



# Treball Final de Grau

**Customizable ultraviolet radiation dosimeter: research and development**

Sheila López Rodríguez

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UNIVERSITAT DE  
BARCELONA



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*El mayor peligro que nos depara el futuro es la  
apatía*

Jane Goodall

Tras finalizar este trabajo quería agradecer a las personas que han estado a mi lado y me han proporcionado ayuda y apoyo durante todo el proceso, para que pudiera continuar avanzando sin perder la sonrisa. En primer lugar quería agradecer a mi tutor José María Gutiérrez por haberme ayudado y resuelto mis dudas con rapidez a pesar de la difícil situación en la que nos hemos visto envueltos durante estos meses. En segundo lugar, quería mostrar mi agradecimiento a una persona muy especial, Sergi Solvas, que me ha dado apoyo moral diariamente, haciéndome ver la luz en los días más oscuros, escuchando todos los problemas y dudas que me surgían, además de aconsejarme y ayudarme en todo lo que estuviera en su mano. Y por último pero no menos importante, a mis padres por haber soportado mi carácter en los momentos de más agobio, haber estado a mi lado tanto en los buenos como en los malos momentos, proporcionándome comprensión y ayuda para poder concentrarme en el trabajo.



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## SUMMARY

Ozone in the stratosphere forms an atmospheric layer that protects life on Earth from ultraviolet rays (UVRs), which are made up of UVA, UVB and UVC rays. Beginning the 1980s, scientists realize of the deterioration of this layer due to chlorofluorocarbons (CFCs). As the ozone layer deteriorates, the protective UVR filter is progressively reduced. Consequently, humans and the environment are exposed to higher levels of UV radiation. This problem leads us to the need to monitor the solar radiation to which we are exposed to ensure that we don't put our health at risk. Therefore, in this work is carried out a bibliographic and market study about the different existing UVR detection devices and selects the most effective and commercially viable. After analyzing the data, a customizable UVR dosimeter is chosen according to each user's skin type, irreversible and spectrally selective from the UVR based on a multi-redox polyoxometalate photoelectrochromic ink and an electronic donor. Subsequently, proposals are carried out to adapt the device to the activity of users, improving its adhesion and wettability to allow the application of sunscreen on its surface, reducing its size and modifying the format so that it doesn't interfere with the tanning. Additionally, the quality indexes are determined to be taken into account at the time of its manufacture in order to satisfy the customer's needs to the maximum, taking into account above all aspects such as resistance, wettability and precision of the device. Lastly, an initial manufacturing proposal is made and the type of reactor to be used for the synthesis of the indicator is determined: a tank reactor agitated with marine propeller blades. Synthesis results in a simple process, with laboratory scale equipment that works at ambient temperature and pressure and that requires a single daily load.

**Keywords:** Product development, sun protection, UV dose indicator, ultraviolet radiation, dosimeter, MED.



## RESUMEN

El ozono en la estratosfera forma una capa atmosférica que protege la vida en la Tierra de los rayos ultravioletas (UVR), formados por rayos UVA, UVB y UVC. A partir de la década de 1980, los científicos se percataron del deterioro de dicha capa a causa de los clorofluorocarbonos (CFC). A medida que la capa de ozono se deteriora, el filtro protector de UVR se reduce progresivamente. En consecuencia, los seres humanos y el medio ambiente están expuestos a niveles más altos de radiación UV. Este problema nos lleva a la necesidad de monitorizar la radiación solar a la que estamos expuestos para asegurarnos de que no ponemos en riesgo nuestra salud. Por ello en este trabajo se realiza un estudio bibliográfico y de mercado sobre los distintos dispositivos existentes de detección de UVR y se selecciona el más efectivo y viable comercialmente. Tras analizar los datos se escoge un dosímetro de la UVR personalizable según el tipo de piel de cada usuario, irreversible y espectralmente selectivo de la UVR basado en una tinta fotoelectrocromática de polioxometalato multirredox y un donante electrónico. Posteriormente, se realizan propuestas para adaptar el dispositivo a la actividad de los usuarios, mejorando su adhesión y mojabilidad para permitir la aplicación de protector solar sobre su superficie, reduciendo su tamaño y modificando el formato para que no interfiera con el bronceado. Adicionalmente, se determinan los índices de calidad a tener en cuenta a la hora de su fabricación para satisfacer al máximo las necesidades del cliente, teniendo en cuenta sobretodo aspectos como la resistencia, la mojabilidad y la precisión del dispositivo. Por último, se realiza una propuesta de fabricación inicial y se determina el tipo de reactor a utilizar para la síntesis del indicador: un reactor tanque agitado por palas de hélice marina. La síntesis resulta en un proceso sencillo, con equipos a escala de laboratorio que trabajan a temperatura y presión ambientales y que requieren una única carga diaria.

**Palabras clave:** Desarrollo de productos, protección solar, indicador de dosis UV, radiación ultravioleta, dosímetro, MED.



# 1. INTRODUCTION. HARMFUL EFFECTS OF UV RADIATION ON HEALTH

The Earth is protected from the sun's rays by the ozone layer, which is located in the stratosphere (15-50 km from the Earth's surface). Sunlight is composed of three types of ultraviolet radiation (UVR): UVA (315–400 nm), UVB (280–315 nm) and UVC (100–280 nm) [1], [2]. When that rays pass through the atmosphere, all UVC rays and approximately 90% of UVB radiation are absorbed by the ozone layer by gas-generated dispersion mechanisms (oxygen, carbon dioxide and ozone) and existing water vapour in the atmosphere [1], [3]. On the other hand, UVA radiation is less affected by these factors, therefore, much of the radiation reaching the Earth's surface is composed of UVA and, in a smaller proportion, UVB [1].

In reduced doses the UVR can be beneficial for people as it helps treat diseases and stimulates vitamin D production. However, long-term exposure to solar radiation can have negative effects on our health [1]. UVA rays penetrate deep into the skin and its overexposure causes skin aging and deterioration [2], [4]. UVB can damage DNA and short bursts of high doses of UVB cause burns and lead to the development of skin cancer and cataracts [2], [5]. Finally, UVC rays, which are the most energetic, can cause fatal damage to all life forms [2].

Table 1. Characteristics of ultraviolet radiation

Radiation type	Wavelength [nm]	Characteristics
UVA	315 - 400	Its excessive exposure promotes skin aging and deterioration.
UVB	280 - 315	It source burns and is the main cause of skin cancer and cataracts.
UVC	100 - 280	It can cause lethal damage to any form of life.

In the 1970s scientists recognized that the presence of nitrogen oxides (NOX), bromine (halocarbons) and chlorine (Cl), from chlorofluorocarbons (CFCs), cause harmful effects on ozone (O<sub>3</sub>). Later, in the 1980s, it was discovered that the ozone layer that protects us was being progressively destroyed, leading to higher levels of UVR reaching the earth's surface and endangering the lives of humans. Because of these facts, governments agreed the Montreal convention establishing legislation to control emissions of compounds that cause ozone depletion. Some studies say that during the period 1979 to 1998, the overall O<sub>3</sub> decreased by 10% to 15%, while between 2000 and 2013 it has regenerated by about 1%. Since then, the ozone layer has continued to degrade despite the measures taken in the Montreal convention, although it has helped promote ozone regeneration and decrease its degradation. However, the discovery of new short-lived compounds hinders its recovery [3].

To study the effects that the reduction of the ozone layer can cause on human health, computational simulations have been conducted predicting that "a 10% decrease in stratospheric ozone could cause an additional 300 000 non-melanoma and 4500 melanoma skin cancers and between 1.6 and 1.75 million more cases of cataracts worldwide every year" [1].

Currently, these conditions promote that one of the most common cancers worldwide keep being skin cancer, which is mainly caused by overexposure to the sun [2], [6]. It is estimated that "between two and three million non-melanoma skin cancers and approximately 132000 melanoma skin cancers occur globally each year" [1]. Specifically, in countries such as Australia, where the ozone layer deteriorates significantly, 2 out of 3 people are expected to be detected before age 70 [2], [7].

Due to the current environmental situation and the increasing incidence of diseases caused by this situation, the need to market a device has been identified that alerts the user to when it has reached levels of ultraviolet radiation dangerous to health.



## **2. OBJECTIVES**

The objective of this work is the development of a personal product that can detect the dose of UV radiation and indicate when a hazardous level for health is reached. In this sense, the sub-objectives to be carried out shall be:

- Product conceptualization. Through a bibliographic study, including patents and a market study to detect products that may exist. The advantages and disadvantages of described or existing products will be analyzed to select the product that is deemed most suitable to meet the needs of the consumer.
- Ingredients selection. The necessary ingredients for the manufacture of the indicator according to the desired characteristics for the product will be selected.
- Quality criteria and indexes. The factors that may influence the perception by the consumer of the quality of the product will be analyzed to establish the quality criteria to be met and the indexes that allow quantifying those criteria.
- Synthesis of process for product manufacturing. From the selected ingredients, the process will be established to obtain the structure and composition of the product, complying with the quality indices.



### 3. PRODUCT CONCEPTUALIZATION

At present, it is necessary to design and market a portable and ergonomic device, accessible to all users, that allows us to determine when we reach excessive exposure to ultraviolet radiation and dangerous to our health, so that it allows us to take precautionary measures such as the application of sunscreen lotion or avoid sun exposure for longer.

The composition and amount of UV radiation reaching the Earth's surface is also affected by situational and environmental factors such as pollution levels, astronomical phenomena (sun position), geographical location, weather conditions such as clouds and reflective surfaces such as sand, water and snow [2], [8]. The usefulness of this device lies in its ability to monitor UVR under any environmental and situational situation, mentioned above. In addition, you should generate a single response that takes into account the combination of different UVRs (UVA, UVB and UVC) [2]. For greater efficacy of the indicator, it should take into account the different skin types of each user and their minimal erythemal dose (MED). The MED value represents the minimum amount of UV (particularly UVB) necessary to produce sunburn on the skin after being exposed to the sun for 24-48 hours [6]. Depending on the skin type more or less elevated MED values are accepted. The skin type of each user can be classified according to the Fitzpatrick scale, which is composed of six skin phototypes ranging from Type I (lighter skin) to Type VI (darker skin), where Type I has the lowest MED value and Type VI the highest, as expressed in Table 2. Skin phototypes that accept lower MED values such as Type I and II, turn out to be the most prone to suffer from skin cancer unlike Type IV ones that accept higher MED values [6] [9].

Table 2. Fitzpatrick scale and risks [6], [9]

Phototype	Phenotype (no sun exposure)	UV response	MED UVA [J/cm <sup>2</sup> ]	MED UVB [mJ/cm <sup>2</sup> ]
I	The skin is bright white. Typical blue or green eyes. They tend to have freckles. British or Northern Europe origin.	Always burns. Never tans.	20 - 35	20 - 30
II	White skin. Blue, hazel or brown eyes. Red, blond or brown hair. European or Scandinavian origin.	Burns easily. Tans minimally.	30 - 45	25 - 35
III	Light Skin. Brown eyes. Dark hair. Central or Southern European origin.	Burns moderately. Average tanning ability.	40 - 55	30 - 50
IV	Light brown skin. Dark eyes. Dark hair. Mediterranean, Asian or Latin origin.	Burns minimally. Tans easily.	50 - 80	45 - 60
V	Brown skin. Dark eyes. Dark hair. East Indian, Native American, Latino or African origin	Rarely burns. Tans easily and substantially.	70 -100	60 - 100
VI	Black skin. Dark eyes. Dark hair. African or Aboriginal descent.	Almost never burns. Tans easily and deeply.	>100	100 - 200

### 3.1. BIBLIOGRAPHIC ANALYSIS

Next, a bibliographic study of today's existing UV radiation indicator devices is then conducted, comparing to determine which is the most effective and functional. To do this, the following aspects of each device will be verified and compared:

- **Efficacy**

- Use of sunscreen: It is checked if the device takes into account the sun protection factor applied to the skin.
- Solar radiation: The types of UVR to which the indicator is sensitive and capable of absorbing.
- Skin type: It is checked whether the device is able to distinguish between the different skin phototypes classified on the Fitzpatrick scale.
- Accuracy: It is determined whether the values provided by the device are accurate or rather indicative.

- **Lifetime**

- Resistance: It is evaluated whether the device is able to continue measuring effectively the UVR after being exposed to water, sweat and high temperatures.
- Reversibility: It is researched whether the indicator can be reusable or it will be disposable after use.
- Expiration: It is checked the stability of the indicator during storage.

- **Usability**

- Format: The shape that can be given to the device (wristband, watch, decal, pin, etc.) and its comfort for the user is evaluated.
- Intuitive design: It is assessed whether the way the device alerts the user when reaching dangerous radiation levels is simple and easy to determine.
- Accessibility: Depending on the type of design and format it is determined whether the device is suitable for use by any user.

Through Google Patent, the UB's patent and journal search website (CRAI) and the search and patent applications website, Espacenet, developed by the European Patent Office together with the member states of the European Patent Organization, a search has been carried out for the UV radiation indicator devices created from 2002 to 2020. From this search, a total of 7 sensors have been obtained, exposed below, whose purpose is to detect UV radiation and alert the user for the adoption of preventive measures.

### **3.1.1.UV indicator to signal the reduction of sunscreen efficiency (2002)**

During the year 2002 patent [US 2002/0124603 A1] was published, in which it is described an abrasion resistant device (i.e. rubbing), soap and water, capable of alerting the user when UV radiation (UVR), essentially formed from UVA and some UVB can become dangerous to our health. A photochromic indicator is used, this means that the molecule changes color in the presence of radiation due to its conformational change and is able to return to its initial structure by ceasing radiation exposure, so that it returns to its original color or very similar after repeated exposure to UV radiation. The indicator can be modified to provide a more or less delayed warning signal depending on the specific skin type (Type I to Type VI according to the Fitzpatrick scale). This invention provides the ability to apply sunscreen on the indicator in such a way the color change of the device alerts the user when the sunscreen applied to the skin and on the indicator no longer acts effectively and must be reapplied. When the user is applied sunscreen again, the indicator returns to its original color as sunscreen prevents most ultraviolet rays from activating the photochromic molecule within the indicator. The indicator used can comprise different levels of photochromic molecules to indicate when the applied sunscreen is decreasing its effectiveness in a staggered way [10].

Said indicator can be applied as a solid film (temporary tattoo) or as a fluid film on the skin (balm bar, a pen, a lotion or similar). It can also take different geometric shapes, drawings, letters, or words, so that as you absorb radiation, said drawings or words may appear to alert the user to the different levels of unprotection to which he is being exposed [10].

Table 3. Characteristics of the patent US 2002/0124603 A1

		<b>Advantages</b>	<b>Disadvantages</b>
<b>Efficacy</b>	<b>Use of sunscreen</b>	<ul style="list-style-type: none"> <li>- Alerts the user when the sunscreen no longer provides sun protection.</li> <li>- Provides an indicator to determine when there is absence of protector.</li> </ul>	<ul style="list-style-type: none"> <li>- Not all sunscreens are suitable.</li> </ul>
	<b>Solar radiation</b>	<ul style="list-style-type: none"> <li>- Measures UVA and UVB radiation (UV).</li> </ul>	<ul style="list-style-type: none"> <li>- Doesn't differentiate between UVA and UVB radiation.</li> <li>- Doesn't take into account the UVC.</li> </ul>
	<b>Skin type</b>	<ul style="list-style-type: none"> <li>- Can differentiate between different skin types (Type I to Type VI).</li> </ul>	
	<b>Accuracy</b>	<ul style="list-style-type: none"> <li>- The indicator changes color when it exposed to UV radiation and alerts us that the protector doesn't provide the same protection and you should reapply it.</li> </ul>	<ul style="list-style-type: none"> <li>- Doesn't act as a dosimeter, therefore, it doesn't indicate how much radiation is building up in your body and whether you have reached a dangerous level of radiation.</li> </ul>
<b>Lifetime</b>	<b>Resistance</b>	<ul style="list-style-type: none"> <li>- It is water and soap resistant so that it can be used when swimming.</li> </ul>	<ul style="list-style-type: none"> <li>- Can only be removed with solvents that could be harmful to the skin if used very frequently.</li> </ul>
	<b>Reversibility</b>	<ul style="list-style-type: none"> <li>- It is capable of returning to its original color several times when it ceases to be exposed to UV radiation.</li> </ul>	-
	<b>Expiration</b>	-	-
<b>Usability</b>	<b>Format</b>	<ul style="list-style-type: none"> <li>- It isn't possible for the indicator to fall or be lost.</li> <li>- Doesn't create any discomfort on the skin.</li> </ul>	<ul style="list-style-type: none"> <li>- It isn't an aesthetic or discreet method.</li> <li>- It can create subtle differences in skin tone owing to lack of tan.</li> </ul>
	<b>Intuitive design</b>	<ul style="list-style-type: none"> <li>- Intuitive, simple and easy to identify designs.</li> <li>- Eye-catching for children.</li> </ul>	-
	<b>Accessibility</b>	<ul style="list-style-type: none"> <li>- It is easy to determine when the user is exposed to UV, thanks to the fast color change.</li> </ul>	<ul style="list-style-type: none"> <li>- Designs that aren't based on the appearance of images aren't suitable for people who are color-blind.</li> </ul>

### 3.1.2. Dose responsive UV indicator (2010)

In patent [WO 2010/070290 A1], published in 2010, designs a UV indicator device that shows accumulated UVR over a period of time, which can also be adjusted to different skin types. It also allows you to apply sunscreen on the device to get a more accurate result of accumulated UV radiation. In this invention UV-sensitive materials are used that are more effective in absorbing UVB light than UVA light, as it is the most harmful. This device uses irreversible components, combining acid releasing agents driven by UVB and/or UVA radiation and a pH indicator that presents an altered color between the deprotonated and acid forms. The UVR-sensitive material used can be modified to exhibit a color change in response to different MED values [11].

