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REVIEW ARTICLE

Sunscreens: An Update

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Abstract Sunscreens have been widely used by the general public for their photoprotective properties, including prevention of photocarcinogenesis and photoaging and management of photodermatoses. It is important to emphasize to consumers the necessity of broad-spectrum protection, with coverage of both ultraviolet A (320–400 nm) and ultraviolet B (290–320 nm) radiation. This review discusses the benefits of sunscreen, different ultraviolet filters, sunscreen regulations and controversies, the importance of broad-spectrum protection, issues of photostability and formulation, and patient education and compliance.

Key Points

Data to support the regular use of sunscreen far outweighs the limited data regarding its possible side effects.

Use a broad-spectrum water-resistant sunscreen with SPF 30 or greater; apply one oz (30 ml) to adequately cover the entire body.

Ultraviolet filters do not protect against visible light and infrared radiation, which have been shown to induce 50% of the free radicals generated in the skin following sun exposure.

1 Introduction

Sunscreens have been widely used by the general public for their photoprotective properties, including prevention of photocarcinogenesis and photoaging and management of photodermatoses. It is important to emphasize to consumers the necessity of broad-spectrum protection with coverage of both ultraviolet (UV) A (UVA; 320–400 nm) and UVB (290–320 nm) radiation.

The basic requirements that sunscreen manufacturers must consider are efficacy, safety, registration, and patent freedom [1]. Ideal sunscreens should have highly efficient filters against both UVB and UVA radiation, be photostable, and be made in formulations that are cosmetically acceptable to the general public. They should have no adverse effect on the environment or on humans. UV filters must be approved by the local regulatory agency for the area in which the products are to be marketed. Obviously, patent infringement must be avoided [1].

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2 Clinical Benefits of Sunscreens

The harmful effects of solar radiation exposure on human skin are well known. Acute effects of UV radiation include erythema, pigment darkening, vitamin D synthesis, tanning, and photoimmunosuppression. Chronic effects include photoaging and photocarcinogenesis. UV radiation leads to DNA damage. UVB radiation results predominantly in the formation of pyrimidine dimers and 6–4 photoproducts, whereas the predominant effect of UVA radiation is oxidative damage to DNA [2]. The American Cancer Society estimated that about 76,000 new cases of invasive melanoma would be diagnosed in the year 2016 in the USA [3].

The role of sunscreens as effective photoprotective agents in preventing the adverse outcomes of exposure to sunlight has been well studied and documented. A landmark study demonstrated that daily use of sunscreen can prevent the development of melanoma. This longitudinal study conducted in Nambour, QLD, Australia, with 1621 individuals aged 25–75 years assessed the effect of sunscreen use on the development of skin cancers. Participants were randomly assigned to the sunscreen intervention group ($n = 812$) or the control group ($n = 809$). The intervention group were given unlimited free SPF 16 sunscreen for 4 years and were asked to apply it to the head, neck, and upper extremities every morning and repeat applications as necessary, whereas the control group were not provided free sunscreen and were instructed to use sunscreen as they usually would with no intervention. The trial participants were monitored three times during the 4.5 years of the trial and screened with questionnaires 10 years after the trial ended. In total, 11 (1.4%) individuals in the sunscreen intervention group and 22 (2.7%) in the control group developed melanoma. Therefore, melanoma risk was reduced by 50% in the sunscreen intervention group at the end of the study period. However, statistical significance was borderline ($p = 0.051$) because of the small numbers of individuals developing melanoma [4].

The same study also evaluated the rates of squamous cell carcinoma (SCC) and basal cell carcinoma (BCC) development. Analysis at 8 years after the initial 4.5-year trial showed that, although the development of BCC decreased by 25% in the sunscreen group compared with controls, this trend was not statistically significant. In contrast, SCC rates were significantly reduced in the sunscreen treatment arm: total number of SCC tumors was 38% lower (81 tumors in the treatment group vs. 142 in the control group: rate ratio 0.59; 95% confidence interval [CI] 0.38–0.90) and the number of people affected with SCC was 35% lower (51 individuals in the treatment group vs. 76 in the control group: rate ratio 0.65; 95% CI 0.45–0.94) [5].

