging - Lip Gloss PAULA'S CHOICE (159)	40	Texture	5	UV Filter	Homosalate, Octisalate, Avobenzone, Octocrylene
		Taste	3	Emollient	Ethylhexyl Palmitate, Polyglyceryl-2 Tetraisostearate, Cocos Nucifera Oil, Lecithin, Octyldodecanol, Isononyl Isononanoate, Isopropyl Myristate, Isopropyl Titanium Triisostearate
		Moisture	4		
		Wearability	5	Vehicle	Ethylhexyl Palmitate, Microcrystalline Wax, Cocos Nucifera Oil, Polyethylene
Lipscreen PAULA'S CHOICE (160)	50	Texture	5	UV Filter	Homosalate, Octisalate, Avobenzone, Octocrylene
		Taste	3	Emollient	Hydrogenated Soybean Oil, Bis-Diglyceryl Polyacyladipate-2, Beeswax, Hydrogenated Jojoba Oil, Theobroma Cacao Seed Butter, Butyrospermum Parkii Butter, Hydrogenated Olive Oil, Hydrogenated Vegetable Oil, Copernicia Cerifera Wax
		Moisture	5		
		Wearability	5	Vehicle	Hydrogenated Olive Oil, Beeswax, Ozokerite, Polyethylene, Microcrystalline Wax
Lip Balm BONDI SANDS (161)	50+	Texture	4	UV Filter	Avobenzone, Octocrylene, Ethylhexyl Triazone, Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine
		Taste	5	Emollient	Ricinus Communis Seed Oil, Octyldodecanol, Hydrogenated Polydecene, Synthetic Beeswax, Cocoglycerides, Cetyl Palmitate, Butyrospermum Parkii Butter, Simmondsia Chinensis Seed Oil
		Moisture	3		
		Wearability	4	Vehicle	Microcrystalline Wax, Ricinus Communis Seed Oil, Synthetic Beeswax
Lip Balm LIPTASTICK (162)	50	Texture	4	UV Filter	Octocrylene, Titanium Dioxide (Nano), Avobenzone
		Taste	3	Emollient	Prunus Amygdalus Dulcis Oil, Hydroxystearic/Linolenic/Oleic Polyglycerides, Ricinus Communis Seed Oil, Helianthus Annuus Seed Cera, Caprylic/Capric Triglyceride, Butyrospermum Parkii Butter, Isopropyl Myristate, Copernicia Cerifera Cera, Argania Spinosa Kernel Oil, Stearic Acid, Helianthus Annuus Seed Oil
		Moisture	3		

		Wearability	1	Vehicle	Helianthus Annuus Seed Cera, Ricinus Communis Seed Oil
Sheen Screen Hydrating Lip Balm **ULTRA VIOLETTE** (163)	50	Texture	5	UV Filter	Ethylhexyl Methoxycinnamate, Octocrylene, Avobenzone
		Taste	3	Emollient	Lanolin, Theobroma Cacao Seed Butter, Beeswax, Butyrospermum Parkii Butter, Helianthus Annuus Hybrid Oil, Olea Europaea Fruit Oil, Ricinus Communis Seed Oil
		Moisture	5		
		Wearability	5	Vehicle	Lanolin, Beeswax
Protector Labial **ISDIN** (164)	50+	Texture	3	UV Filter	Octocrylene, Octisalate, Avobenzone, Ethylhexyl Triazone, Diethylamino Hydroxybenzoyl Hexyl Benzoate
		Taste	3	Emollient	Ricinus Communis Seed Oil, Cocoglycerides, Dibutyl Adipate, Copernicia Cerifera Cera, Octyldodecanol, Lanolin, Caprylyl Glycol, Shorea Stenoptera Seed Butter
		Moisture	3		
		Wearability	4	Vehicle	Ricinus Communis Seed Oil, Cera Microcristallina, Paraffin
The One For Your Lips **HELLO SUNDAY** (165, 166)		Texture	5	UV Filter	Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine, Avobenzone, Octisalate, Ethylhexyl Triazone, Diethylamino Hydroxybenzoyl Hexyl Benzoate, Octocrylene
		Taste	3	Emollient	Caprylic/Capric Triglyceride, Paraffinum Liquidum, Silica Dimethyl Silylate, Diisopropyl Adipate, Squalane, Octyldodecanol, Butyrospermum Parkii Butter, Dicaprylyl Carbonate, Glyceryl Dibehenate, Tribehenin, Glyceryl Behenate, Caprylyl Glycol, Ethylhexyl Palmitate, Hydrogenated Polydecene
		Moisture	5		
		Wearability	4	Vehicle	Polyisobutene, Paraffinum Liquidum, Dimethyl Silylate

