Chemical and Physical Sunscreens

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Abstract

Sunscreens are formulations for skin application that contain substances that can absorb, reflect, or disperse solar radiation, reducing its biological effects on the skin (Schalka et al., An Bras Dermatol, 89:1–74, 2014; Schalka and Reis, An Bras Dermatol, 86:507–15, 2011). They are classified in organic or inorganic filters, based on their respective chemical compositions (Schalka et al., An Bras Dermatol, 89:1–74, 2014; Schalka and Reis, An Bras Dermatol, 86:507–15, 2011; Monteiro, Rev Bras Med, 67:5–18, 2010; Shaat, Sunscreens: regulation and commercial development, Taylor and Francis, Boca Raton, pp. 217–239, 2005). The main objective of this chapter is to differentiate the physical and chemical filters, their different galenical presentations, and their effectiveness.

Keywords

Sunscreen • Organic filters • Inorganic filters • Ultraviolet radiation

Contents

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M.C.A. Issa, B. Tamura (eds.), *Daily Routine in Cosmetic Dermatology*, Clinical Approaches and Procedures in Cosmetic Dermatology 1, DOI 10.1007/978-3-319-12589-3_7

Introduction

The reactions caused by sunlight on the skin are many and may be both positive and negative. They depend, among other factors, on radiation intensity and wavelength, as well as on the type of skin of each individual. The appropriate choice and use of sunscreens are decisive in the correct skin protection against UV radiation, avoiding skin cancer, sunburns, and photoaging (Schalka et al. 2014).

Sunscreens

Sunscreens (or topical photoprotectors) are formulations for skin application, in different presentation forms, that contain substances that can absorb, reflect, or disperse solar radiation, reducing its biological effects on the skin (Schalka et al. 2014; Schalka and Reis 2011).

Initially, they were conceived for the purpose of preventing solar burns during outdoor work, leisure, and sports activities. The first formulations appeared in the 1930s and protected only against UVB rays, those mainly responsible for causing erythema and damage to cell DNA. By the 1980s, the role of UVA radiation in photoaging and carcinogenesis, and the importance of formulations containing filters for this radiation, was demonstrated. Thus, a good photoprotector agent is one that protects against both UVA and UVB rays (Schalka et al. 2014; Schalka and Reis 2011; Monteiro 2010; Shaat 2005).

Sunscreen Formulation

UV Filters

Sunscreens contain filters that are agents with the ability to absorb, reflect, or disperse ultraviolet radiation. Their correct use is the main cosmetic approach to protecting from the harmful effects of solar radiation. These substances are commonly classified as "physical filters" or "chemical filters" (Schalka et al. 2014). However, this designation is not adequate, since the action mechanism of sunscreens usually involves physical processes (Schalka and Reis 2011; Monteiro 2010). Thus, the more appropriate classification is organic filters or inorganic filters, based on their respective chemical compositions (Schalka et al. 2014; Schalka and Reis 2011; Monteiro 2010; Shaat 2005).

An inorganic or physical sunscreen acts as a barrier, reflecting the majority of the radiation. Light falling on inorganic particles is redirected, reflected back, or spread out in different ways. The most common examples of this type of filters are zinc oxide and titanium dioxide (Schalka et al. 2014; Schalka and Reis 2011; Monteiro 2010; Shaat 2005). Depending on the size of the particle, the protection can occur not only by means of reflection. When these filters are in a micronized form, they can also act by diffraction and dispersion (Schalka et al. 2014; Schalka and Reis 2011; Monteiro 2010; Shaat 2005).

Inorganic filters have a minimal potential for allergic sensitivity and high photostability, making them especially important for formulating children's products, for daily use and for persons with sensitive skin (Schalka et al. 2014; Schalka and Reis 2011; Monteiro 2010; Shaat 2005). However, their reflective property can cause excessive shine and a whitish aspect, limiting their exclusive use in preparations due to low cosmetic acceptance. A way to solve this problem was the addition of iron oxide pigment to products, providing a makeup base coloration very well accepted by women (Schalka et al. 2014; Schalka and Reis 2011; Monteiro 2010; Shaat 2005).

Sunscreens with inorganic filters have been improved in recent years, through development of micronized forms of titanium dioxide and zinc oxide and by using polymers to encapsulate them. With their micronization, the size of the particles was reduced to 50–90% of the original size, making it possible to develop formulations that become transparent after application, with a consequent improvement in acceptability (Schalka et al. 2014; Schalka and Reis 2011; Monteiro 2010; Shaat 2005).