A number of clinical studies have demonstrated the protective effects of sunscreen against photoaging. From the same Australian cohort, 903 of the total 1621 adults were selected to evaluate skin aging from baseline to the end of the trial after 4.5 years. There were no differences in sun exposure, smoking, phenotype, other sun-protection measures, or pretrial sunscreen use between the groups. At the end of the follow-up, the sunscreen group had 24% fewer signs of photoaging as measured by skin surface replicas from the back of the left hand using silicone-based impression material [6]. The protective effect of sunscreen on photoaging was demonstrated in another study in individuals aged 20–35 years exposed to solar-simulated radiation (SSR). The use of broad-spectrum photoprotective day cream (SPF information not provided in the original article) decreased the development of effects of UV-induced photoaging, as evidenced by the lack of melanization and elastosis [7].

Sunscreen use has also been shown to protect against UV-induced immunosuppression. Moyal and Fourtanier [8] evaluated varying types of sunscreens against exposure to natural sunlight and SSR. Participants' responses to delayed-type hypersensitivity (DTH) tests were measured by applying a Multitest kit with seven recall antigens (antigens encountered by most participants during childhood immunizations) to participants' backs, then exposing them to UVA, UVA1, and SSR. The results indicated that broad-spectrum protection afforded better response to DTH tests than products with either limited-spectrum protection or no protection, suggesting that the broad-spectrum sunscreens offered better protection from UV-induced immunosuppression. This study also showed that the SPF of a sunscreen indicates protection against only sunburn and that for a sunscreen to be effective against the immunosuppressive effects of UVA radiation, it should also contain a superior UVA-protection factor [8].

Sunscreen use is also important for people with photoaggravated dermatoses such as lupus erythematosus (LE). A study evaluating the photoprotective impact of broad-spectrum sunscreens found that the use of broad-spectrum sunscreens in participating patients with LE lessened the development of cutaneous lesions [9]. Studies have also demonstrated the benefits for organ transplant recipients of regularly using broad-spectrum sunscreens to prevent the development of actinic keratoses and invasive SCC [10].

3 Ultraviolet Filters

UV filters are chemicals that scatter and absorb UV radiation. They are classified as either organic agents or inorganic agents. Organic filters can exist in liquid or solid forms and absorb photons from UVA and UVB rays. These

compounds are aromatic compounds containing series of conjugated π-electron systems on their aromatic rings. The presence of conjugated aromatic rings allows the compound to absorb UV energy, which is then dissipated in the form of heat [11].

There are five main types of organic filters: para-aminobenzoic acid (PABA) derivatives, benzophenones, salicylates, cinnamates, and 'other' (see Table 1) [12–14]. The PABA derivatives are highly effective UVB absorbers. Padimate O is a PABA ester that is a highly effective UVB absorber but causes severe photodegradation when used in conjunction with oxybenzone; it is also a common contact allergen. Therefore, it is very rarely used.

Benzophenones are good UVA2 (320–340 nm) absorbers. Oxybenzone is the most frequently used benzophenone and absorbs both UVB and UVA. It is the most common cause of photoallergic reaction among UV filters. Because of this, in the EU, sunscreens that contain oxybenzone must include "contains oxybenzone" on the label. However, it is still commonly used in the USA because other US FDA-approved filters that provide both photostabilization of avobenzone and UVA2 and UVB protection are lacking.

Salicylates, which include octisalate, homosalate, and trolamine salicylate, are weak UVB absorbers and are primarily used in combination with other organic absorbers. Octinoxate (also known as octylmethoxycinnamate), the most commonly used cinnamate, is a strong UVB absorber that destabilizes avobenzone. There are many other organic absorbers that do not fit in these categories, including octocrylene (UVB filter used to stabilize photolabile agents), ensulizole (photostable UVB absorber), avobenzone (effective but photolabile UVA1 [340–400 nm] filter), and menthyl anthranilate (relatively weak UVA2 filter) [12].

Inorganic filters, specifically titanium dioxide and zinc oxide, are opaque particles that primarily absorb but also reflect and scatter UV photons that reach the skin and can even offer protection into the visible light range. Historically, inorganic agents were cosmetically unacceptable as they give the skin a ghostly white appearance. Starting in the early 1990s, titanium dioxide and zinc oxide have been micronized and nanosized to achieve a cosmetically acceptable appearance [11, 12]. The smaller the particle size, the shorter its peak absorption spectrum [11]. Micronization primarily increases the UVB absorbance of titanium dioxide but does not affect the spectral absorbance distribution of zinc oxide, and decreases scattering and reflection in visible wavelengths. Zinc oxide has a flat absorbance curve throughout the UV in all particle sizes and the same critical wavelength independent of particle size [15]. The above-mentioned absorbance shift for titanium dioxide results in less protection in the UVA range