(a) Consumer rating system: 1: Terrible 2: Bad 3: Correct 4: Good 5: Excellent.
(b) Wearability: Layering with makeup, easy to reapply, "long-lasting (around 2 h)", no white cast

Table 3. Ingredient list and packaging of the sunscreens for the eye contour

Products	Ingredients
Advanced day eye protect MEDIK8 (153) 	Aqua (Water), Diethylamino Hydroxybenzoyl Hexyl Benzoate, Dibutyl Adipate, Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine, Glycerin, C12-15 Alkyl Benzoate, Cetearyl Alcohol, Dicaprylyl Carbonate, Ethylhexyl Triazone, Potassium Cetyl Phosphate, Caffeine, Sodium Polyacrylate, Phenoxyethanol, Butylene Glycol, Carnosine, Xanthan Gum, Sodium Hyaluronate, Tetrahexyldecyl Ascorbate, Glucosyl Hesperidin, Moringa Oleifera Seed Extract, Disodium EDTA, Benzoic Acid, Ethylhexylglycerin, Disodium Phosphate, Theobroma Cacao (Cocoa) Seed Extract, Dehydroacetic Acid, Citric Acid, Ectoin, Dimethicone/Vinyl Dimethicone Crosspolymer, Polysilicone-11, Silica, Laureth-12.
CC Eye cream ERBORIAN (154) 	Aqua/Water, Cyclomethicone, Ethylhexyl Methoxycinnamate, Dipropylene Glycol, Glycerin, Titanium Dioxide, Peg-10 Dimethicone, Methyl Trimethicone, C12-15 Alkyl Benzoate, Ethylhexyl Salicylate, Zinc Oxide-[Nano], Dimethicone, Titanium Dioxide-[Nano], Ci 77492/Iron Oxides, Disteardimonium Hectorite, Magnesium Sulfate, Vinyl Dimethicone/Methicone Silsesquioxane Crosspolymer, Centella Asiatica Extract, Mel/Honey Extract, Mica, Talc, Trihydroxystearin, Butylene Glycol, Polyester-1- Aluminum Hydroxide, Silica Dimethyl Silylate, Palmitic Acid, Stearic Acid, Tocopheryl Acetate, Ethylhexylglycerin, Phenoxyethanol, Methicone, Dimethicone/Vinyl Dimethicone Crosspolymer, Parfum/Fragrance, Hexyl Cinnamal, Alpha-Isomethyl Ionone, Linalool, Citronellol, Geraniol, Eugenol, Limonene, Ci 77491/Iron Oxides, Ci 77499/Iron Oxides
Foto Ultra Age Repair Fusion Water ISDIN (155) 	Aqua (Water), Octocrylene, Propanediol, Butyl Methoxydibenzoylmethane, Ethylhexyl Salicylate, Polymethyl Methacrylate, Dimethicone, Phenylbenzimidazole Sulfonic Acid, Polysilicone-15, Propylene Glycol Dicaprylate/Dicaprate, Tromethamine, Glycerin, Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine, Silica, Dimethicone/Vinyl Dimethicone Crosspolymer, Butylene Glycol, 1,2-Hexanediol, Hydroxyacetophenone, Polysorbate 60, PEG-10 Dimethicone, Sodium Hyaluronate, Tocopheryl Acetate, Xanthan Gum, Caprylyl Glycol, Parfum (Fragrance), Disodium EDTA, PEG-8, Carbomer, Polysorbate 20, Sodium Lactate, Tocopherol, Phenoxyethanol, Tropolone, Lecithin, Plankton Extract, Ascorbyl Palmitate, Sodium Benzoate, Ascorbic Acid, Citric Acid, Palmitoyl Tripeptide-1, Palmitoyl Tetrapeptide-7, Pentapeptide-34 Trifluoroacetate.

Bright-Eyed 100% Mineral Eye Cream SUPERGOOP! (157) 	Zinc Oxide, Water, Caprylic/Capric Triglyceride, Glycerin, Propanediol, Butyloctyl Salicylate, Glyceryl Stearate Citrate, Lauroyl Lysine, Cetyl Esters, Inulin Lauryl Carbamate, Polyhydroxystearic Acid, Cetearyl Alcohol, Potassium Cetyl Phosphate, Griffonia Simplicifolia Seed Extract, Titanium Dioxide, Olive Oil Polyglyceryl-6 Esters, Mica, Triethoxycaprylylsilane, Microcrystalline Cellulose, Glyceryl Glucoside, Hydroxyacetophenone, Polyurethane-79, Diethylhexyl Syringylidenemalonate, Sodium Stearoyl Lactylate, 1,2-Hexanediol, Caprylyl Glycol, Sodium Citrate, Trisodium Ethylenediamine Disuccinate, Camellia Sinensis Leaf Extract, Lactobacillus Ferment Lysate, Punica Granatum Extract, Sodium Stearoyl Glutamate, Xanthan Gum, Cellulose Gum, Iron Oxides, Hedychium Coronarium Root Extract, Lactobacillus Ferment, Caffeine, Leuconostoc/Radish Root Ferment Filtrate, Tin Oxide.
Mineral eye UV defense SKINCEUTICALS (158) 	Dimethicone, Titanium Dioxide [Nano]/Titanium Dioxide, C12-15 Alkyl Benzoate, Hydrogenated Jojoba Oil, Styrene/Acrylates Copolymer, Dimethicone Crosspolymer, Talc, Triethylhexanoin, Isohexadecane, Dimethicone/Vinyl Dimethicone Crosspolymer, Aluminium Hydroxide, Stearic Acid, CI 77419, CI 77492, CI 77499/Iron Oxides, Aluminium Stearate, Polypropylsilsequioxane, Alumina, Polyhydroxystearic Acid, PEG-8 Laurate, Silica Silylate, Isododecane, 2-Oleamido-1, 3-Octadecanediol, Disodium Stearoyl Glutamate.