The size of the particles of inorganic filters is, therefore, a determining factor of their effect. The smaller the particle, the better it covers the skin and, consequently, the better the reflection; however, refraction is worse. Therefore, reflection and refraction are inversely related. The efficiency of inorganic filters is related to the size and dispersion of their particles (Schalka et al. 2014; Shaat 2005). They can be covered with silicone, silica, aluminum oxide, stearic acid, or aluminum stearate, among others, improving their dispersion, avoiding agglomeration of particles, and altering emulsion rheology. Titanium dioxide, for example, can only be associated with avobenzone when covered with silica and dimethicone. On the other hand, only inorganic filters with particles larger than 200 nm are capable of reflecting in the visible light range (Schalka et al. 2014; Schalka and Reis 2011; Monteiro 2010; Shaat 2005).

Organic or chemical filters are molecules capable of absorbing UV radiation and transforming it into energy radiation harmless to humans. With regard to solubility, they can be hydro or liposoluble (González et al. 2008; Palm and O'Donoghue 2007; Schlossman and Sho 2005). In relation to their action mechanism, the molecules of the absorbing filters contained in sunscreens have numerous double links in their configuration, whether in the benzene ring or the linear chain, allowing many of the electrons found in lower-energy orbits to absorb incident UV radiation and be excited to higher-energy orbits, converting the high-energy radiation and short wavelengths that are highly damaging into low-energy radiations and long wavelengths (González et al. 2008; Palm and O'Donoghue 2007; Schlossman and Sho 2005).

The UV energy absorbed by a molecule is released when it returns to its resting state. Furthermore, its release occurs in the form of fluorescent or phosphorescent light and heat, able to decompose and form photoproducts. Therefore, a sunscreen absorbs harmful energy and transforms it into energy forms that do not damage the skin (González et al. 2008; Palm and O'Donoghue 2007; Schlossman and Sho 2005).

In comparison to inorganic filters, they have higher allergic sensitivity potential and lower photostability, depending on their chemical structure and the combination of components in their formula. More recently, a new generation of organic filters has appeared, with higher photostability and lower potential for skin absorption (reducing the risk of developing an allergic reaction) (Schalka et al. 2014; RIBEIRO, Claudio de Jesus 2006).

However, with the development of new organic and inorganic filters, this classification has become incomplete, since we have organic filters today capable of reflecting UVR and inorganic filters with particles so small (less than 100 nm) that they are able to absorb UVR (Schalka et al. 2014; Shaat 2005).

Organic filters can be divided into UVA filters that protect against UVA radiation, UVB filters that protect against UVB radiation, and broad-spectrum filters that protect against both UVA and UVB radiation (Schalka et al. 2014; Shaat 2005).

Usually, commercial sunscreens use a composition of inorganic and organic filters to expand the photoprotection spectrum (UVA and UVB), exploit synergistic properties, and minimize the adverse effects of a specific component (Schalka et al. 2014; Shaat 2005).

In Brazil, sunscreens are categorized by the National Health Surveillance Agency (ANVISA) as cosmetics, making medical prescription unnecessary for their sale. The same occurs in European countries. However, there is regulation that requires studies to verify safety and efficacy. In the USA, regulatory approval of new filters is slow since sunscreens are considered OTC products (drugs that do not need medical prescription). Many UV filters were developed over the last decade to improve efficacy and safety. However, for regulatory reasons, the list of filters approved for sunscreen development can vary from country to country. There are 16 approved UV filters in the USA, 29 in Australia, 28 in the European Union, and 33 in Brazil. In addition, the concentration of active ingredients allowed to be incorporated in the formulations can also vary (Schalka et al. 2014; Shaat 2005; Agência Nacional de Vigilância Sanitária (ANVISA) 2012). Table 1 shows the components regulated by the FDA.

Filters capable of protecting against visible light act only by reflection, having a whitening effect. As an alternative, different pigments as blocking components of this radiation range are