The indicator consists of two materials. The first material presents changes color immediately in response to an initial UVR dose (colorless to green), while the second material changes color in a delayed manner (gradually) in response to an increase in the UVR dose (from yellow to red/pink). Such changes in the color of each material can be displayed separately or alternatively, they are printed on top of each other to observe progressive color changes as in a "traffic light". These methods would use reference patterns corresponding to known UVR doses or causing an image to be revealed or hidden in response to the UVR dose, to help people determine the dose received. It is a disposable device made with low-cost materials that can take the form of a bracelet, label, sticker or ink, and remain stable for months as long as it is protected from sunlight [11].



Table 4. Characteristics of the patent WO 2010/070290 A1

		<b>Advantages</b>	<b>Disadvantages</b>
<b>Efficacy</b>	<b>Use of sunscreen</b>	- Can be covered with sunscreen.	- It isn't specified whether all sunscreens are effective.
	<b>Solar radiation</b>	- Its components are sensitive to UVB and UVA radiation.	- Not sensitive to UVC radiation. - Its main sensor is only sensitive to UVB radiation.
	<b>Skin type</b>	- It adapts virtually all skin types.	-
	<b>Accuracy</b>	- The device can be adapted to get a response to different MED values.	-
<b>Lifetime</b>	<b>Resistance</b>	-	-
	<b>Reversibility</b>	-	- It uses irreversible components, therefore, they are single-use devices.
	<b>Expiration</b>	- It can be kept stable for months, as long as it stays protected from UVR and moisture.	-
<b>Usability</b>	<b>Format</b>	- Wide range of formats that adapt to the needs of consumers (wristband/sticker/label/ink).	- The formats applied directly to the skin aren't very discreet. - It can leave unwanted marks due to lack of tan.
	<b>Intuitive design</b>	- Distinguishes easily between a first dose of UVR and a prolonged dose that allows distinguishing different MED values. - Uses simple and intuitive designs to alert when a dangerous dose has been reached. - In the case of using a color-based indicator, you can compare reference patterns to identify the meaning of the colors.	-
	<b>Accessibility</b>	- Can be used by both children and adults. - Its design can be adapted for the appearance of images and that is suitable for people with color blindness.	- Indicators based on color changes aren't suitable for people with color blindness.

### 3.1.3. Ultraviolet exposure wristband indicator (2014)

In 2014 the patent [WO 2014/135871 A2] was published, describing an electronic bracelet with a sensor that monitors UVA and UVB radiation in a way that helps prevent overexposure to UV radiation by alerting the user that their sunscreen is no longer effective when a specific dose of solar radiation is reached. It contains an electronic indicator that can be programmed to enter the sun protection factor used and alerts the user more accurately when levels of UV radiation dangerous to their skin type are reached using UV index (UVI) [12]. The EPA's (United States Environmental Protection Agency) Ultraviolet Index (UVI) is a standard measurement indicating the intensity of UVR reaching the Earth's surface at each wavelength weighted by its harmful action on man, carried out by the World Health Organization (WHO) in collaboration with the World Meteorological Organization (WMO), the United Nations Environment Programme (UNEP) and the International Commission on Non-Ionizing Radiation Protection (ICNIRP). It standardizes the methods of calculating the index and also provides a color code and graphics to offer the information to the public [1], [13], [14].<sup>1</sup>

This information can be entered either directly by indicating the protection factor value of the product used through a mobile or similar device, or by scanning the product's bar code where all its information is recorded, by the mobile phone or similar device, or, as another option, by pre-designing the device for a single specific protection factor. On the other hand, it also allows you to enter information about the user's skin type, according to the Fitzpatrick scale [12].

Once the user puts on the wristband it activates and every three or four seconds the sun radiation (UVI) is controlled. When the sun's UV rays change, the UV sensor detects it and updates the processor that recalculates the time needed before applying sunscreen again. The device can be connected wirelessly to any smartphone or computer, where at the end of the day the user can collect all the information about the UV exposure, the amount of vitamin D received and the potential risk of sunburn. In addition, it can have a vibrator, speaker and a visual display, configured to indicate to the user when the detected ultraviolet radiation exceeds the predefined dose. An optional feature, is to detect that the user is introduced into the water in order to take into account the remaining time before applying sunscreen again, contemplating

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<sup>1</sup> Go to Appendix 1 for look at UV index (UVI) categories according to the EPA.

the possible degradation of this in the water. The waterproof device is designed to restart after a time afterward the user removes it or by pressing a button [12].

The wristband consists of a flexible bistable spring band and layers of stainless steel sealed inside a fabric, plastic, rubber or silicone cover. The wristband can be straightened, creating tension within the metal elastic band. By tapping the wristband gently against the wearer's wrist it is wrapped around it with lace methods to prevent the case from falling off due to wear. The material can be fabric, plastic, rubber and silicon. In addition, it has a rechargeable battery that supplies power that can be recharged with a solar cell or by induction [12].

Table 5. Characteristics of the patent [WO 2014/135871 A2]

		<b>Advantages</b>	<b>Disadvantages</b>
<b>Efficacy</b>	<b>Use of sunscreen</b>	<ul style="list-style-type: none"> <li>- It takes into account the sun protection factor.</li> <li>- It takes into account variations in UV exposure to recalculate the time needed to reapply sunscreen.</li> </ul>	<ul style="list-style-type: none"> <li>- The protector isn't applied directly on the device, therefore, it makes estimation and by means of a statistical evaluation it guides the user on the effectiveness of the protector, thus it can give a not totally exact answer.</li> <li>- In the case of buying the devices with pre-sets sunscreen options aren't transferable to other people or changes of the sun protector.</li> </ul>
	<b>Solar radiation</b>	<ul style="list-style-type: none"> <li>- It is sensitive to UVA and UVB radiation.</li> </ul>	<ul style="list-style-type: none"> <li>- Doesn't take into account UVC radiation.</li> <li>- Doesn't differentiate between absorbed radiation</li> </ul>
	<b>Skin type</b>	<ul style="list-style-type: none"> <li>- Distinguish between different skin types according to the Fitzpatrick scale.</li> </ul>	-

Table 5. Characteristics of the patent [WO 2014/135871 A2] (Continued)

		<b>Advantages</b>	<b>Disadvantages</b>
<b>Efficacy</b>	<b>Accuracy</b>	<ul style="list-style-type: none"> <li>- It has an omnidirectional reflector that ensures that solar radiation reaches the UV detectors.</li> <li>- Monitors daily sun radiation every 2-3 seconds, detecting variations in UV exposure and recalculating the time needed to reapply the sunscreen.</li> <li>- Detects water and adjusts calculations based on sunscreen degradation.</li> </ul>	<ul style="list-style-type: none"> <li>- The wristband alarm is only designed to be activated at a predetermined level of UV radiation, at which point the protective lotion should be reapplied. The warning doesn't discriminate between several levels of exposure.</li> </ul>
	<b>Resistance</b>	<ul style="list-style-type: none"> <li>- It has fitting methods to prevent it from falling out due to wear.</li> <li>- It is water resistant.</li> </ul>	-
	<b>Lifetime</b>	<ul style="list-style-type: none"> <li>- This is a reversible device that resets when it detects that the wristband isn't attached to the user or when a button is pressed.</li> </ul>	-
	<b>Expiration</b>	<ul style="list-style-type: none"> <li>- When using electronic components, stability isn't altered during storage.</li> </ul>	-
	<b>Format</b>	<ul style="list-style-type: none"> <li>- It is a bracelet with an easy to use closure system when the user has slippery hands.</li> </ul>	<ul style="list-style-type: none"> <li>- Due to its size and location it can leave unwanted marks on the skin due to lack of tan.</li> </ul>
<b>Usability</b>	<b>Intuitive design</b>	<ul style="list-style-type: none"> <li>- Ability to connect to a device wirelessly to display more data.</li> <li>- Alerts easily by acoustic, vibration or display signal.</li> <li>- Display the data obtained on the smartphone or computer.</li> </ul>	<ul style="list-style-type: none"> <li>- The procedure for entering or reviewing data into the device can be complex.</li> <li>- A mobile phone or computer connected to the network and with GPS is required to use all the device options.</li> </ul>
	<b>Accessibility</b>	<ul style="list-style-type: none"> <li>- Diversity in signals (acoustic, vibration or visual) promotes accessibility to users with color blindness.</li> </ul>	<ul style="list-style-type: none"> <li>- The complexity of their procedures can restrict their use only to people who are accustomed to the handling of computer devices.</li> <li>- People who don't have the necessary technology cannot access all its possibilities of use.</li> </ul>

### 3.1.4. Ultraviolet monitoring device (2016)

Patent [US 9476765 B2] of year 2016 refers to a portable and interactive device capable of monitoring a user's exposure to UVR and alerting the person to the need to apply sunscreen. The device's UV sensor has a photodiode that continuously measures a voltage proportional to the UVI. It provides an interface that allows the user to enter personal information using a mobile phone, computer, tablet or other device connected to the network. Information is requested about the skin type on the Fitzpatrick scale, the sun protection factor (SPF) used, what time it was applied, occupation and age. Includes a UV detector coupled to a processing unit that determines the UVI and direction of incoming UV light. This information is available to the user through the mobile device connected to the network by an interactive application and is used to provide recommendations to the individual to reduce the risk of UVR exposure, such as when to reapply sunscreen and what type of clothing to wear. It can also determine the amount of time that has elapsed since the user applied the sunscreen and generate alerts [15].

In this application, the user will be able to view long-term statistics on UV exposure and enter information about sunburn received to allow continuous monitoring. The application also allows the user to enter a location or track it themselves through the GPS of the device connected to the network, to allow them to retrieve a UVI forecast specific to that location obtained via the EPA website and thus be able to compare it to the measured index [15].

In addition, it has an orientation unit that detects the orientation of the UV sensor and emits signals indicating the displacement of the device. The central processor unit (CPU) creates an average of the UVI for each of the direction, which removes noise from the collected data to facilitate accurate monitoring of the user exposure. The UV direction indicator separately shows the user the intensity of UV radiation from multiple different directions and notifies the user of the relative magnitude of the average UV index measured in each of multiple directions. In this way, the user can determine where protection is needed to avoid further exposure. At the end of the day, the user can restart the UVR measurement with a button. In addition, the device has a power supply that provides power, with a rechargeable battery, through USB connection or induction or even could have a solar cell [15].

It can be shaped like a pendant, button, bracelet, etc. The means of attachment can be a band, a strap, a chain, a clip, glue, thread, etc. The UVI information is shown to user in real time through the indicator unit, which can comprise 5 light-emitting diodes (LEDs) that are of the same color, as the color of EPA UVR scale. Once a certain UVI level is reached, the user enters when sunscreen has been reapplied to start a timer that will notify the user when sunscreen should be reapplied [15].

Table 6. Characteristics of the patent [US 9476765 B2]

	<b>Advantages</b>	<b>Disadvantages</b>
<b>Use of sunscreen</b>	<ul style="list-style-type: none"> <li>- The device uses information previously entered in the mobile phone or similar, about the protection factor used to inform the user when to reapply sunscreen.</li> </ul>	<ul style="list-style-type: none"> <li>- By not applying sunscreen directly to the device, it doesn't take into account that the lotion can lose its effectiveness ahead of time, due to abrasion, contact with water or sweat.</li> </ul>
<b>Solar radiation</b>	<ul style="list-style-type: none"> <li>- Measured UV radiation is provided based on UV indices (UVI) calculated by the EPA.</li> <li>- UVI take UVA and UVB radiation into account.</li> <li>- Using GPS it makes a UV index forecast specific to the location in which is the user.</li> </ul>	<ul style="list-style-type: none"> <li>- Doesn't take into account UVC radiation.</li> <li>- It doesn't differentiate between radiations.</li> <li>- It conducts forecasts and measurements that may not match reality, if the information entered isn't entirely correct.</li> <li>- You won't be able to get location forecasts if you are somewhere without a GPS signal.</li> </ul>
<b>Efficacy</b>		
<b>Skin type</b>	<ul style="list-style-type: none"> <li>- It takes into account the skin type based on the Fitzpatrick scale, to obtain recommendations according to your skin.</li> </ul>	-
<b>Accuracy</b>	<ul style="list-style-type: none"> <li>- The device consists of an orientation unit that detects the orientation of the UV sensor and thus obtains accurate results even with the user's movement.</li> <li>- It notifies the user of the average UV index measured in each direction in which it is received, in order to determine where greater protection is required.</li> </ul>	-

Table 6. Characteristics of the patent [US 9476765 B2] (Continued)

		<b>Advantages</b>	<b>Disadvantages</b>
<b>Lifetime</b>	<b>Resistance</b>	-	-
	<b>Reversibility</b>	- It is a reversible electronic device, which allows resuming measurement when desired.	-
	<b>Expiration</b>	- Given that it is an electronic sensor its stability isn't affected during storage.	-
<b>Usability</b>	<b>Format</b>	- It can take various forms such as a pendant, a button, a device that looks like a wristwatch, etc.	- This is a relatively large, few unobtrusive device that isn't suitable for all the user's daily activities. - It can leave unwanted marks on the skin due to lack of tan.
	<b>Intuitive design</b>	- Real-time UV index information is displayed through the indicator unit, using 5 LEDs in the colors of the well-known EPA UV scale. - It provides a lot of useful information through the mobile device, with forecasts and recommendations. Alarms can be programmed to know when to reapply cream or if a too high level of radiation has been reached.	- The procedure for entering or reviewing data into the device can be complex. - A mobile phone or computer, connected to the network and with GPS is required to use all the device options.
	<b>Accessibility</b>	- Adults can get a lot of information clearly and easily through an app and directly from the indicator.	- The complexity of its procedures may restrict its use only to people who are used to handling computer devices. - People who don't have the necessary technology cannot access all its possibilities of use. - Colored LED indicators aren't suitable for people with color blindness.

### **3.1.5. Soft, stretchable, epidermal sensor with integrated electronics and photochemistry for measuring personal UV exposures (2018)**

In 2018, PLOS ONE journal published an article on the design and development of a portable UV sensor that accurately quantifies personal UVR exposure, sunscreen reduction and provides personalized recommendations. The device is an ultra thin, elastic, breathable heart-shaped patch that adapts to the surface of the skin and has similar properties. Therefore, it is compatible with emollients and sunscreens, allowing skin care products and sunscreens to be applied over the patch. The patch consists of a soft, electronic, elastic, ultra-thin functional layer, besides a photosensitive dye. Said irreversible photosensitive dye changes color after exposure to UVR, this change corresponds to the intensity of the UV radiation and is analyzed with a smartphone camera using a quantification algorithm. The algorithm uses a reference color system to allow precise quantification of the color change of the UV dye under different lighting conditions [16].

The device distinguishes between UVA and UVB radiation. The UVB is calculated using a pre-calculated search table that provides the conversion factor as a function of the amount of ozone in the atmosphere, such information is extracted from the website of the National Environmental Prediction Centers of the National Oceanic and Atmospheric Administration (NOAA) and the solar zenith angle (SZA) determined by the location and time of the GPS. The UVA and UVB results are then checked against the maximum expected values for the user's location, determined according to the UVI's forecast web services. This process avoids sporadic and erroneous readings. If no Internet connection is available, the result is checked against search tables that relate the maximum UVI data to the corresponding maximum values for UVA and UVB in different geographical locations and time. Depending on the geometry of the solar position and the orientation of the surface, personal exposure to UV rays can be greater or less than the exposure predicted by UVI, sometimes by factors greater than 30% [16].

Daily safe personal UV doses are calculated based on the skin phototype determined by the Fitzpatrick scale through a simplified questionnaire completed by the user in an interactive application installed on the smartphone, together with the MED [16].

The patch maintains accurate readings even after exposure to ocean water, high temperatures and humidity, excessive sweat, skin care products and sunscreens. The patch structure allows for comfortable skin contact and continuous use for 5 days [16].