Table 4. Ingredient list and packaging of the sunscreens for lips.

Products	Ingredients
Resist Anti-aging - Lip Gloss PAULA'S CHOICE (167) 	Polybutene, Octyldodecanol, Ethylhexyl Palmitate, Homosalate, Ethylhexyl Salicylate, Cera Microcristallina, Polyethylene, Polyglyceryl-2 Tetraisostearate, Cocos Nucifera (Coconut) Oil Butyl Methoxydibenzoylmethane, Octocrylene, Flavor, Silica Silylate, Adenosine, Retinyl Palmitate, Lecithin, Tocopherol, Tocopheryl Acetate, Isononyl Isononanoate, Isopropyl Titanium Triisostearate, Stearalkomium Hectorite, Isopropyl Myristate, Propylene Carbonate, Polyhydroxystearic Acid, Silica, Phenoxyethanol. May Contain: Mica, Tin Oxide, Titanium Dioxide, Iron Oxides, Manganese Violet, Blue 1 Lake, Yellow 5 Lake, Red 6, Red 7, Red 7 Lake, Red 21, Red 22 Lake, Red 28 Lake, Red 30, Red 30 Lake, Red 33 Lake, Red 36, Red 40, Red 40 Lake.
Lipscreen PAULA'S CHOICE (168) 	Hydrogenated Soybean Oil, Bis-Diglyceryl Polyacyladipate-2, Hydrogenated Olive Oil, Polyglyceryl-3 Diisostearate, Beeswax, Ozokerite, Hydrogenated Jojoba Oil, Ethylhexyl Salicylate, Homosalate, Polyethylene, Hydrogenated Polycyclopentadiene, Cera Microcristallina, Butyl Methoxydibenzoylmethane, Theobroma Cacao (Cocoa) Seed Butter, Octocrylene, Silica, Tocopheryl Acetate, Butyrospermum Parkii (Shea) Butter, Olea Europaea (Olive) Fruit Oil, Phytosterols, Tocopherol, Hydrogenated Vegetable Oil, Copernicia Cerifera (Carnauba) Wax, Water (Aqua), Phenoxyethanol.
Lip Balm BONDI SANDS (161) 	Ricinus Communis (Castor) Seed Oil, Octyldodecanol, Synthetic Beeswax, Microcrystalline Wax, Hydrogenated Polydecene, Cocoglycerides, Cetyl Palmitate, Butylene Glycol, Butyrospermum Parkii (Shea) Butter, Simmondsia Chinensis (Jojoba) Seed Oil, Butyl Methoxydibenzoylmethane, Octocrylene, Ethylhexyl Triazone, Aroma (Flavor), Triacontanyl Pvp, Peg-30 Dipolyhydroxystearate, Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine, Bha, Saccharin, Tocopheryl Acetate.
Lip Balm LIPTASTICK (162) 	Prunus Amygdalus Dulcis Oil, Brassica Campestris Seed Oil, Hydroxystearic/Linolenic/Oleic Polyglycerides, Ricinus Communis Seed Oil, Octocrylene, Helianthus Annuus Seed Cera, Caprylic/ Capric Triglyceride, Titanium Dioxide (Nano), Euphorbia Cerifera Cera, Butyrospermum Parkii Butter, Isopropyl Myristate, Copernicia Cerifera Cera, Butyl Methoxydibenzoylmethane, Argania Spinosa Kernel Oil, Alumina, Stearic Acid, Helianthus Annuus Seed Oil, Tocopherol