Table 1 Sunscreen active ingredients currently approved in the FDA monograph

Active ingredients	Maximum concentration (%)	Peak absorption λ (nm)	UV action spectrum
Organic filters			
UVA filters			
Benzophenones			
Oxybenzone (benzophenone-3)	6	288.325	UVB, UVA II
Sulisobenzone (benzophenone-4)	10	366	UVB, UVA II
Dioxybenzone (benzophenone-8)	3	352	UVB, UVA II
Dibenzoylmethanes			
Avobenzone (butyl methoxydibenzoylmethane, Parsol 1789)	3	360	UVA I
Anthralates			
Meradimate (menthyl anthranilate)	5	340	UVA II
Camphors			
Ecamsule * (terephthalylidene dicamphor sulfonic acid, Mexoryl SX)	10	345	UVB, UVA
UVB filters			
Aminobenzoates (PABA derivatives)			
PABA (para-aminobenzoic acid)	15	283	UVB
Padimate-O (octyl dimethyl PABA)	8	311	UVB
Cinnamates			
Cinoxate (2-ethoxyethyl p-methoxycinnamate)	3	289	UVB
Octinoxate (octyl methoxycinnamates [OMC])	7.5	311	UVB
Salicylates			
Octisalate (octyl salicylate)	5	307	UVB
Homosalate (homomenthyl salicylate)	15	306	UVB
Trolamine salicylate (triethanolamine salicylate)	12		UVB
Others			
Octocrylene	10	303	UVB, UVA II
Ensulizole (phenylbenzimidazole sulfonic acid)	4	310	UVB
Inorganic filters			
Titanium dioxide	25		UVB, UVA
Zinc oxide	25		UVB, UVA

used, providing a “base” appearance to the formulation (Schalka et al. 2014; Shaat 2005).

Sunscreens able to protect against infrared radiation do so through addition of ingredients capable of reducing cell or molecular damage caused by this radiation (Schalka et al. 2014; Shaat 2005).

Galenic Formulation

Topical sunscreens can be transmitted in different pharmaceutical forms. Pharmaceutical formulas consist of a main component (substance that provides the desired therapeutic benefit), a vehicle (responsible for incorporating the other components), and excipients such as emollients, solvents, emulsifiers, preservatives, and fragrances, among others (Schalka et al. 2014; Palm and O’Donoghue 2007; Teixeira 2012; Chorilli et al. 2006).

The appropriate choice of vehicle and other components for a sunscreen formulation is as important as the main component itself, contributing to a satisfactory final result, stability, and efficacy of the formula (Schalka et al. 2014; Palm and O’Donoghue 2007; Teixeira 2012; Chorilli et al. 2006).

Excipients are essential in preparing formulations – they must be inert but contribute to the appearance, stability, and safety of sunscreens. Examples of excipients include emulsifiers, preservatives, and fragrances, among others. The use of polymers in formulations can improve spreadability, absorption, and film formation on the skin. In other cases, the use of emulsifiers to incorporate organic filters into the vehicles can interfere with the absorption curve of the main component (Schalka et al. 2014; Palm and O'Donoghue 2007; Teixeira 2012; Chorilli et al. 2006).

The vehicle also does not have pharmacological action, but it is responsible for incorporation of the other components. Its choice influences the stability and efficacy of the formulation, contributing to an effective SPF level. In addition, the physical-chemical composition and state of the vehicle influence the cosmetics, thus determining which type of skin is appropriate for each formulation (Schalka et al. 2014; Palm and O'Donoghue 2007; Teixeira 2012; Chorilli et al. 2006).

The choice of appropriate vehicle should take the treatment objective and characteristics of each patient into consideration and increase the efficacy of the formula and adherence of the sunscreen. There are a number of presentation forms, such as oils, gels, emulsions, mousses, aerosols, sticks, compact powder, and bases (Schalka et al. 2014) (Table 2).

Table 2 Various presentations of sunscreens and their characteristics

Presentation	Skin sensation	Water resistant	Need for reapplication
Cream/lotion (emulsion)	Pleasant	Yes	Less frequent
Mousse	Pleasant	Yes	Less frequent
Oily gel	Oily	Yes	Less frequent
Aqueous gel	Pleasant	No	Frequent
Hydroalcoholic gel	Pleasant	Yes	Less frequent
Gel-cream	Pleasant	Yes	Less frequent
Sticks	Greasy	Yes	Less frequent
Spray/aerosol	Oily	Yes	Less frequent
Oil	Oily	Yes	Less frequent

Adapted source: Teixeira SMMCG 2012

Oils

Oils are single-phase vehicles that can be easily manipulated and quite stable for incorporation of liposoluble components. When applied to the skin, they have good spreadability and are quite water resistant. However, they are limited cosmetically since they are oily, leave an excessive shine on the skin and soil clothing, and are difficult to remove. In addition, the easy application leads to only a fine transparent layer of the product on the skin, achieving reduced SPF values (Schalka et al. 2014; Palm and O'Donoghue 2007; Teixeira 2012; Chorilli et al. 2006).