Table 7. Characteristics of the device described in POLT ONE

		<b>Advantages</b>	<b>Disadvantages</b>
<b>Efficacy</b>	<b>Use of sunscreen</b>	- The user can apply sunscreen on the patch and get results on its effectiveness.	-
	<b>Solar radiation</b>	- Its components are sensitive to UVB and UVA radiation. - It distinguishes between UVB and UVA radiation. - For the calculation of the radiation, it takes into account the amount of ozone and the position of the sun where the user is.	- It is not sensitive to UVC radiation. - For a good UV comparison, a mobile device, internet and GPS signal are required.
	<b>Skin type</b>	- It takes into account the different skin types.	-
	<b>Accuracy</b>	- Accurate results are obtained under different environmental conditions and with the use of skin products. - Average multiple square readings for improved data accuracy.	-
	<b>Resistance</b>	- It is resistant to water, sweat, sunscreens, skin products and high temperatures.	-
<b>Lifetime</b>	<b>Reversibility</b>		- Ink is irreversible.
	<b>Expiration</b>	- The components used can be kept stable during storage prior to use.	-
<b>Usability</b>	<b>Format</b>	- Ultra thin, elastic and breathable patch that adheres to the skin.	- It is a relatively large and little unobtrusive device. - It can leave unwanted marks on the skin due to lack of tan.

Table 7. Characteristics of the device described in POLT ONE (Continued)

		<b>Advantages</b>	<b>Disadvantages</b>
<b>Usability</b>	<b>Intuitive design</b>	<ul style="list-style-type: none"> <li>- It is an intuitive design as the user only has to capture an image of the patch with his mobile device. It collates and calculates the UV dose and provides that information to the user along with protection advice.</li> </ul>	<ul style="list-style-type: none"> <li>- The color change is quantified by a mobile phone, which means having a camera phone that correctly captures images of the patch at a fixed angle to avoid glare and shadows.</li> <li>- The mobile phone needs to be connected to the network and have a GPS signal, for full use.</li> </ul>
	<b>Accessibility</b>	<ul style="list-style-type: none"> <li>- Given that it is not necessary for the user to analyze the color change, it is suitable for anyone despite having color blindness.</li> </ul>	<ul style="list-style-type: none"> <li>- This device is only suitable for people who are used to using computer devices.</li> <li>- Users must have the necessary technology to use the indicator.</li> </ul>

### 3.1.6. Skin color-specific and spectrally-selective naked-eye dosimetry of UVA, B and C radiations (2018)

In the journal *Nature Communications*, an article was published in 2018 regarding a disposable device that acts as a UVR dosimeter and allows spectrally selective calorimetric differentiation of different UV radiation using a photoelectrochromic ink that, under different UV sources, provides a response in the form of color change from colorless to blue. The high energy UVC produces a faster response in indicator color change, followed by the UVB and UVA, respectively. Combine this ink with simple components that allow naked eye monitoring of UVR, even at low doses [2].

In order to the UV sensor alerts more accurately to the users about excessive UV exposure, it is covered with transparent films such as optical filters (TFF) that alter the dose of UVR received, allowing six customized sensors to be designed for different skin types according to the Fitzpatrick scale and their corresponding MED [2].

This device has a wristband shape in which four faces are represented with different moods, the drawing of which increases in intensity with rising time of exposure to UV rays. The first two faces have a smiley design and represent the exposure to 25% and 50% of MED, respectively. The third is a neutral face representing exposure at 75% of MED, while the fourth is a sad face that warns the user that he has approached the maximum safe exposure limit and should

therefore take protective measures to avoid overexposure. The sensor shows more than 95% accuracy for all UV doses tested at 10 J·m<sup>-2</sup> increments [2].

The ink used to prepare the smiley sensors remains stable for more than 8 weeks obtaining an accuracy of more than 98% at all doses tested [2].

Table 8. Characteristics of the device described in Nature Communications journal

		<b>Advantages</b>	<b>Disadvantages</b>
	<b>Use of sunscreen</b>	-	-
	<b>Solar radiation</b>	<ul style="list-style-type: none"> <li>- It takes into account UVA, UVB and UVC radiation.</li> <li>- It has the ability to spectrally differentiate UVR.</li> </ul>	-
<b>Efficacy</b>	<b>Skin type</b>	<ul style="list-style-type: none"> <li>- Customized devices can be produced for different skin types (from type I to type VI) so that users with different skin phototypes can control their maximum solar radiation limits.</li> </ul>	-
	<b>Accuracy</b>	<ul style="list-style-type: none"> <li>- The sensor shows an accuracy of more than 95% for all UV doses.</li> <li>- Indicates when we should take measures to avoid overexposure to sunlight.</li> </ul>	-
<b>Lifetime</b>	<b>Resistance</b>	<ul style="list-style-type: none"> <li>- Due to its polymer coating, the device is waterproof and sweat resistant.</li> </ul>	-
	<b>Reversibility</b>	-	- It is irreversible and disposable.
	<b>Expiration</b>	<ul style="list-style-type: none"> <li>- PMA-LA ink and paper sensors have high specificity, durability, stability and reliability under storage conditions. Remains stable for more than 8 weeks.</li> </ul>	-

Table 8. Characteristics of the device described in Nature Communications journal (Continued)

	<b>Advantages</b>	<b>Disadvantages</b>
<b>Format</b>	<ul style="list-style-type: none"> <li>- The wristband format is easy to put on and take off.</li> <li>- Can be adapted to other formats.</li> </ul>	<ul style="list-style-type: none"> <li>- May leave unwanted marks due to lack of tan.</li> </ul>
<b>Usability</b>	<ul style="list-style-type: none"> <li>- The design is based on faces that are simple and easy to understand.</li> <li>- Given its intuitive design, it is easy to determine when a dangerous UV dose is reached for both adults and children.</li> </ul>	-
<b>Accessibility</b>	<ul style="list-style-type: none"> <li>- Since it isn't based on a device with color degradation, but on lighting or the appearance of drawings, this sensor is suitable for people with color blindness.</li> </ul>	-

### 3.1.7. Ultraviolet indicators, formulations and sun care kits comprising the same (2020)

In January 2020 a patent [WO 2020/006153 A2] was published describing UVR-sensitive inks capable of informing the user of real-time UV exposure with a built-in sun protection kit. The UVR-sensitive sensor is applied to the user's skin and allows sunscreen to be worn on the skin and on the sensor to show when it is losing effectiveness. Full spectrum or broadband photochromic dyes with high UVB and low UVA reactivity are used. In addition, it is a stable chemical compound capable of changing color after photon irradiation due to reversible structural changes, therefore, once the radiation ceases or sunscreen is applied to the sensor, the dye returns to its initial color and structure. It can be incorporated into an adhesive on the skin that resists rubbing and moisture (water or sweat), although it could also be adapted to be incorporated into stickers, bracelets, jewelers and similar [17].

Preferably, the indicator is colorless in the absence of UVR and changes to visible colors when exposed to UVR, by combining multiple UV indicators that respond to UV indices (UVI) of 3, 6, 8 and 11. In addition, non-photochromic reference colors can be put to make it easier for the user to identify when a certain level of radiation has been reached [17].

Table 9. Characteristics of the patent [WO 2020/006153 A2]

		<b>Advantages</b>	<b>Disadvantages</b>
<b>Efficacy</b>	<b>Use of sunscreen</b>	- Allows using sunscreen directly on the photo-sensitive dye, to alert when it is no longer adequately protected.	-
	<b>Solar radiation</b>	- Selectively detects UVA and UVB radiation.	- It doesn't take into account UVC radiation. - It focuses more on protection against UVB radiation.
	<b>Skin type</b>	-	- The UV sensor isn't designed to distinguish between different skin phototypes, it is based on the protection factor of the photoprotectors.
	<b>Accuracy</b>	- Dye selectivity allows the user to be accurately informed of UVB exposure.	-
<b>Lifetime</b>	<b>Resistance</b>	- Can resist rubbing and moisture (water or sweat).	-
	<b>Reversibility</b>	- The UV indicator is reversible and can return to its original shape several times when exposure to radiation is ceased or reduced.	- When you reapply sunscreen, the indicator returns to its initial state or similar, therefore, doesn't serve as a dosimeter and doesn't warn of the accumulated radiation in your body.
	<b>Expiration</b>	- Components remain stable during storage.	-
<b>Usability</b>	<b>Format</b>	- It is applied directly to the skin, utterly adapting to the user. - It can be adapted to be incorporated in stickers, wristbands, jewels and similar. - It is designed to create a kit with sunscreen and indicator.	- For the format applicable directly on the skin, its removal can be abrasive to the skin, as it is water resistant. - The indicator must be relatively large in size to properly appreciate the color change. - It can leave subtle marks on the skin due to lack of tan.
	<b>Intuitive design</b>	- It is a simple design based on color changes, easy to identify with reference colors. - It is also intuitive as it follows the EPA's UV index scale.	-

Table 9. Characteristics of the patent [WO 2020/006153 A2] (Continued)

		Advantages	Disadvantages
<b>Usability</b>	<b>Accessibility</b>	- Given its simple and intuitive design it can be easily used by both children and adults.	- People with color blindness may find it difficult to identify absorbed radiation.

### 3.1.8. Comparative of the bibliographic study

After the analysis of the different patented devices, is desired to perform a first sifting and thus obtain the three best sensors so far described with the help of Table 10. It has been considered that the most efficient device should have the following features:

- Allow the sunscreen to be applied directly to the device to obtain a more truthful result on wear and loss of protection factor effectiveness (SP).
- That the UVR sensitive indicator reacts to UVA, UVB and UVC radiation, due to ozone layer wear and the increasing incidence of skin cancer (R).
- Distinguish between different skin types according to the Fitzpatrick scale, as each one admits different MED values (ST).
- Gives accurate results based on the actual UVR the user is exposed to according to his environmental situation (AC).
- The device must be water and sweat resistant in order to be used without restrictions (RS).
- That the indicator used is reversible and reusable (RV).
- The indicator must be stable so that it can remain stored until its used (E).
- That it uses a format that is comfortable, discreet and non-invasive on the skin (F).
- That it uses a simple and intuitive design, for easy understanding and use by both children and adults (ID).
- That the design and way of warning the user is accessible for children, adults and people with color blindness (A).

Table 10. Comparative of patented devices from 2002 to 2020

Devices	Efficacy				Lifetime			Usability			
	SP	R	ST	AC	RS	RV	E	F	ID	A	
<b>UV indicator to signal the reduction of sunscreen efficiency</b>	✓	○	✓	✓	○	✓	-	○	✓	✓	
<b>Dose responsive UV indicator</b>	✓	○	✓	✓	-	○	✓	✓	✓	✓	
<b>Ultraviolet exposure wristband indicator</b>	○	○	✓	✓	✓	✓	✓	○	○	○	
<b>Ultraviolet monitoring device</b>	○	○	✓	✓	-	✓	✓	○	○	○	
<b>Soft, stretchable, epidermal sensor with integrated electronics and photochemistry for measuring personal UV exposures</b>	✓	○	✓	✓	✓	○	✓	○	○	○	
<b>Skin color-specific and spectrally-selective naked-eye dosimetry of UVA, B and C radiations</b>	-	✓	✓	✓	✓	○	✓	✓	✓	✓	
<b>Ultraviolet indicators, formulations and sun care kits comprising the same</b>	✓	○	○	✓	✓	✓	✓	✓	✓	○	

a) Each tick (✓) corresponds to the compliance of a feature described in section 3.1.8., being the maximum of ticks in the case of efficacy, 4 (✓✓✓✓) and 3 in the case of lifetime and usability (✓✓✓). Otherwise, a circle will appear (○) and if there isn't information about a feature a dash will be added (-).

As can be seen in Table 10, the device described in the Nature Communications article [2], Skin color-specific and spectrally-selective naked-eye dosimetry of UVA, B and C radiations is the one that gathers the more number of desired characteristics, therefore, becomes the main candidate for production. After carrying out the market study, the viability of its commercialization will be assessed, comparing its characteristics with those of the products currently on sale.

## 3.2. MARKET STUDY

According to a study conducted in 2019 by the World Tourism Organization (UNWTO), Spain is the second most visited country in the world [18]. Along these lines, data provided by the National Institute of Statistics determine that between 2016 and 2019, Spain received a total of 280 million international tourists, with the busiest periods occurring in July and August. Specifically, in the month of August our country welcomes up to 9.5 million tourists, of which approximately 8 million travels to autonomous communities characterized by their beach tourism, as now Andalusia, Catalonia or the Balearic Islands. In the national scene there are also clear preferences for this type of tourism in the summer months: of the 25 million holiday trips that took place in July and August within the territory, approximately 16 million went to autonomous communities famous for concentrating most of the tourist activity on its coasts (Catalonia, Valencia Community, Balearic Islands, Canary Islands, Andalusia and the Region of Murcia), which is practically equate to 64% of the total. If these data are framed in the area of Catalonia, it is obtained that in the months of July and August it receives 23.56% of the quota of international tourists and 13.63% of the national tourism.<sup>2</sup> The set of data analyzed seems to indicate a trend in tourism towards places with sun and beach, besides to some preference for Catalonia as a tourist destination. This trend is supported by a survey conducted in 2018 by the Centre for Sociological Research (Centro de Investigación Sociológica, CIS), which asked 2128 people their opinions on various current issues and determined that 50% of those survey respondent chose these destinations as their first or second choice when travelling [19].

Once the importance of sun and beach tourism in our society has been demonstrated, it has proceeded to analyze the habits of photoprotection and the general attitudes towards the sun of the population. In an online survey carried out by the Industria Farmacéutica Cantabria (IFC) to 5965 people, it was obtained that 58.27% of those survey respondent used a sun protection factor (SPF) equal to or higher than 50, 31.06% an SPF of 30, 8.58% an SPF lower than 30 and

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<sup>2</sup> Go to Appendix 2 to see the tables of data on tourism in Spain obtained in: National Institute of Statistics (Instituto nacional de estadística, INE), [Online]. Available: [https://www.ine.es/dyngs/INEbase/es/categoria.htm?c=Estadistica\\_P&cid=1254735570703](https://www.ine.es/dyngs/INEbase/es/categoria.htm?c=Estadistica_P&cid=1254735570703). [Accessed: 24-Mar-2020].



only 2.09% didn't use sun protection. In addition, 74% of people who use sunscreen reapply it twice or more. This survey also considers the timing of sunscreen use, showing that although approximately 65% of respondents use it occasionally, the remaining 35% use it throughout the year [20]. On the other hand, in another survey conducted by a student of the Faculty of Medicine of the University of Malaga (M. de Troya Martín), with a sample of 1054 people from both Spaniards and foreigners, it was obtained that 56.70% of those respondents like to sunbathe, 65.50% understand this practice as healthy for the body and 57.70% feel that it improves their state of mind. If we consider the photoprotection habits of this sample, we find that 91.40% of people believe it is worth using sunscreen to avoid problems in the future, 68.10% use an SPF equal to or greater than 15, and 61.30% habitually carry out three or more sun protection practices (use of umbrella, sunglasses, hat or cap, avoid midday, use photoprotection, etc.) [21]. These data demonstrate a community attitude quite favorable to sunbathing, besides the fact that photoprotective behaviors are widespread among the population. These behaviors are also favored by the opinion of the health sector, as 77% of the doctors surveyed by the IFC actively recommend photoprotection, all year round (88%) and with an SPF of 50 or more (84%) [20].

Finally, it has been purposed to extract information about those who are most likely to carry out photoprotection behaviors and to show a more positive attitude towards the practice of sunbathing. Taking as a reference the survey conducted by the student of the Faculty of Medicine of Malaga, significant differences have been observed between men and women. Women like to sunbathe more than men and carry out more photoprotection habits, besides, there is a higher percentage of women who use photoprotectors with an SPF  $\geq 15$  and are more aware of the benefits of using sunscreen to avoid problems in the future. Significant differences in the population have also been obtained depending on their age. People aged 30 and under enjoy sunbathing more, take it at peak radiation hours (midday) and carry out in less photoprotection practices, such as now using SPF sunscreen  $\geq 15$ . Participants in this age group are less aware that sunscreen can prevent problems in the future and this is reflected in a higher incidence of sunburn [21].

Analyzing the set of data presented, it is deduced the importance of sun and beach tourism in our society (and, more specifically, in Catalonia) and the wide acceptance this practice has in our country, both by Spaniards and foreigners. It also shows the high incidence of sun

protection habits in the population and the high degree of awareness, both by society and by the health authorities, of the impact of the sun's rays on our health. Lastly, it has been detected that women and people over 30 years old show more photoprotective behaviors and are also more aware of the impact of such practices on their health, thus they could be a wide target in terms of distribution and marketing of the product.

Next, a search is carried out of the UVR indicator products that are currently on sale through online platforms, in order to analyze their market and points of sale prices, as shown in Table 11. The characteristics of each device will also be compared in the Table 12, according to the criteria described above in section 3.1.8, excluding the expiration section.

Table 11. Marketed UVR indicators.