Sheen Screen Hydrating Lip Balm **ULTRA VIOLETTE** (163) 	Lanolin, Theobroma Cacao (Cocoa) Seed Butter, Ethylhexyl Methoxycinnamate, Octocrylene, Beeswax, Butyl Methoxydibenzoylmethane, Butyrospermum Parkii (Shea) Butter, Helianthus Annuus Hybrid Oil (Helianthus Annuus (Sunflower) Seed Oil), Olea Europaea (Olive) Fruit Oil, Ricinus Communis (Castor) Seed Oil, Aroma, Tocopherol, May Contain +/- CI 19140, CI 15850, CI 77891, CI 77491, CI 17200, CI 45410, CI 77492, CI 77499, CI 42090.
Protector Labial **ISDIN** (164) 	Ricinus Communis (Castor) Seed Oil, Cera Microcristallina (Microcrystalline Wax), Cocoglycerides, Octocrylene, Dibutyl Adipate, Paraffin, Ethylhexyl Salicylate, Butyl Methoxydibenzoylmethane, Copernicia Cerifera (Carnauba Wax) Cera, Ethylhexyl Triazone, Octyldodecanol, Diethylamino Hydroxybenzoyl Hexyl Benzoate, Lanolin, Glycol Montanate, 1,2-Hexanediol, Parfum (Fragrance), Caprylyl Glycol, Shorea Robusta Resin, Shorea Stenoptera Seed Butter, Tocopheryl Acetate, CI 77891 (Titanium Dioxide), Bisabolol, BHT, Tropolone, Triethoxycaprylylsilane, Tocopherol, CI 15850 (Red 6 Lake)."
The One For Your Lips **HELLO SUNDAY** (165) 	Polyisobutene, Caprylic/Capric Triglyceride, Paraffinum Liquidum, Silica Dimethyl Silylate, Diisopropyl Adipate, Squalane, Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine, Butyl Methoxydibenzoylmethane, Ethylhexyl Salicylate, Ethylhexyl Triazone, Octyldodecanol, Diethylamino Hydroxybenzoyl Hexyl Benzoate, Octocrylene, Butyrospermum Parkii Butter, Dicaprylyl Carbonate, Glyceryl Dibehenate, Synthetic Beeswax, Tribehenin, Glyceryl Behenate, 1,2-Hexanediol, Bisabolol, Caprylyl Glycol, Stearalkonium Hectorite, Tocopherol, Ethylhexyl Palmitate, Propylene Carbonate, Hydrogenated Polydecene, Butylene Glycol, Pentylene Glycol, Dunaliella Salina Extract, Sodium Hyaluronate.

APPENDIX 2: COLOR TONE SELECTION

To choose a nude color that will flatter the widest range of skin tones, multiple lipstick colors available on the market were analyzed, afterwards the color 'Runway Royalty' of Charlotte Tilbury lipsticks, shown in Figure 1, was selected because it suits different skin tones.

Figure 1. Swatches of The Super Nude lipstick, color Runway Royalty (169).

Once the color was selected, Microsoft Publisher was used to find a Pantone color similar to it. Rectangle figures were inserted and, through the 'Sample Fill Color' tool applied on the lipstick color of Figure 1 was obtained the sample color, subsequently some Pantone colors were chosen and compared with the sample color (Figure 2).

Figure 2. Comparison of different Pantone colors with the sample color.

Finally, Figure 3 shows the comparison of the Pantone selected (Pantone 21-3-2 CP), which is “Nuevo” on Figure 3, to the sample color, which is ‘Actual’.

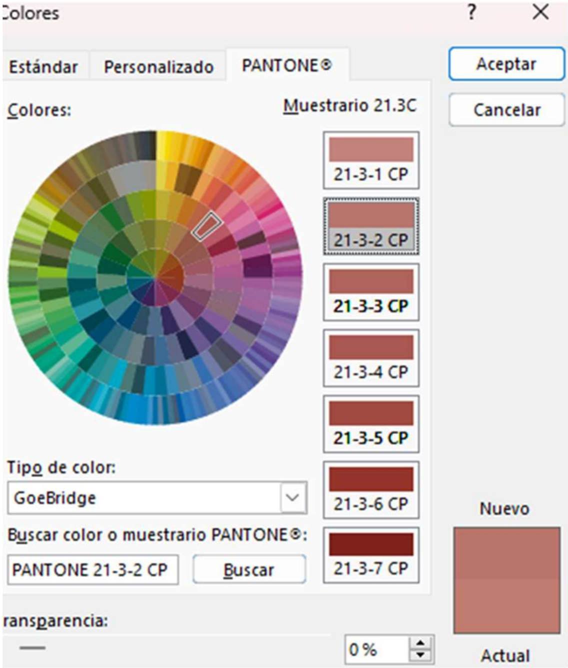

Figure 3. Pantone color wheel and comparison of the 21-3-2 CP to the sample color.