Gels

A gel is a semisolid preparation formed primarily by polymers dispersed in a liquid medium. The liquid phase, in general, is composed of water or alcohol, while the solid phase is represented by gelling agents. Hydrogels are easily applied and provide a dry and transparent film over the skin; however, they are not water resistant and do not provide high SPF values. Alcohol gels are cosmetically similar to hydrogels, providing higher SPF levels; however, they can cause skin dehydration and should be avoided by people with skin xerosis and sensitive skin. On the other hand, oil gels or gel-creams have characteristics similar to oils and are water resistant. Moreover, they leave a denser film on the skin than do oils, providing stronger photoprotection (Schalka et al. 2014; Palm and O'Donoghue 2007; Teixeira 2012; Chorilli et al. 2006).

Emulsions

Emulsions are dispersions of two immiscible phases (aqueous and oily), which form a homogeneous and stable system through the action of an emulsifier. Emulsions can be classified in different ways, for example, taking the proportion between the aqueous and oily phases into account. In water-in-oil (W/O) emulsions, the continuous phase of the emulsion is the oil and the disperse phase the water, resulting in more oily formulations that leave a shine on the skin and are more water resistant. The oil/water (O/W) emulsions are less greasy, dry quickly, and are easier to remove with water. This is a vehicle with versatile properties, cosmetically pleasing and compatible with the incorporation of lipo- and water-soluble substances, making it one of the most prescribed pharmaceutical forms. They can be divided into liquid emulsions (fluid or lotion emulsions) or pasty emulsions (creams) depending on their physical aspect (Schalka et al. 2014; Palm and O'Donoghue 2007; Teixeira 2012; Chorilli et al. 2006).

Silicone-in-water emulsions should also be highlighted. Silicones allow incorporation of large content in the aqueous internal phase and replace oils with the advantage of having greater chemical inertia, and when well structured, the oily characteristic disappears (Schalka et al. 2014; Palm and O'Donoghue 2007; Teixeira 2012; Chorilli et al. 2006).

Gel-Cream

Gel-cream is an emulsion that contains a high percentage of aqueous phase and low oil content, stabilized by hydrophilic colloids. They are cosmetically pleasing, combining the sensory effect of gels with the emollience of emulsions. It is a vehicle commonly used in tropical countries and appropriate for oily skin since it allows incorporation of oil-sequestering agents (Schalka et al. 2014; Palm and O'Donoghue 2007; Teixeira 2012; Chorilli et al. 2006).

Mousses

A mousse is a fluid emulsion, conditioned in a special packaging with a valve that when squeezed forms an elegant foam, easily spreadable (Schalka et al. 2014; Palm and O'Donoghue 2007; Teixeira 2012; Chorilli et al. 2006).

Aerosols

Aerosols are colloidal dispersions of a liquid in a gas. They provide a continuous and homogeneous flow, are easy to apply, and provide an interesting presentation for the scalp, hairy areas, hard-to-reach areas, or large surfaces. Aerosols in general are oily and easily spread over the skin, leaving a fine but oily layer. Formulas containing silicone are more accepted cosmetically, however questionable in relation to the uniformity of coverage (Schalka et al. 2014; Palm and O'Donoghue 2007; Teixeira 2012; Chorilli et al. 2006).

Sticks

Sticks are solid forms made up of waxes and oils, very water resistant and ideal for small areas such as the lips, nose, and cheeks. Liposoluble inorganic and/or organic sunscreens can be incorporated, and they are quite effective; however, they can leave an oily appearance and are expensive (Schalka et al. 2014; Palm and O'Donoghue 2007; Teixeira 2012; Chorilli et al. 2006).

Powders and Bases

These are cosmetic products which incorporate sunscreens. They have a very useful makeup effect, ensuring a uniform color to the skin, reducing shine, and providing photoprotection. Organic and inorganic filters can be added to compact powders and bases, while only inorganic filters are generally incorporated in powders (Schalka et al. 2014; Palm and O'Donoghue 2007; Teixeira 2012; Chorilli et al. 2006).

Other Ingredients

Recently, different components with antioxidant action have been incorporated in sunscreen formulations, with biological action to reverse oxidative damage caused by radiation. These components have no direct action on incident radiation, like the ultraviolet filters mentioned above, but they interfere in a secondary manner, at the cellular or molecular level, neutralizing reactive oxygen species (ROS) (Schalka et al. 2014; Gonzalez et al. 1996; Kenneth and Palefsky 2005).

In addition to antioxidants, new components have been proposed, with biological actions that go beyond antioxidant action. Two examples of these components are *Polypodium leucotomos* extract, with antioxidant action and a modulator of the immunological response resulting from

Table 3 Main antioxidant components used in sunscreen formulations

Antioxidant component	Source
Vitamin C	Fruits, vegetables
Vitamin E	Vegetable oil, seeds
Green tea polyphenols	Green tea fractions
Soy isoflavones	Soybeans, Ginkgo biloba
Caffeic acid and Ferulic acid	Coffee beans, propolis
Selenium	Corn, soybeans, wheat
Pycnogenol	Pine bark extract
Resveratrol	Grape skin and seeds
Polypodium leucotomos	Extract from a tropical fern variety

solar radiation, and *Photolyase*, with photo-chemopreventive action, repairing DNA damaged by the effect of radiation (Schalka et al. 2014; Gonzalez et al. 1996; Kenneth and Palefsky 2005).