Brand	Devices	Online distributors	Market price [€]	Unit price [€]
Everyday Baby	Sun protection indicator, SUN HERO (10 uds)	Bebes y mami / Everyday baby	9.95 - 9.99	1.00
Smart lab	Smart UV Checker FUV-001 (1 uds)	Amazon / Ebay	28.02 - 31.90	28,02 - 31,90
Sanitec	Smartsun, solar indicator wristband (5 uds)	Promofarma / Amazon	6.86 - 7.50	1.37 - 1.50
ISIDIN	CitroBand +UV Tester (1 uds)	Farmacia morlan / Linefarma / Farmacia Paracuellos	9.95 - 12.42	9.95 - 12.42
/	UV-Tester (1 uds)*	Solostocks	0.36 - 0.74	0.36 - 0.74
/	UV measuring wristband (10 uds)	Ebay / Amazon	15.59 - 16.99	2.99

\* The device has been found on a website selling merchandising for companies, therefore, it is intended for wholesale.

To search for devices on sale online, websites of Spanish pharmacies, supermarkets and large surfaces such as Caprabo, Carrefour, Alcampo, Aldi, Mercadona and Ldl have been used, as well as drugstores such as Clarel or Druni. A search has also been carried out through online distributors such as Amazon, Ebay, Solostocks, Bebes y mami or Everyday baby. After this search it is observed that it is a product little marketed and exploited, due to its scant variety and few distributors. Currently, these devices can only be obtained from pharmacies and some

online distributors. It is also proven that there is a wide range of prices (from 1.00 € to 31.90 € per unit), ranging from the most expensive (Smart UV Checker FUV-001), due to its electronic technology, to the cheapest (UV-Tester or SUN HERO sun protection indicator), for its simplicity and low cost materials.

Table 12. Characteristics of the devices for sale<sup>3</sup>

Device	Efficacy				Lifetime		Usability		
	SP	R	ST	AC	RS	RV	F	ID	A
Sun protection indicator, SUN HERO	✓	○	○	✓	✓	✓	○	✓	○
Smart UV Checker FUV-001	○	○	○	✓	○	✓	○	✓	○
Smartsun, solar indicator wristband	✓	○	○	✓	✓	○	○	✓	○
CitroBand +UV Tester	-	○	○	✓	✓	✓	○	✓	○
UV-Tester	-	○	○	✓	✓	-	○	✓	○
UV measuring wristband	✓	○	○	✓	-	✓	○	✓	○

a) Each tick (✓) corresponds to the compliance of a feature described in section 3.1.8., being the maximum of ticks in the case of efficacy, 4 (✓✓✓✓), 2 in the case of lifetime (✓✓) and 3 in usability (✓✓✓). Otherwise, a circle will appear (○) and if there isn't information about a feature a dash will be added (-).

As a summary, the devices found in this search are composed of indicators sensitive to UVA and UVB radiation, don't take into account the user's skin type and show the results obtained in a simple and understandable way. Such devices warn the user of the radiation reached through gradual color changes, which is a disadvantage for all those with color blindness, except the Smart UV Checker FUV-001, which alerts through the mobile phone with specific messages. The disadvantage of the latter is that it requires a mobile phone and basic knowledge of its use, which limits the age range to which the sale of the device can be directed. On the other hand, the indicators take mostly form of wristband, with the exception of the sun protection indicator SUN HERO which is a skin adhesive and the Smart UV Checker FUV-001 which is connected directly to the mobile phone. In the case of wristbands and stickers, these

<sup>3</sup> In Appendix 3 you will find the sales URLs of UVR indicator devices.

are very little discreet formats that can leave unwanted marks due to lack of tan on the skin, and in the case of the device connected to the mobile phone, it doesn't provide real values of the radiation dose received by the user as it isn't always found exposed to sunlight in the same way as the user would.

From this analysis it has been detected that the UVR indicator devices currently on the market lack features such as differentiation of different skin types and sensitivity to UVC radiation, besides use designs that aren't accessible to all users with undesirable formats for the tan and not all of them admit the application of sunscreen.

### **3.3. SELECTION OF THE DEVICE TO DESIGN**

Taking into account the comparative conducted in the bibliographical analysis and the market study, the decision to choose for its production the device described in the article Skin color-specific and spectrally-selective naked-eye dosimetry of UVA, B and C radiations is reaffirmed. Said device stands out for its functionality and versatility with respect to formats, for allowing the spectrally selective calorimetric differentiation of UVA, UVB and UVC and for being able to adjust to react to different values of MED simulating the different skin types according to the Fitzpatrick scale. In addition, the method of alerting the user is very simple, based on a change in the color of the indicator to make an image appear (from invisible to blue) that warns of the different MED values that your body is being exposed to. Finally, the wide variety of shapes the device can take makes it easy to use for people who are color blindness and of all ages, from children to the elderly.

Nevertheless, this device isn't without its disadvantages. On the one hand, it uses an irreversible indicator. However, the indicator ink used is combined with materials such as filter paper and transparent sheets, making it a low-cost disposable sensor. On the other hand, the indicator coating used is hydrophobic which avoid some sunscreens or similar from being spread on it correctly. Despite this, there are currently hydrophilic treatments that could be carried out on the surface of the device in such a way that the aforementioned inconvenience would be solved, since the sunscreen could be applied without being repelled by it.

### 3.3.1. Device description

The UVR indicator device<sup>4</sup> uses a photoelectrochromic ink consisting of two components. On the one hand, the multi-redox polyoxometalate (POM), more specifically the phosphomolybdic acid, also known as PMA, that generates a unique response to specific UV wavelengths (UVA, UVB and UVC). On the other hand, an electronic donor (Lactic Acid or LA) that can induce differentiable levels of reduction of the PMA under different UV sources (multi-step photo-electroreduction from Mo (VI) to Mo (V)), thus causing a color change in the ink. PMA is practically colorless (light yellow), while photo-excited PMA becomes a heteropoly blue, characteristic of reduced POMs, showing a greater response to high energy UVC and less to UVB and UVA, respectively.

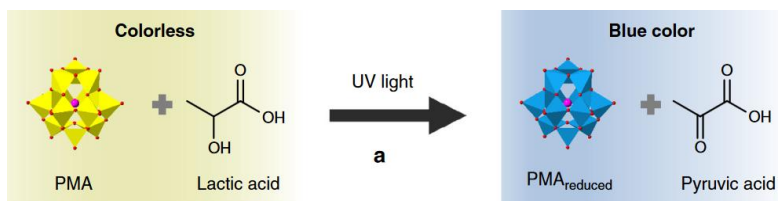


Figure 1. Reaction of PMA ( $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ ) with lactic acid ( $\text{C}_3\text{H}_6\text{O}_3$ ) under UV light. (Image extracted of W. Zou et al., ref. 2)

In relation to the way of alerting the user, an improvement of the design has been valued so that maintaining an intuitive and accessible appearance, the device is more compact with respect to the original design (60 mm wide) and also avoids the duplication of icons when symbolizing two different values of the MED. Concretely, filter paper will be impregnated with PMA-LA ink and shaped into four growing bars like those representing mobile phone coverage. After the ink is dried by the evaporation of water from the solution, each of the sensor bars will be placed on a 1 mm thickness plastic sheet, that will serve as a support, and will be covered with an increasing number of transparent films such as optical filters (TFF) of 100 microns

<sup>4</sup> Most of the characteristics and properties set forth in this section are taken from the article in Nature Communications, Skin color-specific and spectrally-selective naked-eye dosimetry of UVA, B and C radiations [2].

thickness, being the smaller bar the containing less film and the larger one the containing more. The TFF serve to alter the UVR dose received by the sensor and allow the adjustment of the sensor response time based on the UV dose received. As the number of TFF films increases, the UV dose received by the indicator decreases and the sensor response time enlarges. In this way, the drawing of each of the bars will gradually appear as the exposure time to the UVR increases. When the sensor is exposed to sunlight the first two bars, starting with the smallest one, turn blue, indicating that 25% and 50% of the MED has been reached, respectively. On the other hand, the appearance of the third bar represents 75% of the MED to which the user has been exposed. Lastly, the fourth and of the largest bar is an alert indicating that you are close to the maximum safe exposure limit and that you should take measures not to overexpose yourself to the sun, such as covering up or looking for shade. The evolution of the indicator according to your exposure to the sun is shown in figure 2.

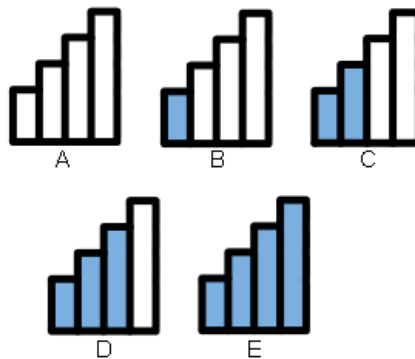


Figure 2. Example of the color change of the device when exposed to sunlight (drawing made from Autocad program). Figure A, indicates that it has not been exposed to UVR. Figure B, C and D indicate that the user has reached 25%, 50% and 75% of the MED, respectively, while figure E indicates 100% of the maximum UVR dose that the user accepts due to his skin type and is a warning signal to take precautionary measures.

The method of addition of transparent films mentioned in the previous paragraph will also be used to design six sensors to simulate the different skin types described according to the Fitzpatrick scale and the MED associated with each of them. The number of transparent films required to simulate each skin type is shown in Table 13.

Table 13. Number of transparent films for each skin type

Skin type	Number of transparent films			
	25% MED	50% MED	75% MED	100% MED
I	0	1	2	3
II	0	2	3	4
III	0	2	4	5
IV	1	4	5	6
V	2	5	6	7
VI	4	6	7	8

Given that 25% of the MED sensors of skin phototypes I, II and III aren't protected from the environment by TFF films, it will be covered by a thinner layer of 12 microns thickness that doesn't represent a significant UV blockage.<sup>5</sup>

In relation to the coating (TFF), Polyethylene Terephthalate (PET) has been selected, the same used in the UV indicator device of W. Zou et al. [2], for being a thermoplastic abundant in the market (it represents more than 50% of the synthetic fibers produced worldwide), that requires little energy for its processing and manufacture and has low cost, besides being strong, durable, resistant to radiation and recyclable [22], [23].

As for the format of the device, it will be adapted so that it doesn't hinder the tan and can be worn in a discreet place. It will consist of a pin with a plastic base (16 mm in diameter) and a metallic safety pin (stainless) that can be placed on the clothing or on the swimsuit. At the top of the plastic base four holes shall be made, one for each bar and of variable thickness, where each of the TFF coated filter paper bars will be placed and glued, increasing from left to right and separated from each other by a distance of 1.5 mm, as shown in Figure 3. In this way it is possible to palliate some of the disadvantages of the original patent wristband format, such as

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<sup>5</sup> The effectiveness of the addition of the new coating will be determined experimentally as described below in section 5.3., about optimization of the TFF coating.

now unwanted marks on the tan, greater possibility of impact on the device when wearing it close to the hand and difficulty of use in cold weather due to the possibility of being covered by clothing. Nevertheless, in an additional invention it would be easy to adapt the format to a wristband by joining the plastic base to a strap made of the same material, for all those users who find it more comfortable in their daily life or who due to their practices cannot place it on their clothes.

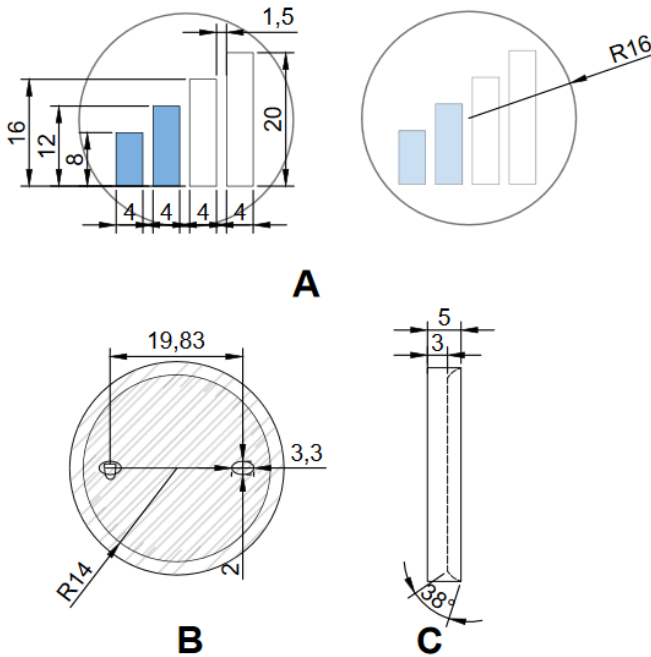


Figure 3. The measurements in millimeters of the pin to be designed are shown (drawing made with the Autocad program). Figure A, represents the front part, while figure B is the back part. Figure C, refers to the thickness of the device.

Additionally, in order to facilitate the visualization of the sensor indicators could be added under each of the bars to otherwise express the degree of exposure to UVR. For example, could be fixed under each bar the MED value to which it corresponds once it is colored (25%, 50%, 75% and 100%) or reference colors to express the danger to which the user is being



exposed when the bars appear, for example, a green color for the 25% bar, yellow for the 50% bar, orange for the 75% bar and red for the 100% bar.

### 3.3.2. Proposals for improvement

As mentioned in the introduction to section 3.3., the coating of the UV-indicator device is hydrophobic, which makes it difficult to apply certain sunscreens to it. In order to address this fact and the motive that cause it, it is necessary to review the meaning and properties of polar and apolar molecules (or little polar).

Apolar molecules are those formed by equal atoms (same electronegativity), the composed by atoms of similar electronegativity or those whose composition is formed by different atoms but with a symmetrical structure such that the polarity is annulled. On the other hand, polar molecules are those that have the electrical charge distributed so that one part of the molecule is negatively charged and the other positively, due to the difference in electronegativity between the elements [24].

Often the term hydrophobic is used to refer to an apolar substance as these don't dissolve in water, but repel it. This is owing to the fact that the water is a polar substance and, therefore, can only be mixed with other polar substances [24].

Based on this, it can be said that polyethylene (PE) is a simple and apolar molecule due to the symmetry of its molecules and the low electronegative difference between carbon and hydrogen. By introducing an aromatic group into the main chain, polyethylene terephthalate (PET) can be formed by slightly increasing its polarity [25]. However, the molecule remains highly apolar and, therefore, hydrophobic.

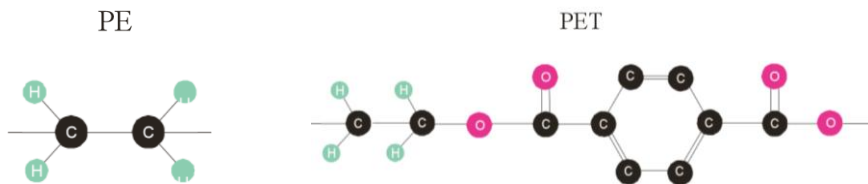


Figure 4. Molecular structure of Polyethylene (PE) and Polyethylene Terephthalate (PET).  
(Image extracted of M. Beltrán and A. Marcilla, ref. 25)

Following the information gathered above, it is concluded that the coating of the UV-indicating device (PET) may present a lack of adhesion and difficulty in spreading some sunscreens homogeneously. When sunscreen is applied to the skin, it acts as a barrier to UVA and UVB radiation, prolonging the time of exposure to the sun without cause damage to the skin [26]. For this reason, the fact that the same protection factor can be applied both on the skin and the indicator is so important, as only in this way will the indicator provide an accurate and real warning of the MED corresponding to the skin type of each user. To solve such disadvantage three possible solutions are proposed:

- Conduct a hydrophilic treatment on the device surface with plasma.
- Conduct a hydrophilic treatment on the device surface with UV radiation and ozone.
- Use the device exclusively with W/O (water in oil) sunscreen.

### 3.3.2.1. Low pressure plasma treatment

Low pressure plasma treatment improves the adhesion and wettability of a surface through removing low molecular weight substances and surface contaminants, of the production of new groups that increase the surface energy of the compound and by crosslinking surface polymer chains [27].

The procedure consists of feeding the chamber with a process gas (e.g. air, oxygen, argon, argon-hydrogen, tetrafluoromethane-oxygen and argon-oxygen) at low pressure that is created by means of a vacuum pump [27], [28]. The working pressure is approximately 0.1 to 1.0 mbar [28]. Once this pressure is reached the generator is turned on, working with a radio frequency of 13.56 MHz or 2.53 GHz, and the process gas is ionized creating the plasma [27], [28]. Plasma

is an excited gas composed of atoms, molecules, free radicals, electrons, ions, excited species and UV radiation [27]. The surface to be treated is bombarded with the energetic species of the plasma, transferring its energy to it, resulting, according to Yáñez, "in a specific modification with a penetration from several nanometers to  $10\mu\text{m}$ , without changing the properties of the substrate" [27]. This system continuously receives new gas while the contaminated gas is sucked in [28].

Plasma treatment is an environmentally friendly, energy-efficient, economical and method applicable to all plastics [27], [28]. Furthermore, plasma doesn't increase the surface temperature of substrates as ions and neutral particles are at room temperature or similar, and electrons show very few collisions with molecules [27].