APPENDIX 3: DURABILITY TEST

To better visualize the difference in light absorption, Figure 1 shows the pictures obtained with the JANUS-II before and after applying sunscreen. A liquid sunscreen with SPF 50+ and broad-spectrum was applied on the face, and the Bondi Sands lip balm SPF 50 was applied on the lips.

The light zones represent the reflection of the UV light, while the dark zones are due to light absorption. In the left picture the melatonin absorbs the light, this is the reason why the inner zone of the lips is brighter, as there is no melatonin there, meanwhile, in the right picture the whole face is dark because of the absorption provided by the UV-filters.

Figure 1. Photographs with UV light. Left: Without any product applied. Right: With sunscreen.

Two durability tests were carried out to compare the performance of two lip products with different textures and SPF.

To perform the durability test, 7 photographs with UV light were taken over a 2-hour period, the first photograph represents the skin without UV protection (1), the second is obtained just after applying the sunscreen (2), and the next 4 photographs are taken every 30 minutes to obtain the degradation of UV protection (3, 4, 5, 6), and the last one was shot after removing the excess product by pressing the lips with the back of the hand (7). During the test the lips were not rubbed, and the subjects did not eat or drink.

The evaluated the degradation of the UV protection, the light absorption is going to be analyzed considering that the percentage of UVB light absorption is related with the SPF by Equation 4.4, which is represented in Figure 2.

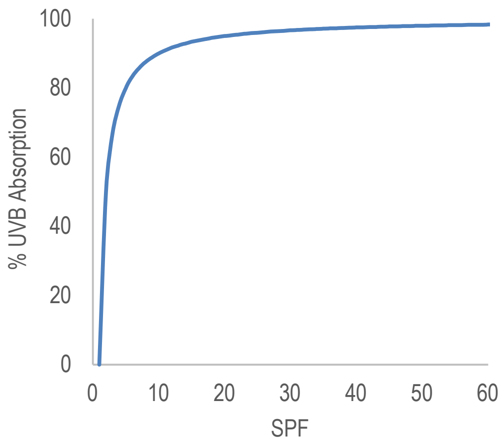

Figure 2. Representation of the UVB absorption provided by the SPF.

Consequently, the photographs were colored in a grey scale to quantify the lightness through the HSL (Hue, Saturation, and Lightness) model of Microsoft Publisher, and then be able to calculate the remaining SPF.

Figure 3 shows the durability test of the Bondi Sand lip balm SPF 50 (A), which is more liquid than the product applied for the durability test presented in Figure 4, which is the Piz Buin sun lipstick SPF 30, broad-spectrum (B).

The values of Lightness of each photograph, obtained from the point 'X' marked in Figure 3 and Figure 4, are shown in Table 1, with their equivalent values of percentage of UVB absorption and SPF. The absorption (y) is calculated by interpolation (Equation 1) with the value of the first (x_1, y_1) and second (x_2, y_2) photographs, and the SPF is estimated with Equation 4.4.

$$y = y_1 + (x - x_1)\frac{(y_2 - y_1)}{(x_2 - x_1)} \quad (1)$$

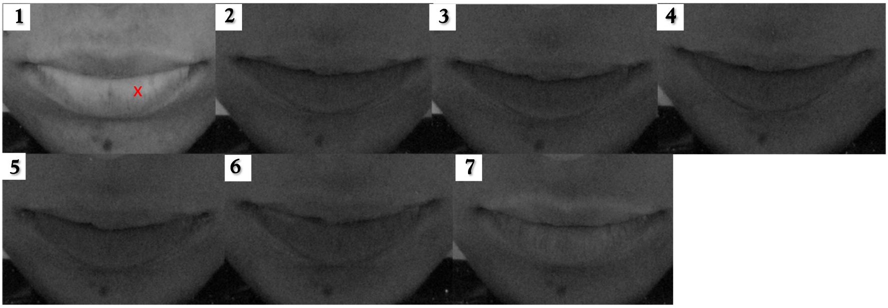

Figure 3. Photographs in grey scale of the product A durability test.

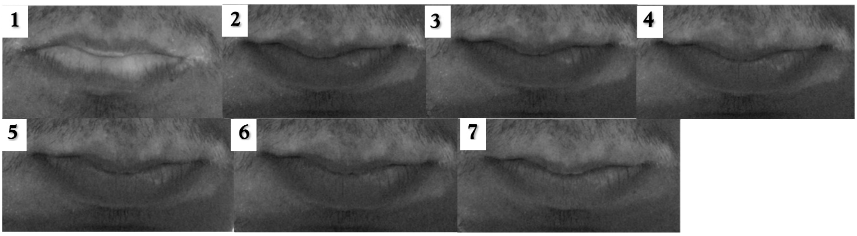

Figure 4. Photographs in grey scale of the product B durability test.