There are also components with the ability to protect mitochondrial DNA, particularly against the effects of infrared radiation, as in the case of *Artemia salina* plankton extract (Schalka et al. 2014; Gonzalez et al. 1996; Kenneth and Palefsky 2005).

Table 3 shows some of the main antioxidant components used in sunscreen formulations.

Assessment of Sunscreen Efficacy

The first method described, and still considered a reference for assessment of the photoprotection efficacy of sunscreens, is the sun protection factor (SPF) that is based on evaluation of the minimum erythematous dose between the skin protected by a sunscreen (application of 2 mg/cm^2) and unprotected skin, conducted with a group of volunteers exposed to radiation-emitting equipment with a spectrum similar to sunlight. The SPF is a measurement capable of essentially quantifying protection against UVB radiation, with little interference on the evaluation of protection against UVA (Schalka et al. 2014; Diffey and Kochevar 2007; DeBuys et al. 2000; Lui and Anderson 2007; Schalka et al. 2009).

For quantification of UVA protection, Moyal et al. (2000) presented a method called "persistent pigment darkening" (PPD) for evaluation of protection in the UVA range. This method, today called UVA protection factor (UVA-PF), is considered the most adequate method for determining protection in the UVA range and can be conducted in vivo or through spectrophotometry (in vitro). The target biological event of the UVA-PF method is immediate pigmentation resulting from oxidation of the melanin formed, an event resulting from UVA radiation (Moyal et al. 2000a; Moyal et al. 2000b; Yaar 2007).

For a sunscreen to be qualified to provide balanced UVA/UVB protection, it must have a minimum UVA-PF of 1/3 of the SPF and a critical wavelength (spectrophotometry method) greater than 370 nm (Schalka et al. 2014; Moyal et al. 2000a; Moyal et al. 2000b; Yaar 2007).

In addition to ultraviolet radiation, waves of greater length, like infrared radiation and primarily visible light, are capable of triggering photobiological phenomena on the skin. In particular, the action of visible light in triggering pigmentation has been demonstrated (Mahmoud 2008; Rhodes and Lim 2007).

So far, there are no substances capable of absorbing visible light, and protection against it can only be provided by particles (inorganic filters) or pigments capable of reflecting or dispersing visible light by means of optical mechanisms. Reliable methods capable of quantifying protection against visible light have not yet been found (Mahmoud 2008; Rhodes and Lim 2007).

Studies also show the effect of type A infrared radiation (760–1,000 nm) on the production of oxygen reactive species through mitochondrial action. Antioxidant components can reduce the production of these reactive species, demonstrating, therefore, antioxidant action against infrared radiation. There are methods capable of measuring the antioxidant efficacy in cellular cultures when exposed to type A infrared radiation (Mahmoud 2008; Rhodes and Lim 2007).

Take-Home Messages

- Sunscreens contain substances that can absorb, reflect, or disperse solar radiation, reducing its biological effects on the skin.
- Sunscreens are commonly classified as "physical filters" or "chemical filters." However, this designation is not adequate, and the more appropriate classification is organic or inorganic filters.
- An inorganic sunscreen acts as a barrier, reflecting the majority of the radiation. The most common examples of this type of filters are zinc oxide and titanium dioxide.
- Organic filters are molecules capable of absorbing UV radiation and transforming it into energy radiation harmless to humans.
- Topical sunscreens can be transmitted in different pharmaceutical forms (gels, emulsions, gel-cream, spray, powder, among others), and the appropriate choice of the product contributes to the efficacy of the formula.
- Antioxidants and modulators of the skin immunological response have been incorporated in sunscreen formulations.
- The efficacy of sunscreens depends on the SPF, the UVA-PF, the ratio UVA/UVB, and the critical wavelength.
- Filters capable of protecting against visible light have a whitening and unpleasant effect. As an alternative, different pigments are used providing a "makeup base" appearance to the formulation.
- Sunscreens able to protect against infrared radiation do so through addition of ingredients capable of reducing cell or molecular damage caused by this radiation.

Cross-References

▶ Oral Photoprotection
▶ Photoprotection: Concept, Classification, and Mechanism of Action
▶ Vitamin D and Photoprotection

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