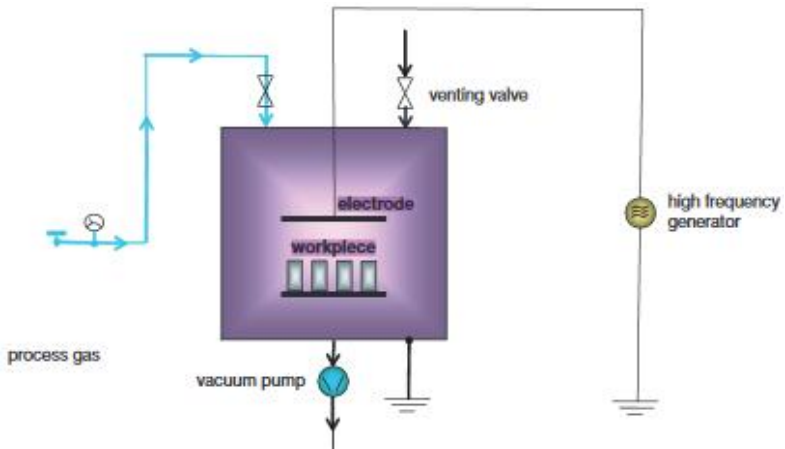


Figure 5. Diagram of a plasma system.  
(Image extracted of Diener Electronic, p. 7, ref. 28)

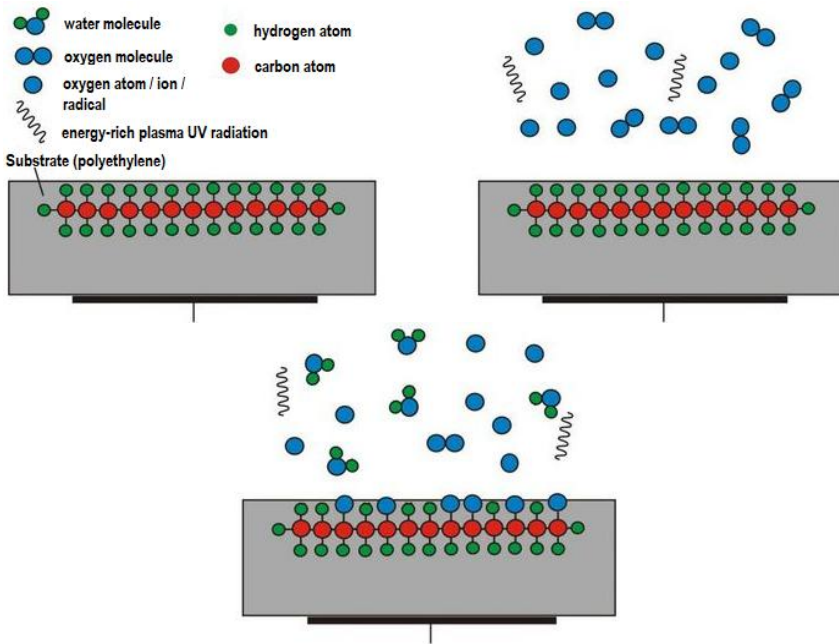


Figure 6. A plasma reaction during plastic activation.

(Image extracted of Diener Electronic, "Activación con plasma." [Online]. Available: <https://www.plasma.com/es/activacion-con-plasma/>. [Accessed: 11/04/2020])

### 3.3.2.2. Treatment with UV-ozone radiation

Surface treatment with ultraviolet radiation and ozone (UV-ozone) increases the wettability and adhesion of a substrate by promoting the removal of contaminants and modifying of its surface chemistry [27].

To carry out this treatment, low pressure mercury discharge tubes are used that emit radiation at two wavelengths, at 184.9 nm and 253.7 nm. Contrary to the wavelength of 253.77 nm, the wavelength of 184.9 nm is absorbed by oxygen causing the generation of ozone. The reactions induced by this treatment generate ions and radicals that can oxidize the surface of the polymer [27]. As described by Yáñez:

UV/ozone treatment generates a radiation intense enough to break most C-C bonds and can even induce chain breaks and crosslinks on the polymers surfaces. Photons that produce UV radiation can interact with oxygen to form ozone and with ozone to form atomic oxygen radicals, and both ozone and atomic oxygen radicals can react with the surface of polymers to remove low molecular weight pollutants and modify surface chemistry. UV treatment can incorporate water into treated surfaces forming highly polar groups such as hydroxyl, carbonyl and/or carboxyl. With UV-ozone radiation treatment new C-O, C=O and COOH/COOR groups are created that are incorporated on the surface of the polymers, leading to a decrease in contact angle values and improved adhesive properties [27]

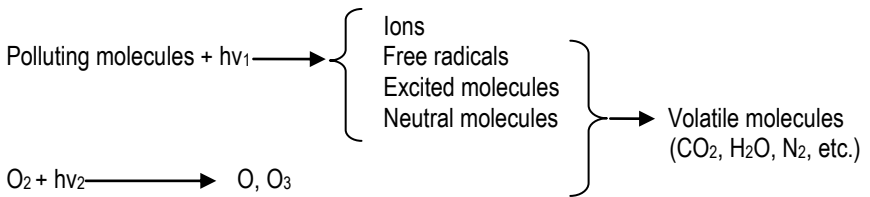


Figure 7. Reactions produced in the treatment of UV-Ozone.  
(Image extracted of A. J. Yáñez Pacios, ref. 27)

To carry out this treatment, the assembly indicated in figure 8 is used. On the other hand, the process can be optimized by modifying the distance between the UV lamp and the compound, besides of varying the exposure time [27].

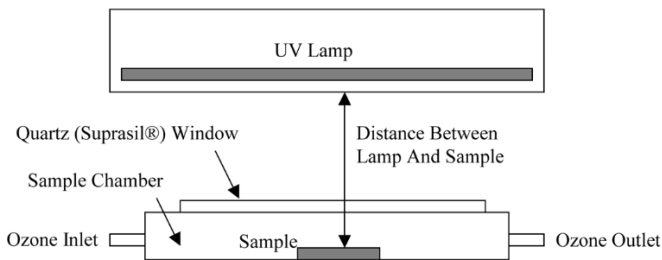


Figure 8. Diagram of the UV-Ozone treatment system.  
(Image extracted of A. J. Yáñez Pacios, ref. 27)

This treatment is effective and fast, as it allows polymer surfaces to be cleaned in less than 1 minute. Its procedure is simple and applicable in both vacuum systems and ambient conditions. Moreover, it is environmentally friendly [27].

### 3.3.2.3. Solar protectors W/O

In the case that the hydrophilic treatments mentioned in the previous paragraphs aren't experimentally viable, the use of sunscreens based on an apolar emulsion compatible with the surface of the PET (apolar) would be considered, in such a way that it could be spread on the device in a homogeneous manner. An emulsion is a mixture of two immiscible liquids, forming a two-phase system in which one of the liquids is dispersed in the form of drops (colloid) [29]. Emulsifiers are composed of a polar group (hydrophilic), the head, and a apolar group (hydrophobic), the tail. Therefore, such emulsifiers are attracted to both polar and apolar compounds [30]. The liquid remaining inside is the dispersed phase while the liquid remaining outside is the continuous phase [29]. There are two types of protectors depending on their emulsion:

- Oil-in-water emulsion (O/W) in which the dispersed phase is an oil of lipophilic (hydrophobic) character and the continuous phase is an aqueous liquid of hydrophilic (water) character. Therefore, it would be a more related protector with polar surfaces like water [29].
- Water-in-oil emulsion (W/O) in which the dispersed phase is an aqueous liquid of hydrophilic (water) character and the continuous phase is an oil of lipophilic (hydrophobic) character. Therefore, it would be a water resistant and more akin to a protector with apolar surfaces [29].

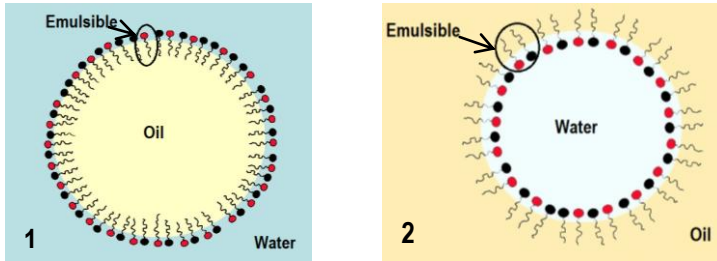


Figure 9. In picture 1 the action of the O/W emulsion is represented, on the other hand, picture 2 represents the action of the W/O emulsion.  
(Image extracted of R. C. Pasquali, ref. 29)

In view of these data we can conclude that the best protective lotion will be the one made with a W/O emulsion (water resistant products), because its continuous phase is apolar with a lipophilic character and will facilitate the application on the device. In this sense, the marketing of the UV indicator could be done together with that of the creams whose emulsion will be W/O.

#### 3.3.2.4. Choice of improvement

Finally, the purpose of this search is to find the solution that allows the use of any sunscreen, for that reason the hydrophilic treatments, that increase the polarity of the surface, as well as the wettability and the adhesion, are the best option. On the other hand, both treatments are equally acceptable for their effectiveness, as well as being economical and environmentally friendly. Therefore, it has been decided to carry out the treatment with low pressure plasma due to its ease of integration in production processes and due to the variety of companies that carry out this treatment for the improvement and activation of polymeric surfaces.





## 4. INGREDIENTS AND MATERIAL NEEDED TO PRODUCE THE DEVICE

For the development of the UV indicator devices will be required the following products:

- Phosphomolybdic acid solution (PMA) of concentration 5 mM [2].
- Lactic acid solution (LA) of concentration 300 mM [2].
- Filter paper approximately 0.15 mm thickness (4 mm x 8 mm, 4 mm x 12 mm, 4 mm x 16 mm and 4 mm x 20 mm).
- PET sheets of 1 mm thickness to serve as individual support for the bars drawn on filter paper.
- Transparent films filters (TFF) of PET of 9 thicknesses (12, 100, 200, 300, 400, 500, 600, 700 and 800 microns) that will cover the bars drawn together with the PET sheets. The thickness of film that each bar of the device will cover will vary depending on the phototype for which it is designed.
- Prefabricated PET support where the coated bars fit <sup>6</sup>.
- Safety pin.

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<sup>6</sup> The design of the indicators bars support can be found in Appendix 4.



## 5. OPTIMIZATION AND DEVELOPMENT OF THE DEVICE

Before developing the final product, it is necessary to carry out a series of experiments that corroborate its usefulness and good functioning due to possible variations in the response of the indicator after modifying its format and the origin of the products, besides to having carried out the plasma treatment to permeabilize the coating of de same.

### 5.1. OPTIMIZATION OF THE MOLAR RATIO OF THE INDICATOR

To optimize the response of the indicator when exposed to UVR, solutions of PMA and La at different concentrations will be made. Next, 100  $\mu\text{L}$  of PMA solution and 100  $\mu\text{L}$  of LA solution will be taken with a micropipette to make mixtures with LA:PMA molar ratios close to the optimal ratio determined by Zou et al. (60:1) [2], since the change of product isn't expected to generate a large difference in the final result. The chosen molar ratios will be of 45:1, 50:1, 55:1, 60:1, 65:1, 70:1 and 75:1. Similarly, the chosen values of PMA concentration will be of 4, 5, 6 and 8 mM, all close to the one selected by Zou et al. (5 mM) [2]. Then, each of the samples (a total of 28, result of multiplying each of the chosen molar ratios by the chosen PMA values) shall then be exposed to different radiation (UVA, UVB or UVC), with a cumulative UV dose of 2.700  $\text{J}/\text{m}^2$ , using UV lamps of 15  $\text{W}/\text{m}^2$  intensity, for 3 minutes. Thirty replicates of the experiment will be carried out for each type of radiation which represents a total of 2520 tests.

Next, the absorbance of each sample will be measured with a spectrophotometer at a wavelength of 700 nm corresponding to the reflected light of blue-green color [2], [33]. The optimum mixture will be the one with the highest absorbance [33].

Once the optimal mixture ratio has been determined it would be convenient to check the response of the indicator to low UVR doses, which are important for measuring the MED of the UVB of lighter skin types. For this, 120 samples of the optimal mixture will be made and exposed independently to UVA, UVB and UVC radiation (40 samples for each radiation) with an

intensity of  $5 \text{ W/m}^2$  during 200 s (equivalent to the maximum MED of phototype VI,  $1000 \text{ J/m}^2$ ). Each  $10 \text{ J/m}^2$  of exposure (5 seconds), will be measured the solution absorbance at 700 nm, making 30 replicates (3600 tests in total).

Finally, the mean, the standard deviation and the 90% confidence interval will be calculated for the absorbance values obtained in the different replicates for each type of UV radiation (UVA, UVB and UVC) and accumulated dose (equivalent to the time of exposure), from which the accuracy of the indicator will be known. As a result of the data obtained will be estimated whether this accuracy is suitable for the functionality of the device, providing an appreciable color change to the human eye, and whether significant changes are seen as the accumulated dose of UVR increases. These changes will be evaluated using the Student T, comparing the average values obtained for each type of UV radiation and exposure time, so that it is allow to know the exposure time from which significant changes in the absorbance values of the indicator ink start to be produced. Using also the Student T, it will be checked that exist significant differences, even at low radiation doses ( $\leq 50 \text{ J/m}^2$ ), between the average absorbance values of the indicators exposed independently to UVA, UVB and UVC radiation in a specific exposure time. In this way, it will be possible to corroborate that the solution differentiates correctly between the different types of UV radiation.

## 5.2. ESTIMATION OF THE REFLECTANCE CORRESPONDING TO THE COLOR CHANGE

Once the optimum molar ratio has been obtained and its effectiveness has been corroborated, it is necessary to determine what is the indicator's reflectance value when it clearly shows the change in color (from white to blue) once the percentage of the maximum MED of each indicator (bar of filter paper impregnated with PMA - LA solution) is reached.

For this purpose, an experiment will be carried out consisting of exposing 3 uncoated indicators (bars) to simulated solar conditions by means of lamps (UVB intensity of  $1 \text{ W}\cdot\text{m}^{-2}$ ) and monitoring, by means of a spectrophotometer<sup>7</sup>, its reflectance profile after a UVR dose of 50,

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<sup>7</sup> A possible spectrophotometer would be Agilent's Cary 7000 Universal Measurement Spectrophotometer (UMS) (UV-Vis & UV-Vis-NIR Systems) with a wavelength range of 190-2800 nm [31].

63, and 75 J/m<sup>2</sup> (50, 63, 75 seconds, respectively) corresponding to the minimum values represented in skin phototypes I, II, and III (25% of the MED of these phototypes). This experiment will be repeated 30 times for each dose of radiation, thus conducting a total of 90 tests. Given that the radiation difference between the three phototypes to that percentage of MED is small and according to the article by Zou et al. [2], neither of them is coated, it will be assumed that the average reflectance of the three doses corresponds to the change in color of each indicator (bar) when the percentage of MED associated is reached, before the next bar begins to appear.

Finally, the mean, the standard deviation and the 90% confidence interval of the reflectance values obtained at 50, 63 and 75 s will be calculated, thus determining the accuracy of the measurements.

### 5.3. COATING OPTIMIZATION (TFF)

It would be appropriate to optimize the thickness of TFF as its characteristics could vary from those used by Zou et al. [2], depending on the supplier and the treatments applied. Furthermore, in this invention it is desired to include a thinner TFF layer (12 micron) that doesn't significantly influence the UV measurement of the 25% MED indicator of skin phototypes I, II and III, thus protecting the filter paper from environmental conditions and homogenizing its appearance. With the objective of optimize the thickness of TFF applied to each sensor and to check that the 12 micron film doesn't significantly influence the UVR measurement, will be determined the reflectance shown by the sensor at a specific radiation dose experimentally as a function of its coating.

The experiment will consist of the measurement of the reflectance of 10 sensors with coatings of 0, 12, 100, 200, 300, 400, 500, 600, 700 and 800 microns thickness. The sensors will be irradiated for 1000 seconds with a 1 W/m<sup>2</sup> intensity lamp that simulates sunlight. This dose would be equivalent to an accumulated radiation of 1000 J/m<sup>2</sup> (the maximum MED of phototype VI).

Next from the 40 seconds of exposure, by means of a spectrophotometer, the reflectance of the sensors with a frequency of 5 seconds will be measured. Thirty replicates of the experiment will be carried out that which entails a total of 57 000 tests.

In order to optimize the TFF thickness of each indicator the exposure time necessary to reach the percentage of the MED corresponding to each skin type (25%, 50%, 75% and 100%) will be taken as a reference, checking, in such times, which sensors have reached the value of reflectance associated with the color change and the TFF thickness that composes their coating. The sensor reflectance value when the color change occurs, that is to say, when the UVR dose associated with each percentage of the MED corresponding to the different skin types is reached, it has been estimated to be approximately 84% (this value should be experimentally corroborated as indicated in section 5.2.)<sup>8</sup>. In this sense, will be chosen that indicator that is closest to the estimated reflectance value and will be understood as optimal, for that percentage of MED given, the thickness of TFF that cover it.

For example, the phototype I sensor reaches 25% of the MED (without TFF) after 50 s which is equivalent to 50 J/m<sup>2</sup> showing approximately 84% reflectance, while 25% of the phototype V must reach 84% reflectance when exposed to 150 s equivalent to 150 J/m<sup>2</sup>, therefore, the thickness of the TFF corresponding to that measurement will be determined (2 TFF (200 microns) according to Zou et al. [2])

On the other hand, in order to corroborate that the 12 micron film doesn't influence in an important way the UVR measurement, will be compared, by calculating the Student T, the average reflectance values of the uncoated group of sensors and of the group with coated of 12 micron, obtained in each of the determined times.