Figure 3 and Figure 4 show that the absorption decrease with time especially in the oral commissure or inner border of the lips, and that after pressing the lips the central area lose more coverage. To have a better estimation of the sun protection remaining it would be better to analyze different reference points, e.g. commissure, central point of the bottom lip and of the top lip, outer edge (vermillion border).

For this example, the points selected (x) correspond to the lightest area, and therefore with the lowest light absorption.

Table 1. Results of the durability test of two lip products.

Product	Photograph	Lightness	Absorption	SPF
Bondi Sands Lip balm SPF 50 (A)	*1*	120	0	1
	2	31	98	50
	3	32	97	32
	4	32	97	32
	5	33	96	24
	6	33	96	24
	7	58	68	3
Piz Buin Lipsticks SPF 30 Broad-spectrum (B)	*1*	123	0	1
	2	45	97	30
	3	46	95	22
	4	46	95	22
	5	48	93	14
	6	53	87	8
	7	57	82	5

With the values presented in Table 1, product A shows a smaller decrease in absorption during the durability test (2 % in front of 10 %), while product B presents a smaller decrease after the lip pressure (6 % in front of 29 %).

These results can be affected by many variables as different subjects, therefore different skin types and habits; different product formats, including a more liquid product which affect the application and durability; different SPF, which results in different light absorption. Therefore, these tests are presented only as an example of the methodology to be followed with the product to be developed, and not to compare or validate these results, as the properties are not the same and the exact SPF of the products tested is unknown.

APPENDIX 4: ITERATIONS OF UV FILTERS

The UV filters were selected using the BASF sunscreen simulator (91), which gives a variety of parameters including the SPF and the UVA rating according to the concentration by weight of each UV filter.

Figure 1 and Figure 2 show the results from the simulator, where the SPF mimics the result of the in vivo test (ISO 24444), the SPF rating is given according to the European Commission recommendation for labeling, where if the SPF tested is between 30.0 and 49.9 the rating should be SPF 30, whereas if the SPF obtained is in the range 50.0 - 59.9, the SPF rating is 50, and is the SPF tested is above 60.0 the SPF rating should be 50+ (62). Finally, the UVA circle is shown when the ratio 1/3 UVA-PF/SPF is met, with the UVA-PF calculated according to the ISO 24442 method.

The iterations made to select the UV filters of the eye cream sunscreen are presented in Figure 1 as follows:

a) The first iteration was based on the patent US 2009/009887 A1 (89), which recommends including 15 % zinc oxide (ZnO), 7.5 % octinoxate (EHMC), and 5 % octisalate (EHS), by weight. The SPF of this combination is lower than the specified SPF for this product, which is an SPF 50,

b) The second iteration consist of changing the inorganic UV filter to titanium dioxide (TiO2) to increase SPF, and, although it provides a high SPF, protects mainly against UVB rays, as do octinoxate and octisalate, therefore the resulting UVA-PF/SPF ratio is lower than the required 1/3.

c) To maintain the required SPF but achieve the UVA rating, the initial concentration of ZnO was included, and the minimum quantity of TiO2 was added until achieving an SPF 50, but the UVA rating is lower than 1/3.

d) The bis-ethylhexyloxyphenol methoxyphenyl triazine (BEMT) and the butyl methoxydibenzoylmethane (BMDBM) were added to increase the UVA-PF while increasing the SPF, because they are high effective and mainly UVA filters.

e) There are two types of BEMT, the one included in the iteration 'd' (BEMT aq), which is water-soluble, and the BEMT included in the iteration 'e', which is oil soluble. Comparing results of iteration e and d, the BEMT aq provides a higher SPF with the required UVA-PF/SPF ratio, therefore the BEMT aq is selected.

f) For this iteration the BMDBM and the TiO2 were eliminated to reduce the total quantity of UV filters, showing that with this combination of filters the SPF and the UVA-PF/SPF ratio are satisfactory.

g) The last iteration was made with the same combination as in the previous iteration but lowering the quantities proportionally, which leaded to obtain the final combination.

	Max.	a	b	c	d	e	f	g
FILTER SELECTION								
BEMT	10%	0.00%	0.00%	0.00%	0.00%	6.00%	0.00%	0
BEMT aq	10%	0.00%	0.00%	0.00%	6.00%	0.00%	6.00%	5.5
BMDBM	5%	0.00%	0.00%	0.00%	2.00%	2.00%	0.00%	0
EHMC	10%	7.50%	7.50%	7.50%	7.50%	7.50%	7.50%	7
EHS	5%	5.00%	5.00%	5.00%	5.00%	5.00%	5.00%	4.5
TiO2 (nano) aq	25%	0.00%	15.00%	6.00%	2.00%	2.00%	0.00%	0
ZnO (nano) oil or aq	25%	15.00%	0.00%	15.00%	15.00%	15.00%	15.00%	14
Total:		27.50%	27.50%	33.50%	37.50%	37.50%	33.50%	31.00%
SPF (SUN PROTECTION FACTOR)								
SPF:		30.2	65.3	51.4	66.0	60.6	59.4	54.5
Rating:		30	50+	50	50+	50+	50	50
Filter Efficiency:		1.1	2.37	1.53	1.76	1.62	1.77	1.76
UVA-METRICS								
EU, AUS, MERCOSUR								
Rating:		-	-	-	UVA	UVA	UVA	UVA

Figure 1. UV filters iterations for the eye cream sunscreen on the BASF simulator.