Lastly, to check that the accuracy of the indicator ink has not been affected by the TFF coating, will be recalculated the mean, standard deviation and 90% confidence interval of the reflectance values obtained every 5 seconds, taking each coating into account in an independent manner. Based on the results it will be assessed whether the accuracy achieved is sufficient for the user to appreciate a significant color change in the indicator. Subsequently, changes in the reflectance of the indicator ink will be evaluated as the cumulative dose of UVR

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<sup>8</sup> Such value is estimated from the reflectance data obtained by Zou et al. [2], after exposing the sensors to a solar simulator with a UVB intensity of 1 W·m<sup>-2</sup>. The calculation can be found in Appendix 5.

increases. By means of calculating the Student T, the average values obtained for each exposure time and each coating will be compared, so that the exposure time from which significant changes in the reflectivity of the indicator are produced will be estimated.

## 5.4. FUNCTIONALITY OF THE DEVICE

Once the molar ratio has been determined and the indicator coating has been optimized, will be proceed to make prototypes of the device, by performing the assembly the filter paper impregnated with the indicator ink on the PET support and, in turn, assembling the four coated indicator bars (sensors) on the plastic pin.

In order to check that the design of the device and its assembly doesn't interfere with its accuracy, will be exposed 6 devices, one for each type of skin, to a lamp of  $1 \text{ W/m}^2$  intensity that simulates sunlight for 1000 s. This dose would be equivalent to an accumulated radiation of  $1000 \text{ J/m}^2$  (the maximum MED of phototype VI). The reflectance of each device shall be measured by the spectrophotometer four times, once for each bar when they reach their maximum percentage of the MED (Table 9 of Appendix 5 indicates the accumulated UV dose for each sensor as a function of skin type which is proportional to the cumulative exposure time). This procedure will be replicated 30 times, with which giving a total of 720 measurements.

Subsequently, by means of the calculating the Student T, the average reflectance obtained for each bar with those obtained in the experiment of the section 5.3 will be compared, taking as a reference the number of TFF covering the indicator and its associated maximum UVR dose.

Once it is verified that the design of the device and its assembly doesn't interfere with the measurement, the average, the standard deviation and the 90% confidence interval will be calculated for the reflectance values obtained in each replica for the different sensors of the same device, taking as a reference the maximum UVR associated to each sensor (bar).

Lastly, to corroborate that the change in color of the four bars when the previous bar has reached its maximum MED percentage is subjectively appreciated by the user, the devices will be exposed to a sample of 100 people in which they will be asked to categorize, on the one hand, the visibility of the bar that has already reached 100% of its maximum dose and, on the other hand, the visibility of the bars that still should change color. The response options will be

4; nothing visible, little visible, visible and very visible. It will be accepted as adequate that, at least, 95% of the sample has categorized the color change as visible or very visible, while the remaining bars have been categorized as little or nothing visible.



## 6. QUALITY INDEXES

For evaluate the quality of the UV radiation device, a series of resistance and precision factors will be taken into account to provide security to the customer when buying the product and to guarantee their satisfaction. To evaluate compliance with these factors, 1 device will be selected out of each 1000 produced to be subjected to different experimental tests. In this sense, 0.1% of the daily production will be evaluated and, in the case that 98% of the chosen products pass the tests, will be proceed to distribute the products manufactured on that day. The quality factors proposed are:

- 1) UV dosimetry. This factor will assess the accuracy and correct display of indicators under normal conditions of use. The index of this factor corresponds to the color reflectance acquired by the different sensors (4 independent bars associated with the percentage of maximum MED for a given skin type), which will be measured by the spectrophotometer. The experiment to determine whether such factor is met will consist of exposing the devices to simulated solar conditions using lamps (UVB intensity of  $1 \text{ W}\cdot\text{m}^{-2}$ ) and monitoring with the spectrophotometer its reflectance profile 4 times, once for each cumulative exposure time corresponding to the percentage of the maximum MED of each sensor. If the reflectance of the sensors when reaching the maximum MED percentage is within the 90% confidence interval calculated in section 5.4., according to its coating, the device will be categorized as accurate, otherwise it will be categorized as not accurate and, therefore, would not comply with the quality index being unsuitable. On the other hand, if the result has been unsuitable, the thickness of the TFF of each bar will be checked to rule out a possible coating failure.
- 2) Water resistance. This factor will ensure the functionality and resistance of the device after it has been wet. To this end, the devices shall be introduced for two hours in salt water, fresh water and chlorinated water, respectively, extracting and introducing the devices from the water at ten-second intervals by simulating vertical movements using

- an automated machine. After completion of the test it shall be assessed that no physical damage has occurred and the dosimetry shall be monitored in the same way as in point 1. If the device is damaged or fails the dosimetry test it will be considered unsuitable.
- 3) Resistance to high temperatures. With this factor we want to ensure the functionality and resistance of the device when exposed to high ambient temperatures. It will be subjected to temperatures of 50°C for 8 hours in an oven and then assessed that physical damage haven't been produced and will be monitored the dosimetry in the same way as in point 1. If the device is damaged or fails the dosimetry test it will be considered unsuitable.
  - 4) Wettability. This factor allows to assuring that sunscreens can be applied to the device in a homogeneous way. The indicator of this factor will consist in measuring the contact angle of a drop of standard liquid on the surface by means of an electronic goniometer<sup>9</sup>. If the angle that the drop forms with respect to the surface is less than 90° it means that the wettability of the surface is favorable, while in the opposite case it is considered insufficient and, therefore, unsuitable [27].
  - 5) Resistance to movement. Through of this factor will confirm the resistance of the device during daily physical activity. To determine this factor, the device shall be placed on a fabric and subjected to continuous high-speed vertical movement for 8 hours, by using an automated machine. If the device is dropped before 8 a.m. it shall be considered unsuitable.
  - 6) Mechanical resistance. This factor shows the resistance of the device to the action of opening and closing the pin. In this test the device shall be subjected to a mechanical stress carried out by an automated machine that will open and close the pin for 4 hours to confirm that breakage due to wear wouldn't be possible. In this case, if breakage shall be happened before 4 hours, it shall be considered unsuitable.

All those devices that have not been qualified as unsuitable will be considered suitable. In this line, for calculate the general quality index for each daily sampling will be used the following formula (1):

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<sup>9</sup> The automatic goniometer 68-76 PGX could be used [32].

$$QI = \frac{N^{\circ} \text{ of suitable devices}}{N^{\circ} \text{ of devices analyzed}} \times 100 \quad (1)$$

As already mentioned previously, in order to consider that all the products manufactured on that day are marketable, the quality index (QI) must be equal to or higher than 98%.



## 7. UVR INDICATOR MANUFACTURING PROCESS

On the basis of the data set out previously in the market study, it has been decided to market the device in the Autonomous Community of Catalonia and to focus the greatest production efforts on the months of June, July, August and September (these will be the months taken into account for the selection of the mixer of the indicator and the calculation of loads).

The initial production of the UVR dosimeter has been estimated from two data sources. On the one hand, those collected by the National Institute about the Statistics on Tourism in Catalonia which records, from 2016 to 2019, the arrival of an average of 3.66 million national and international tourists. On the other hand, the data obtained from the survey conducted by M. de Troy Martin on sun protection habits have been taken into account [21]. By means of this survey, it is estimated that of the total tourists extracted, at least 61.30% (percentage of people taking 3 or more sunscreen measures) could be especially interested in the purchase of the device [21]. Based on the mentioned data, it is estimated that during the months of June to September an average of 2.24 million devices can be reach produce monthly, which would be equal to 74 800 daily.

In a similar way and through the surveys carried out by M. de Troya Martin and Industria Farmacéutica Cantabria on skin phototypes, the production of the devices based on this factor has been estimated, just as shown in Table 14 [20], [21]. It is expected to be better marketed to those with more sensitive skin, so 90% of the production will be for phototypes from I to IV. The remaining 10% will be distributed equally between phototypes V and VI<sup>10</sup>.

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<sup>10</sup> The device's monthly and daily production tables are shown in Appendix 6.

Table 14. Monthly and daily production of UVR indicator device based on skin phototype

Phototype	Monthly average of devices	Daily average of devices
I	130,409	4347
II	422,823	14094
II	715,237	23,841
IV	751,143	25,038
V	112,201	3740
VI	112,201	3740

## 7.1. DAILY LOAD OF THE INDICATOR

In order to be able calculate the required quantity of PMA and LA for the daily production of 75 000 devices approximately, the specific quantity for the manufacture of a single device must be known. In the article by Zou et al., it is mentioned that 100  $\mu\text{L}$  of PMA and 100  $\mu\text{L}$  of LA are used to carry out experiments with the indicator [2], however, in order to optimize the amount of indicator ink needed to completely cover the filter paper in the form of bars (of four different sizes), has been conducted the calculation of the volume of each of the bars supposing that the impregnation of the paper will be 100% (Figure 10).

<ul style="list-style-type: none"> <li>• 25% bar: 4 mm width <math>\times</math> 8 mm height <math>\times</math> 0.15 mm thickness = 4.8 mm<sup>3</sup> = 4.8 <math>\mu\text{L}</math></li> <li>• 50% bar: 4 mm width <math>\times</math> 12 mm height <math>\times</math> 0.15 mm thickness = 7.2 mm<sup>3</sup> = 7.2 <math>\mu\text{L}</math></li> <li>• 75% bar: 4 mm width <math>\times</math> 16 mm height <math>\times</math> 0.15 mm thickness = 9.6 mm<sup>3</sup> = 9.6 <math>\mu\text{L}</math></li> <li>• 100% bar: 4 mm width <math>\times</math> 20 mm height <math>\times</math> 0.15 mm thickness = 12 mm<sup>3</sup> = 12 <math>\mu\text{L}</math></li> <li>• Indicator ink amount per device: 4.8 <math>\mu\text{L}</math> + 7.2 <math>\mu\text{L}</math> + 9.6 <math>\mu\text{L}</math> + 12 <math>\mu\text{L}</math> = 33.6 <math>\mu\text{L}</math></li> </ul>
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Figure 10. Calculation of the volume of indicator ink required to completely cover the bars as a function of their size.

With the purpose of making up for possible losses of indicator ink during the impregnation of the filter paper, it was decided to round up the value obtained to 40  $\mu\text{L}$  of indicator (20  $\mu\text{L}$  of PMA dissolution and 20  $\mu\text{L}$  of LA dissolution).

20 $\mu\text{L}$ of PMA [5 mM]	$\left\{ \begin{array}{l} \text{PMA molecular weight} = 1825.25 \text{ g/mol} \\ \text{H}_3[\text{P}(\text{Mo}_3\text{O}_{10})_4]x\text{H}_2\text{O} \text{ (solid)} \\ \text{Density (25}^\circ\text{C)} = 1.62 \text{ g/cm}^3 \end{array} \right.$
20 $\mu\text{L}$ of LA [300 mM]	$\left\{ \begin{array}{l} \text{LA molecular weight} = 90.08 \text{ g/mol} \\ \text{C}_3\text{H}_6\text{O}_3 \text{ (solid), 98\% de purity} \\ \text{Density (20}^\circ\text{C)} = 1.200 \text{ g/cm}^3 \\ \text{Viscosity (25}^\circ\text{C)} = 5 - 60 \text{ mPa}\cdot\text{s} \end{array} \right.$

Figure 11. PMA and LA chemical data. The data have been extracted from their technical sheets [34], [35], [36].

In this sense, it is calculated that for the daily production of 75.000 devices will be required a total of 3 L of PMA-LA indicator ink, meaning, 1.5 L of PMA solution [5 mM] mixed with 1.5 L of LA solution [300 mM].

By means of the data shown in Figure 11, it has been calculated that the production of 1.5 L of PMA solution [5 mM] will require 14 g of PMA and 1.5 L of deionized water per day. The solid PMA will be obtained from Sigma-Aldrich and will have a monthly cost of 710.0 € for 500 g [37]. On the other hand, for the manufacturing of 1.5 L of LA [300 mM], 42 g of LA and 1.5 L of deionized water per day will be required. The solid LA used with a purity of 98 % will also be obtained from Sigma-Aldrich and will entail a monthly cost of 15 080.0 for 1300 g [38].

## 7.2. INDICATOR MIXER TANK

To produce the indicator will be used three cylindrical agitated tank reactors with rounded bottoms to avoid straight edges where the fluid flows wouldn't penetrate and an agitator mounted on the central axis of the container and driven by an electric motor [39]. Two of the reactors will be destined for the preparation of the dissolution of PMA (5 mM) and LA (300 mM), independently. Each reactor will have a capacity of two liters, in this way can be prepared the solution needed to make the one-day indicator ink in a single charge (1.5 L of PMA and 1.5 L of LA). The third reactor will be of three liters capacity and will be used to form the PMA-LA indicator ink, mixing the two previous solutions.

Both substances (PMA and LA) are highly soluble in water at ambient temperature (lactic acid is reported as infinite miscibility in the Manual del Ingeniero Químico de Perry) [40], [41]. In addition, it can be supposed that the mixture will be of low viscosity, similar to that of water due to the low concentration of the solutions, therefore, the reactors will work at normal conditions of environmental temperature (20-25°C) and atmospheric pressure (1 bar). To produce these solutions it won't be necessary to dimension the reactors to be used, due to their reduced size the standardized ones like a used in laboratories can be bought. Bürchiglauster's stainless steel Polyclave reactor with high acid resistance, excellent heat transfer and efficient agitation for low and high viscosity media has been selected in two different sizes (two 2 L and one 3 L reactor) [42].

An important feature to take into account at the time of carrying out dissolution and a homogeneous mixture is the type of agitator to be used. Essentially there are four types of agitators: anchor, propeller, paddle and turbine [43]. Given that the fluid to be mixed is of low viscosity, the most appropriate agitators for homogenization would be propeller or paddle agitators, these latter having an inclination of the paddles of less than 90° with the plane perpendicular to the axis [43], [44]. These types of agitators generate axial flows (fluid circulation in a plane parallel to the axis), ideal for suspensions, solid-liquid solutions (as it prevents solid particles from being deposited at the bottom of the tank), liquid mixing and homogenization [43], [44].



Table 15. Comparative of the characteristics of propeller type agitators and paddles with an angle of less than 90° to the shaft [43]

Agitator type	Characteristics
<b>Propeller</b>	The propeller type agitators can be used for the processes of suspension, dispersion and homogenization for low-viscosity products, where it is necessary to work at medium and high speed (between 3 and 15 m/s).
<b>Paddles (angle less than 90°)</b>	Paddle agitators can be used in suspension, dispersion and homogenization processes for low and medium viscosity products. The agitation speed is low-moderate (between 2 and 7 m/s).

Both the propeller and the paddle agitators can be effective agitators for the process of dissolving and homogenizing a product with low viscosity. In addition, due to the low viscosity of the indicator, mixing can be carried out at medium or moderate speed with turbulent flow. [44], [45]. However, the propeller agitator will be used as it has a greater range of speeds. More concretely, the marine propeller has been chosen for its multiple applications in the treatment of milk, mixing of liquids (with the same or different viscosities), solids solutions, etc. [43].



## 8. CONCLUSIONS

In this work, an irreversible device has been developed that alerts the user of the dose of UV radiation to which he is being exposed, in order to protect him before reaching his maximum daily dose (MED) and prevent possible health problems. The development has been made through the following stages:

- On the basis of a bibliographic and market study in which the characteristics present in the UV radiation indicator products that exist today have been reviewed and compared, a dosimeter has been conceived based on an irreversible photoelectrochromic ink that is spectrally selective of the UVR, standing out from the rest for its functionality, versatility and simplicity. Such ink, coated with transparent layers of polyethylene terephthalate (PET) to simulate the skin type, alerts the user by means of a change in color when a determined UVR level has been reached.
- It has been proposed several improvements to the device with respect to the original design: its format has been modified so that it doesn't interfere with the tanning and to avoid shocks to a greater extent, giving it the shape of a round pin to be placed on the clothes; the user alert mode has been changed, using four increasing bars, to reduce the size of the device while maintaining its simplicity and intuitive design; it has been decided to subject PET coatings to a low-pressure plasma treatment that would improve their wettability and adhesion, thus allowing some sunscreens to be more easily spread on the device; and, lastly, a thinner coating (12 microns) has been added to the sensor of the 25% of the MED of phototypes I, II and III, initially uncoated, in order to protect them from environmental factors without representing a significant blockage of the UVR.
- The ingredients required for the response of the device have been selected: a 5 mM phosphomolybdic acid (PMA) solution and a 300 mM lactic acid (LA) solution. On the other hand, the materials used in their manufacture are low cost: filter paper impregnated with the indicator ink, PET coatings and supports and a safety pin.

- Product quality factors have been established, i.e. parameters that must be met to ensure perceived quality and customer satisfaction. These factors would be accuracy, water resistance, resistance to high temperatures, resistance to fast movements, mechanical resistance of the clasp and wettability of the device to sunscreen.
- The indicator synthesis process has been developed. Two dissolutions will be carried out in independent reactors, one of PMA 5 mM and the other of LA 300 mM, and, subsequently, both dissolutions will be mixed in a third reactor. This production will be carried out avoiding sunlight or UVR, so that the mixture doesn't react.
- Three laboratory scale stainless steel reactors Polyclave from Bürchiglauster (two 2L and one 3L) have been chosen to produce both the low viscosity solutions as well as the indicator ink. These reactors shall operate at ambient temperature and pressure using an agitator with a marine propeller that works at moderate speed and produces a turbulent flow rate for the production of a low viscosity homogeneous mixture.

To conclude, this work highlights the importance and need for further progress in the field of sun protection, both at the level of research and the design of new products to adjust to individual needs, supplying the current market lack. On the other hand, it is essential to delve into the limitations of indicators already marketed or patented, of which the device to be developed isn't exempt, in order to solve them, such as the selective differentiation of the three types of UVR radiation or the irreversibility of the indicator. It would be useful to find a way to develop a product capable of discriminating between UVA, UVB and UVC radiation, that would also be reversible, differentiate between different skin types and to which sunscreen could be applied as, in this way, it would perhaps be possible to extend its use among the population and, therefore, reduce the incidence of diseases produced by the sun.

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## ACRONYMS

A: Accessibility

AC: Accuracy

CFC: Chlorofluorocarbon

CIS: Centro de Investigaciones Sociológicas (Sociological Research Center)

Cl: Atomic chlorine

CO<sub>2</sub>: Carbon Dioxide

CPU: Central Processor Unit

CRAI: Centro de Recursos para el Aprendizaje y la Investigación (Resource Center for Learning and Research)

DNA: Deoxyribonucleic acid

E: Expiration

EPA: Environmental Protection Agency

F: Format

GPS: Global Positioning System

$h\nu$ : Incident photon energy

H<sub>2</sub>O: Water molecule

ICNIRP: International Commission on Non-Ionizing Radiation Protection

ID: Intuitive design

IFC: Industria Farmacéutica Cantabria (Pharmaceutical Industry Cantabria)

INE: Instituto Nacional de Estadística (Statistics National Institute)

LA: Lactic acid

LED: Light Emitting Diode

MED: Minimal Erythema Dose

N<sub>2</sub>: Nitrogen

NOX: Nitrogen oxides

NOAA: National Oceanic and Atmospheric Administration

O: Atomic oxygen

O<sub>2</sub>: Oxygen

O<sub>3</sub>: Ozone

O/W: Oil in Water

PE: Polyethylene

PET: Polyethylene terephthalate

PMA: Phosphomolybdic acid

POM: Photoelectrochromic polyoxometalate

QI: Quality index

R: Radiation

RS: Resistance

RV: Reversibility

SPF: Sun Protection Factor

SP: Sun Protection

ST: Skin Type

SZA: solar zenith angle

TFF: Transparent films filters

UNEP: United Nations Environment Programme

UNWTO: World Tourism Organization

USB: Universal Serial Bus

UV: Ultraviolet

UVA: Ultraviolet A

UVB: Ultraviolet B

UVC: Ultraviolet C

UVI: Ultraviolet Index

UVR: Ultraviolet radiation

W/O: Water in Oil

WHO: World Health Organization

WMO: World Meteorological Organization

%: Percent

°: Degree

°C: Centigrade degree

μL: Microliter

L: Liter

mm<sup>3</sup>: cube millimeter

g: grams

g/mol: gram per mole

g/cm<sup>3</sup>: gram per cubic centimeter

mPa·s: Millipascal per second

mM: Milimolar

GHz: Gigahertz

MHz: Megahertz

J/m<sup>2</sup>: Joule per square meter

W/m<sup>2</sup>: Watt per square meter

nm: Nanometer

s: second

m/s: Meter per second

# APPENDICES

# APPENDIX 1: GLOBAL SOLAR UV INDEX

EXPOSURE CATEGORY	UVI RANGE
LOW	< 2
MODERATE	3 TO 5
HIGH	6 TO 7
VERY HIGH	8 TO 10
EXTREME	11+

Figure 1. UV radiation exposure categories

(Extracted image of World Health Organization, "Global solar UV index, a practical guide." 2002)

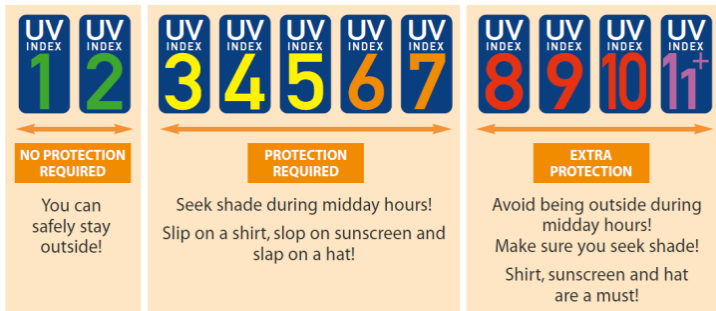


Figure 2. Recommended sun protection scheme.

(Extracted image of World Health Organization, "Global solar UV index, a practical guide." 2002)

## APPENDIX 2: SPANISH TOURISM

Table 1. National tourism in Spain and autonomous communities with beach in 2019

Andalusia		Balearic Islands		Canary Islands		Catalonia	
Leisure, break and vacation		Leisure, break and vacation		Leisure, break and vacation		Leisure, break and vacation	
2019M09	1 554 292	2019M09	245 010	2019M09	387 089	2019M09	1 102 439
2019M08	3 257 318	2019M08	333 464	2019M08	687 035	2019M08	1 741 845
2019M07	2 574 288	2019M07	308 359	2019M07	526 350	2019M07	1 683 421
2019M06	1 676 906	2019M06	206 071	2019M06	358 063	2019M06	1 841 110
2019M05	1 316 646	2019M05	111 492	2019M05	207 208	2019M05	1 267 454
2019M04	1 356 872	2019M04	187 424	2019M04	313 163	2019M04	1 461 610
2019M03	1 213 932	2019M03	127 444	2019M03	290 266	2019M03	1 205 996
2019M02	1 147 630	2019M02	73 669	2019M02	245 010	2019M02	1 147 182
2019M01	905 983	2019M01	62 636	2019M01	164 552	2019M01	906 574
Valencia Community		Murcia		Spain			
Leisure, break and vacation		Leisure, break and vacation		Leisure, break and vacation			
2019M09	887 003	2019M09	130 944	2019M09	7 592 799		
2019M08	2 347 352	2019M08	405 814	2019M08	14 046 289		
2019M07	1 789 090	2019M07	304 533	2019M07	11 076 186		
2019M06	1 273 658	2019M06	230 295	2019M06	8 799 684		
2019M05	842 971	2019M05	192 092	2019M05	6 865 606		
2019M04	1 051 489	2019M04	162 248	2019M04	8 252 258		
2019M03	614 127	2019M03	83 078	2019M03	6 302 132		
2019M02	451 213	2019M02	89 307	2019M02	5 460 023		
2019M01	535 106	2019M01	.	2019M01	4 753 926		



Table 2. Percentages of national tourism in Spain in 2019

<b>Total number of national tourists in Spain during the months of July and August</b>	<b>Number of national tourists that go to the autonomous communities with beach during the months of July and August</b>	<b>% of tourists who travelled to Spain during July and August for beach tourism</b>
25 122 475	15 958 869	63.52

Table 3. International tourism in Spain and autonomous communities with beach in 2016

	<b>National total</b>	<b>Andalusia</b>	<b>Balearic Islands</b>	<b>Canary Islands</b>	<b>Catalonia</b>	<b>Valencia Community</b>	<b>Murcia</b>
<b>2016M12</b>	<b>3 115 937</b>	365 132	76 709	1 223 876	674 049	279 305	43 713
<b>2016M11</b>	<b>3 251 951</b>	452 758	122 438	1 128 790	742 423	303 346	37 911
<b>2016M10</b>	<b>6 100 455</b>	963 363	1 181 312	1 236 398	1 237 816	663 303	69 931
<b>2016M09</b>	<b>7 057 857</b>	1 019 166	1 806 672	971 258	1 607 456	698 118	66 092
<b>2016M08</b>	<b>9 296 900</b>	1 280 539	2 253 257	1 099 833	2 341 344	1 024 460	146 295
<b>2016M07</b>	<b>8 664 754</b>	1 083 913	2 315 144	1 118 838	2 137 830	946 718	88 021
<b>2016M06</b>	<b>6 591 364</b>	916 943	1 871 448	912 300	1 540 307	644 688	74 802
<b>2016M05</b>	<b>6 078 190</b>	912 210	1 508 172	882 784	1 358 848	637 563	48 630
<b>2016M04</b>	<b>4 921 015</b>	743 189	709 379	1 043 627	1 187 552	527 132	85 638
<b>2016M03</b>	<b>3 747 057</b>	562 959	340 695	1 172 829	814 900	399 478	48 044
<b>2016M02</b>	<b>2 814 264</b>	354 913	141 577	1 092 324	635 264	283 558	38 011
<b>2016M01</b>	<b>2 671 999</b>	352 572	83 723	1 073 252	608 028	237 567	21 655

Table 4. International tourism in Spain and autonomous communities with beach in 2017

	<b>National total</b>	<b>Andalusia</b>	<b>Balearic Islands</b>	<b>Canar, Islands</b>	<b>Catalonia</b>	<b>Valencia Community</b>	<b>Murcia</b>
<b>2017M12</b>	<b>3 217 373</b>	397 623	75 363	1 221.915	652 851	316 289	46 270
<b>2017M11</b>	<b>3 676 581</b>	494 020	154 597	1 221 648	735 375	375 566	60 601
<b>2017M10</b>	<b>6 331 811</b>	1 000 840	1 188 368	1 285 656	1 236 433	663 419	80 953
<b>2017M09</b>	<b>7 949 343</b>	1 189 637	1 968 264	1 094 163	1 728 274	883 143	70 964
<b>2017M08</b>	<b>9 596 016</b>	1 307 500	2 313 522	1 145 676	2 376 536	1 073 941	129 873
<b>2017M07</b>	<b>9 427 961</b>	1 211 834	2 428 593	1 167 334	2 264 701	1 082 218	111 314
<b>2017M06</b>	<b>7 401 577</b>	1 014 945	2 045 534	1 003 676	1 709 489	759 416	63 949
<b>2017M05</b>	<b>6 895 568</b>	1 015 274	1 622 027	964 380	1 596 482	783 760	53 739
<b>2017M04</b>	<b>6 065 684</b>	878 909	932 185	1 237 916	1 491 114	645 887	80 116
<b>2017M03</b>	<b>3 995 086</b>	557 883	290 633	1 264 982	878 563	420 439	65 645
<b>2017M02</b>	<b>3 387 506</b>	442 318	138 050	1 168 042	793 234	350 226	37 063
<b>2017M01</b>	<b>3 142 597</b>	411 772	83 391	1 162 993	629 897	310 481	28 461

Table 5. International tourism in Spain and autonomous communities with beach in 2018

	<b>National total</b>	<b>Andalusia</b>	<b>Balearic Islands</b>	<b>Canary Islands</b>	<b>Catalonia</b>	<b>Valencia Community</b>	<b>Murcia</b>
<b>2018M12</b>	3 571 407	431 221	138 487	1 225 685	782 263	347 500	38 520
<b>2018M11</b>	3 763 368	497 009	157 927	1 160 015	835 919	426 529	44 252
<b>2018M10</b>	6 707 426	989 967	1 225 283	1 227 091	1 455 496	734 143	96 607
<b>2018M09</b>	7 987 061	1 124 739	1 945 824	1 021 229	1 792 634	906 337	99 259
<b>2018M08</b>	9 370 729	1 298 595	2 147 195	1 083 251	2 282 784	1 088 715	133 611
<b>2018M07</b>	9 070 322	1 238 504	2 274 239	1 104 285	2 143 927	1 039 141	133 758
<b>2018M06</b>	7 508 130	1 044 950	1 951 190	981 915	1 796 302	805 450	92 928
<b>2018M05</b>	7 149 584	1 086 904	1 608 129	944 669	1 618 218	803 605	93 349
<b>2018M04</b>	5 782 796	952 051	871 385	1 079 494	1 259 688	648 405	91 499
<b>2018M03</b>	4 341 659	628 792	349 163	1 322 096	900 043	512 214	55 959
<b>2018M02</b>	3 458 372	468 570	134 306	1 170 262	811 508	347 709	34 586
<b>2018M01</b>	3 462 200	455 107	103 973	1 159 764	703 556	362 365	38 115

Table 6. International tourism in Spain and autonomous communities with beach in 2019

	<b>National total</b>	<b>Andalusia</b>	<b>Balearic Islands</b>	<b>Canary Islands</b>	<b>Catalonia</b>	<b>Valencia Community</b>	<b>Murcia</b>
<b>2020M01</b>	3 381 620	451 670	88 971	1 081 211	677 878	349 188	37 020
<b>2019M12</b>	3 539 334	416 674	103 968	1 169 913	801 553	363 791	28 408
<b>2019M11</b>	3 824 438	481 865	156 171	1 143 298	827 499	458 252	42 487
<b>2019M10</b>	6 661 237	1 065 469	1 154 716	1 127 874	1 447 456	791 376	72 128
<b>2019M09</b>	8 005 561	1 238 575	1 952 595	932 744	1 759 813	911 050	99 574
<b>2019M08</b>	9 452 928	1 293 800	2 219 081	1 031 576	2 213 472	1 174 870	137 068
<b>2019M07</b>	8 984 595	1 151 190	2 302 976	1 014 337	2 130 363	1 106 523	121 589
<b>2019M06</b>	7 806 132	1 088 556	1 996 995	910 544	1 797 712	844 252	90 409
<b>2019M05</b>	6 946 340	1 029 391	1 644 306	845 126	1 532 627	776 521	77 064
<b>2019M04</b>	6 232 096	994 497	1 008 189	1 086 432	1 438 017	714 828	89 273
<b>2019M03</b>	4 682 261	704 270	327 307	1 309 403	1 020 639	501 250	44 777
<b>2019M02</b>	3 550 385	473 375	146 219	1 158 625	814 247	377 008	42 572
<b>2019M01</b>	3 440 353	450 480	106 800	1 134 278	745 603	310 000	36 417

Table 7. Percentages of international tourism in Spain in 2019

<b>Total international tourism in Spain from 2016 to 2019</b>	<b>International tourism in Spain in July and August 2019</b>	<b>% of international tourism in Catalonia in July and August 2019</b>
280 697 560	18 437 523	23.56