In the case of the lip sunscreen, the iterations that were made are shown in Figure 2, according to the following:

a) The most used UV filters for lip products are octisalate (EHS), avobenzone (BMDBM), octocrylene (OCR), and ethylhexyl triazone (EHT), therefore the maximum allowed concentrations were included in the first iteration, and although it achieves the previously mentioned criteria, it represents a high concentration, which limits the choice of other ingredients.

b) c) and d) reduce the concentration of the UVB filters by 2.5 %, with the objective of choosing to reduce the concentration of the UV filter that decreases the SPF the least, which is the EHS.

e) BEMT was added for the final iteration to increase the SPF without decreasing the UVA-PF/SPF ratio, this allowed to reduce the concentration of the UVB filters, reducing in this way the total quantity of UV filters while meeting the established criteria.

	Max.	a	b	c	d	e
FILTER SELECTION						
BEMT	10%	0.00%	0.00%	0.00%	0.00%	5
BMDBM	10%	10.00%	10.00%	10.00%	10.00%	4
EHS	10%	10.00%	7.50%	10.00%	10.00%	6.5
EHT	5%	5.00%	5.00%	2.50%	5.00%	4.5
OCR	10%	10.00%	10.00%	10.00%	7.50%	6.5
Total:		35.00%	32.50%	32.50%	32.50%	26.50%
SPF (SUN PROTECTION FACTOR)						
SPF:		50.0	48.5	41.0	45.2	51.1
Rating:		30	30	30	30	50
Filter Efficiency:		1.43	1.49	1.26	1.39	1.93
UVA-METRICS EU, AUS, MERCOSUR						
Rating:		UVA	UVA	UVA	UVA	UVA

Figure 2. UV filters iterations for the lip sunscreen on the BASF simulator.

APPENDIX 5: PIGMENT COMPOSITION

Microsoft Publisher and the Color Mixer tool from the web site Color designer (170) were used to estimate the pigment composition.

The pigments selected (Figure 1) were based on some of the pigments used on the Charlotte Tilbury lipstick (169) and checked on the Annex IV of the Regulation 1223/2009/EC (172) to confirm that they can be used on the lips.

Figure 1. Powder pigments from left to right: Blue CI 42090 (173), Red CI 15850 (174), Red iron oxide CI 77491 (175), Yellow iron oxide CI 77492 (176), Titanium dioxide CI 77891 (177).

Firstly, Publisher was used to know the proportions of each pigment according to the CMYB (cyan, magenta, yellow, and black) color model, and the RGB (red, green, and blue) color model, as shown in Figure 2.

The Gauss-Jordan method was applied to estimate the quantity that should be added of each pigment. The CMYB and green proportions are used as the equations, the green was added to have 5 equations because there are 5 unknowns, which are the quantities of the 5 pigments, and the solution is the CMYB and green proportions of the lip sunscreen color (Pantone 21-3-2 CP). The resulting proportions, which were included in the matrix for the calculation, are shown in Table 1.

Figure 2. Color tool of Publisher. Left: CMYK color model. Right: RGB color model.

Table 1. Cyan, magenta, yellow, black, and green proportions of the pigments and the lip sunscreen color.

Color	CI 42090	CI 15850	CI 77491	CI 77492	CI 77891	21-3-2 CP
Cyan	96	0	10	7	5	15
Magenta	66	100	98	47	17	63
Yellow	3	98	91	91	24	51
Black	16	2	7	1	0	7
Green	77	50	54	142	207	112

There are negatives in the results of the equations, which is not possible, therefore 1 was added to the results to made them all positives and the percentage of each one was calculated, which were 17 % CI 42090, 9 % CI 15850, 35 % CI 77491, 14 % CI 77492, and 25 % CI 77891.

The Color Mixer tool allows mixing different colors that are added by creating them with the RGB proportions of each one. Consequently, the pigment colors were added and mixed in the above quantities, the result was a color slightly darker that the Pantone 21-3-2 CP (Figure 3).

Therefore, the percentages of CI 42090, CI 15850, CI 77492, were lower by 1, and the CI 77491 by 2, to have a lighter color, adding the rest to the CI 77891. The result is shown in Figure 4, with a color more similar to the Pantone 21-3-2 CP.