## APPENDIX 3: POINTS OF SALE OF UVR INDICATOR DEVICES

Table 8. URLs address of the sale of UVR detection devices visited on 18/03/2020

Device	Online distributors	URL address
UV measuring wristband	Ebay and Amazon	<a href="https://www.ebay.es/i/222190798843?chn=ps&amp;norover=1&amp;mk_evt=1&amp;mkrid=1185-146825-5486-0&amp;mkcid=2&amp;itemid=222190798843&amp;targetid=908485731114&amp;device=c&amp;mktype=pla&amp;googleloc=1005427&amp;poi=&amp;campaignid=9557020751&amp;mkgroupid=96291106697&amp;rlsarget=pla-908485731114&amp;abclid=1139526&amp;merchantid=116424900&amp;gclid=Cj0KCQjwpfHzBRCiARIsAHHzyZrMtA5LGc7q3JtIBwVBXyQFI5NEY_h_gzteRXwVKWn_tI7NXG9y8owaApS-EALw_wcB">https://www.ebay.es/i/222190798843?chn=ps&amp;norover=1&amp;mk_evt=1&amp;mkrid=1185-146825-5486-0&amp;mkcid=2&amp;itemid=222190798843&amp;targetid=908485731114&amp;device=c&amp;mktype=pla&amp;googleloc=1005427&amp;poi=&amp;campaignid=9557020751&amp;mkgroupid=96291106697&amp;rlsarget=pla-908485731114&amp;abclid=1139526&amp;merchantid=116424900&amp;gclid=Cj0KCQjwpfHzBRCiARIsAHHzyZrMtA5LGc7q3JtIBwVBXyQFI5NEY_h_gzteRXwVKWn_tI7NXG9y8owaApS-EALw_wcB</a>
		<a href="https://www.ebay.es/itm/10x-UV-METRO-MUNEQUERAS-SOLAR-SUN-INDICADOR-SENSOR-PROTECCION-VACACIONES/322417358736?trkparms=aid%3D1110001%26algo%3DSPLICE.SIM%26ao%3D2%26asc%3D20160908110712%26meid%3D6966361288a741a58749d1a8e6c38ffb%26pid%3D100677%26rk%3D4%26rkt%3D5%26mehot%3Dnone%26sd%3D222190798843%26itm%3D322417358736%26pmt%3D0%26noa%3D1%26pg%3D2386202%26alqv%3DDefault&amp;trksid=p2386202.c100677.m4598">https://www.ebay.es/itm/10x-UV-METRO-MUNEQUERAS-SOLAR-SUN-INDICADOR-SENSOR-PROTECCION-VACACIONES/322417358736?trkparms=aid%3D1110001%26algo%3DSPLICE.SIM%26ao%3D2%26asc%3D20160908110712%26meid%3D6966361288a741a58749d1a8e6c38ffb%26pid%3D100677%26rk%3D4%26rkt%3D5%26mehot%3Dnone%26sd%3D222190798843%26itm%3D322417358736%26pmt%3D0%26noa%3D1%26pg%3D2386202%26alqv%3DDefault&amp;trksid=p2386202.c100677.m4598</a>
		<a href="https://www.amazon.es/Giftsbynet-Mu%C3%B1equeras-Indicadores-Seguridad-Vacaciones/dp/B00V6BDQNA/ref=sr_1_14?dchild=1&amp;keywords=medidor+uv&amp;qid=1585222173&amp;sr=8-14">https://www.amazon.es/Giftsbynet-Mu%C3%B1equeras-Indicadores-Seguridad-Vacaciones/dp/B00V6BDQNA/ref=sr_1_14?dchild=1&amp;keywords=medidor+uv&amp;qid=1585222173&amp;sr=8-14</a>
CitroBand +UV Tester	Online pharmacies	<a href="https://www.linefarma.es/tienda/solar/proteccion-solar-infantil/citroband-isdin-kids--uv-tester-pulsera-c-2-recarga-168356.html?virtuemart_currency_id=47&amp;lang=es">https://www.linefarma.es/tienda/solar/proteccion-solar-infantil/citroband-isdin-kids--uv-tester-pulsera-c-2-recarga-168356.html?virtuemart_currency_id=47&amp;lang=es</a>
		<a href="https://farmaciaparacuellos.es/repelentes/14913-citroband-isdin-kids-uv-tester-pulsera-edicion-bella-y-bestia?qclid=Cj0KCQjwyPbzBRDsARIsAFH15JZEP7UCxEWoC8oVfH5L0E4hueXdKsgnQ-hZfIUzhL1SSRtV_sBxDcaAvyJJEALw_wcB">https://farmaciaparacuellos.es/repelentes/14913-citroband-isdin-kids-uv-tester-pulsera-edicion-bella-y-bestia?qclid=Cj0KCQjwyPbzBRDsARIsAFH15JZEP7UCxEWoC8oVfH5L0E4hueXdKsgnQ-hZfIUzhL1SSRtV_sBxDcaAvyJJEALw_wcB</a>
		<a href="https://www.farmacia-morlan.com/isdin-citroband-tester-pulsera-recargable-antimosquitos-1ud2pastillas-p-8179.html">https://www.farmacia-morlan.com/isdin-citroband-tester-pulsera-recargable-antimosquitos-1ud2pastillas-p-8179.html</a>

Tabla 8. URLs address of the sale of UVR detection devices visited on 18/03/2020 (Continued)

Device	Online distributors	URL address
Smartsun, solar indicator wristband	Online pharmacies and Amazon	<a href="https://www.promofarma.com/es/smartsun-pulsera-indicador-solar-5u/p-89075">https://www.promofarma.com/es/smartsun-pulsera-indicador-solar-5u/p-89075</a>
		<a href="https://www.amazon.es/Sanitec-Filtro-solar-corporal-gr/dp/B00M9B67GE">https://www.amazon.es/Sanitec-Filtro-solar-corporal-gr/dp/B00M9B67GE</a>
UV-Tester	Solostocks	<a href="https://www.solostocks.com/venta-productos/mobiliario-infantil/otro-mobiliario-infantil/pulsera-de-pvc-indicadora-de-nivel-de-rayos-uv-38078011">https://www.solostocks.com/venta-productos/mobiliario-infantil/otro-mobiliario-infantil/pulsera-de-pvc-indicadora-de-nivel-de-rayos-uv-38078011</a>
		<a href="https://www.solostocks.com/venta-productos/regalos-promocionales-personales/llaveros-promocionales/llavero-medidor-radiacion-uv-level-39086706">https://www.solostocks.com/venta-productos/regalos-promocionales-personales/llaveros-promocionales/llavero-medidor-radiacion-uv-level-39086706</a>
Smart UV Checker FUV-001	Ebay and Amazon	<a href="https://www.ebay.es/itm/Smart-Lab-FUV-001-Smart-UV-Checker-Ftlab-Ultraviolet-For-Smartphone-/201275199861">https://www.ebay.es/itm/Smart-Lab-FUV-001-Smart-UV-Checker-Ftlab-Ultraviolet-For-Smartphone-/201275199861</a>
		<a href="https://www.amazon.es/Smart-FUV-001-Smartphone-dispositivo-ultravioleta/dp/B01BAJIER0">https://www.amazon.es/Smart-FUV-001-Smartphone-dispositivo-ultravioleta/dp/B01BAJIER0</a>
Sun protection indicator, SUN HERO	Bebes y mamis and everyday baby	<a href="https://bebesymamis.com/INDICADOR-PROTECCION-SOLAR-SUN-HERO-EVERYDAY-BABY-10-uds">https://bebesymamis.com/INDICADOR-PROTECCION-SOLAR-SUN-HERO-EVERYDAY-BABY-10-uds</a>
		<a href="https://everydaybaby.com/collections/popular-products/products/sunhero-sunscreen-indicator-10-pack">https://everydaybaby.com/collections/popular-products/products/sunhero-sunscreen-indicator-10-pack</a>

## APPENDIX 4: POLYMERIC SUPPORT OF UV INDICATOR BARS

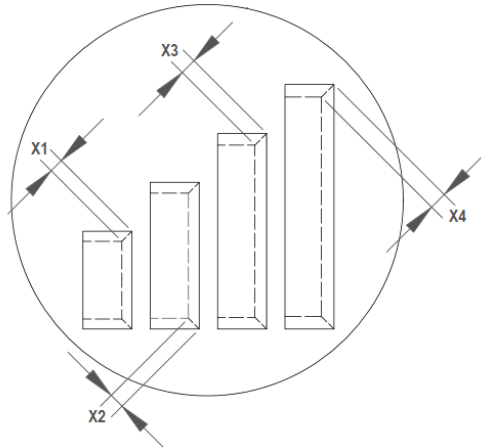


Figure 4. Scheme of the support of the UV indicator bars, where X1, X2, X3 and X4, represent the thicknesses of the bars of 25%, 50%, 75% and 100%, respectively, depending on the type of skin and indicated in Table 11 (drawing made with the Autocad program).

Table 11. Approximate thickness of the UV indicator bars after being coated by the TFF (approximately 1 mm PET sheet + 0.15 mm filter paper + TFF thickness)

Skin type	X1 (mm)	X2 (mm)	X3 (mm)	X4 (mm)
I	1.162	1.25	1.35	1.45
II	1.162	1.35	1.45	1.55
III	1.162	1.35	1.55	1.65
IV	1.25	1.55	1.65	1.75
V	1.35	1.65	1.75	1.85
VI	1.55	1.75	1.85	1.95

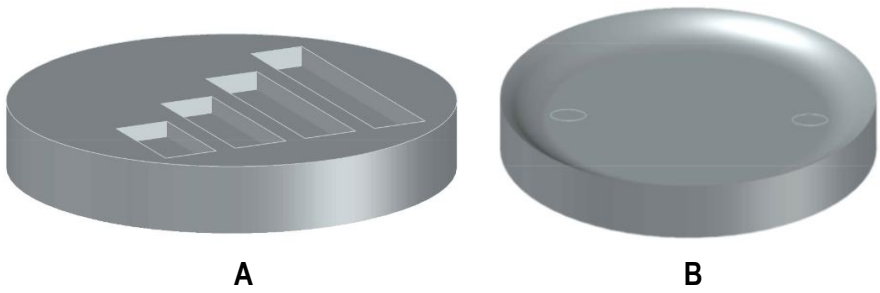


Figure 5. 3D representation of the support of the UV indicator bars (drawing made with Autocad program). Image A is the front side while image B is the back side of the support.

## APPENDIX 5: REFLECTANCE OF THE UVR INDICATOR SENSORS

To estimate the approximate percentage of reflectance associated with the color change of a sensor just before the change of the next sensor is produced, it is necessary to know the accumulated UVR dose that each one represents (25%, 50%, 75% and 100%) according to the MED corresponding to its skin type. In this sense, Table 9 shows the accumulated UVR dose ( $J/m^2$ ) associated with the percentage of MED depending on skin type according to the Fitzpatrick scale, beside indicating the number of TFF (100 microns thickness each) associated with each percentage.

Table 9. Accumulated UVR dose and number of TFF from each sensor according to skin type [2]

TYPE I	UVB MED VALUE [ $J/m^2$ ]	%MED (N°TFF)			
	200	25(0)	50(1)	75(2)	100(3)
	UVR dose [ $J/m^2$ ]	50	100	150	200
TYPE II	UVB MED VALUE [ $J/m^2$ ]	%MED (N°TFF)			
	250	25(0)	50(2)	75(3)	100(4)
	UVR dose [ $J/m^2$ ]	63	125	188	250
TYPE III	UVB MED VALUE [ $J/m^2$ ]	%MED (N°TFF)			
	300	25(0)	50(2)	75(4)	100(5)
	UVR dose [ $J/m^2$ ]	75	150	225	300
TYPE IV	UVB MED VALUE [ $J/m^2$ ]	%MED (N°TFF)			
	450	25(1)	50(4)	75(5)	100(6)
	UVR dose [ $J/m^2$ ]	113	225	338	450
TYPE V	UVB MED VALUE [ $J/m^2$ ]	%MED (N°TFF)			
	600	25(2)	50(5)	75(6)	100(7)
	UVR dose [ $J/m^2$ ]	150	300	400	600
TYPE VI	UVB MED VALUE [ $J/m^2$ ]	%MED (N°TFF)			
	1000	25(4)	50(6)	75(7)	100(8)
	UVR dose [ $J/m^2$ ]	250	500	750	1000



Table 9 shows that, unlike the rest of the sensors, those that represent 25% of the MED of skin types I, II and III, don't have of any TFF that blocks UV radiation and, therefore, all the radiation to which it is exposed will be equal to that which it accumulates. Next, by means of the graph in figure 3, the percentage of reflectance can be seen to decrease as the accumulated radiation dose increases over time (1s represents 1 J/m<sup>2</sup> of UVB radiation), which would imply an increase in the visualization of the sensor. Therefore, it can be deduced that when 50, 63 and 75 s of exposure to simulated sunlight have passed, the sensors of 25% of the MED of Type I, II and III, respectively, will have reached their maximum radiation and the percentage of reflectance at that time will be that corresponding to the change in color before the color of the next sensor begins to appear.

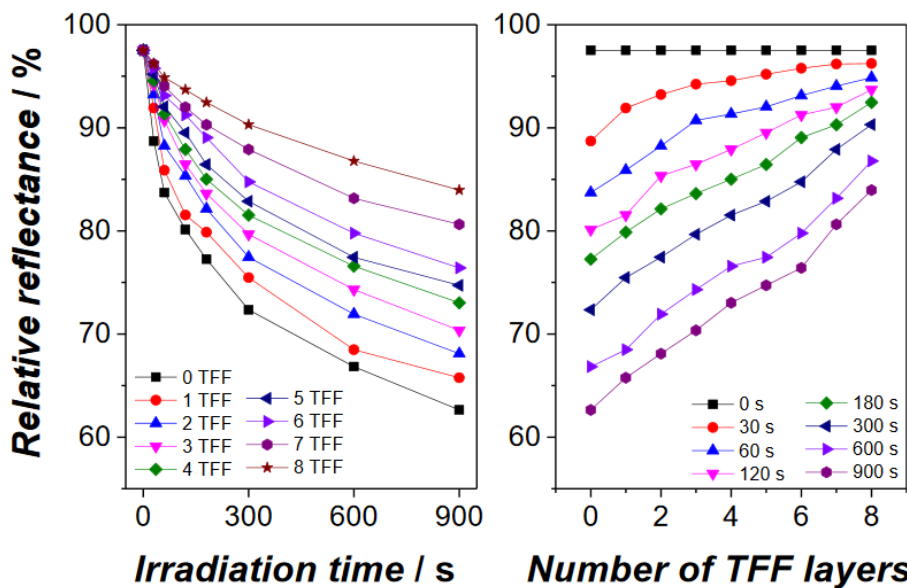


Figure 3. Correlation between the TFF numbers used to prepare the paper-based smiling sensors and the relative reflectance of the blue indicator generated by exposure to the solar simulator. In these experiments, 1 s of simulated solar irradiation corresponds to 1 J·m<sup>-2</sup> equivalent to the UVB.  
 (Extracted image of supplementary information of W. Zou et al., ref. 2)

Finally, by using the interpolation formula indicated in figure 4, the reflectance data of these sensors has been obtained and the average reflectance of approximately 84% by means of the values of the graph in figure 3. The results are shown in table 10 [2].

$$y = y_0 + \frac{y_1 - y_0}{x_1 - x_0} (x - x_0)$$

Figure 4. Linear interpolation formula to find the value "y" associated to a value "x" that is between the known values of "x<sub>0</sub>" and "x<sub>1</sub>" associated to the values "y<sub>0</sub>" and "y<sub>1</sub>", respectively.

Table 10. Sensor reflectance percentages of 25% of the MED of skin types I, II and III obtained by interpolation

Skin type	UV dose at 25% of the MED [J/m <sup>2</sup> ]	% reflectance	% average reflectance
I	50	85.36	83.99
II	63	83.69	
III	75	82.91	

## APPENDIX 6: MAXIMUM DEVICE PRODUCTION

Table 12. Total production estimated on the basis of the number of tourists received in Catalonia according to the INE (Appendix 2) and the 61.3% of people surveyed by M. de Troya Martín who would carry out 3 or more sun protection practices [21]

Estimated monthly production (30 Days)					
Month 9	Month 8	Month 7	Month 6	Total	Monthly average
1 787 863	2 659 395	2 412 440	2 116 351	8 976 050	<b>2 244 012</b>
Estimated daily production					
Month 9	Month 8	Month 7	Month 6	Total	Daily average
59 595	88 647	80 415	70 545	299 202	<b>74 800</b>

Table 13. Participants in the surveys conducted by the IFC and M. de Troya Martín (MTM) according to skin phototype [20], [21]

Survey results				
Phototype	IFC participants	MTM participants	Total	%
I	311	143	454	<b>6.46%</b>
II	1237	235	1472	<b>20.94%</b>
III	2132	358	2490	<b>35.41%</b>
IV	2297	318	2615	<b>37.19%</b>
	5977	1054	7031	

Table 14. Estimated weightings according to the skin phototype for the calculation of total production. The 90% will be destined to the phototypes of skin from I to IV and the other 10% will be distributed equally between phototypes V and VI

<b>Weighting of phototypes</b>		
<b>Phototype</b>	<b>Weighting</b>	<b>%</b>
I	5.8	<b>5.8%</b>
II	18.8	<b>18.8%</b>
III	31.9	<b>31.9%</b>
IV	33.5	<b>33.5%</b>
V	5.0	<b>5.0%</b>
VI	5.0	<b>5.0%</b>

Table 15. Estimated monthly and daily production of the device according to the skin phototype and its weighting corresponding

<b>Estimated monthly production for phototype</b>						
<b>Phototype</b>	<b>Month 9</b>	<b>Month 8</b>	<b>Month 7</b>	<b>Month 6</b>	<b>Total</b>	<b>Monthly average</b>
I	103 900	154 548	140 197	122 990	521 635	<b>130 409</b>
II	336 874	501 090	454 558	398 769	1 691 292	<b>422 823</b>
III	569 848	847 633	768 920	674 547	2 860 948	<b>715 237</b>
IV	598 455	890 184	807 521	708 410	3 004 570	<b>751 143</b>
V	89 393	132 970	120 622	105 818	448 802	<b>112 201</b>
VI	89 393	132 970	120 622	105 818	448 802	<b>112 201</b>
<b>Total</b>	<b>1 787 863</b>	<b>2 659 395</b>	<b>2 412 440</b>	<b>2 116 351</b>	<b>8 976 050</b>	<b>2 244 012</b>
<b>Estimated daily production for phototype</b>						
<b>Phototype</b>	<b>Month 9</b>	<b>Month 8</b>	<b>Month 7</b>	<b>Month 6</b>	<b>Total</b>	<b>Daily average</b>
I	3 463	5 152	4 673	4 100	17 388	<b>4 347</b>
II	11 229	16 703	15 152	13 292	56 376	<b>14 094</b>
III	18 995	28 254	25 631	22 485	95 365	<b>23 841</b>
IV	19 948	29 673	26 917	23 614	100 152	<b>25 038</b>
V	2 980	4 432	4 021	3 527	14 960	<b>3 740</b>
VI	2 980	4 432	4 021	3 527	14 960	<b>3 740</b>
<b>Total</b>	<b>59 595</b>	<b>88 647</b>	<b>80 415</b>	<b>70 545</b>	<b>299 202</b>	<b>74 800</b>