This combination was tried with pigments in oil to confirm that the result is the desired, and the result was satisfactory, nevertheless the final color may vary due to the color of the lip sunscreen base, so adjustment will probably have to be made in the first production.

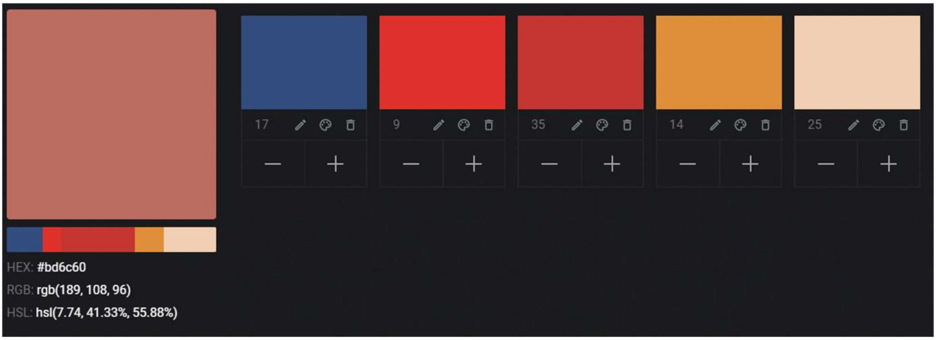

Figure 3. Color result of the first mixing of pigments on the web site Color designer.

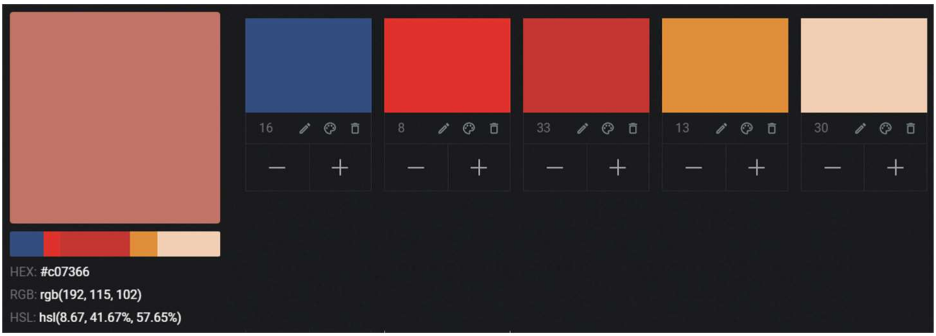

Figure 4. Color result of the final mixing of pigments on the web site Color designer

APPENDIX 6: MIXING VESSEL CAPACITIES

There are heuristics to select the capacity of mixing vessels (146), where the liquid level should be equal to the vessel diameter.

To estimate the capacity of each vessel, the volume of the mixture (V_m) is calculated with Equation 1.1, with the values presented in Table 1, which are the quantities of each ingredient (m_i) for a batch of 150 kg, and the following densities (ρ_i): xanthan gum (178), glycerin (179), water, freeze dried aloe vera powder (180), ricinus communis (Castor) seed oil (181), simmondsia chinensis (Jojoba) seed oil (182), CI 77491 (183), CI 77891 (184), CI 42090 (185), CI 77492 (186), CI 15850 (187).

$$V_m = \sum \frac{m_i}{\rho_i} \tag{1.1}$$

Table 1. Cyan, magenta, yellow, black, and green proportions of the pigments and the lip sunscreen color.

Classification	Ingredient	Quantity (kg)	Density (kg/L)	Volume (L)
Dispersion of Xanthan gum (a)	Glycerin	7.50	1.26	6.01
	Xanthan gum	0.45	8.00	
B ingredients (b)	Water	3.75	1.00	8.57
	Glycerin	3.75	1.26	
	Aloe vera	0.75	0.41	
E ingredients (c)	Castor Seed Oil	22.50	0.95	27.38
	CI 77491	1.98	5.25	
	CI 77891	1.80	3.9	
	Jojoba Seed Oil	1.50	0.87	
	CI 42090	0.96	1.48	
	CI 77492	0.78	4.26	
	CI 15850	0.48	1.59	

Considering that the vessels are cylinders, and that the vessel diameter (d_v) should be the same as the liquid level of the mixture, Equation 1.2 is applied to calculate the vessel diameter, with the volumes of the mixtures (V_m).

$$d_v = \sqrt[3]{\frac{4 \cdot V_m}{\pi}} \quad (1.2)$$

The vessel diameters for the mixtures a, b, and c are the following: 197 mm, 222 mm, 327 mm. These results are added to the criterion of a 20 % oversizing of the volume, to conclude, based on vessels available on the market, that the capacity of the vessel for the mixtures a (188), b (189), and c (190) are 8 L, 10 L, and 35 L.