Table 1 Ultraviolet filters [12]

UVB filters	Aminobenzoates: padimate O, PABA	Cinnamates: octinoxate, cinoxate	Salicylates: octisalate, homosalate, trolamine salicylate	Others: octocrylene, ensulizole, enzacamene, octyl triazone, amiloxate, diethylhexyl butamido triazone
UVA filters	Benzophenones: oxybenzone, dioxybenzone, sulisobenzone	Others: avobenzone, meradimate, ecamsule, drometrizole trisiloxane (also a UVB filter), bemotrizinol (also a UVB filter), bisoctrizole (also a UVB filter), menthyl anthranilate		
Inorganic agents	Zinc oxide, titanium dioxide			

PABA para-aminobenzoic acid, *UVA* ultraviolet A, *UVB* ultraviolet B

Table 2 Ultraviolet filters pending approval by the US FDA in the USA

Filter	Peak absorption (nm)	500 Da
UVA		
Ecamsule (Mexoryl SX)	345	+
UVB		
Octyl triazone = ethylhexyl triazone	314	+
Amiloxate = isoamyl methoxycinnamate	308	
Diethylhexyl butamido triazone	311	+
Enzacamene = 4 methyl benzylidene camphor	300	
UVA/UVB		
Drometrizole trisiloxane (Mexoryl XL)	303/341	+
Bemotrizinol (Tinosorb S)	310/343	+
Bisoctrizole (Tinosorb M)	305/360	+

UVA ultraviolet A, *UVB* ultraviolet B

and little to no protection in the visible light range. Both titanium dioxide and zinc oxide are approved by the FDA.

4 Sunscreen Regulations

Regulation of sunscreens varies widely around the world. Sunscreens in the USA are regulated as over-the-counter drugs. In Australia, beach sunscreens are regulated as therapeutic drugs, whereas daily-wear moisturizer sunscreens are regulated as cosmetics. However, in the European markets, sunscreens are classified as cosmetics and are therefore not held to the same regulatory norms that are prevalent in the USA. Authorities in Japan regulate sunscreen as 'quasi-drugs' with regulations on the types of UV filters and concentrations allowed [11, 16]. The USA has the least and Europe and Australia have the most UV filters available to them when formulating sunscreen [17]. In the USA, only 16 UV filters are approved by the FDA and included in the sunscreen monograph; an additional filter, ecamsule, was approved through a New Drug Application process, and therefore is not included in the list in the FDA monograph. No new UV filters have been approved in the USA for more than 10 years [17]. There has been consistent effort by the US sunscreen industry to urge the FDA to approve the eight new UV filters (Table 2) currently waiting for approval under the Time and Extent Application (TEA) process. In fact, the Sunscreen Innovation Act was signed into law in 2014 with this specific objective, but no new UV filters have yet been approved [18].

Because the US sunscreen manufacturers do not have access to these new UV filters, there is concern that US sunscreen may not offer broad-spectrum UV protection comparable to those in other parts of the world. This is shown in two recent studies. One study examined SPF 50 products sold in Europe compared with those in the USA and found that US SPF 50 sunscreens transmitted three times more UVA [19]. Another study evaluated 20 US sunscreens (all broad spectrum; SPF 15–100+); 19 of the 20 products had a critical wavelength of $\geq$370 nm, the FDA requirement for a product to be labeled "broad spectrum." However, only 11 of the 20 products fulfilled an EU standard for the "broad spectrum" definition, which is a ratio of UVA protection factor over SPF of >1:3 [20].

The "500 Da rule" refers to the new filters that are in line with the general trend of sunscreen filters moving toward higher molecular weights (i.e., >500 Da), thereby minimizing percutaneous absorption. The objective with sunscreens is to keep the UV filter on, rather than in, the skin, which contrasts with many other topical dermatological therapies or percutaneous systemic therapies for which skin penetration is the goal, meaning compounds <500 Da are ideal [21].

5 Sunscreen Controversies

Several controversies have surfaced around the potential harms seen in UV filters in sunscreens [11]. One particularly heated controversy concerns oxybenzone. A limitation of oxybenzone is its photoallergenicity; it should be noted that although it has the highest rate of photoallergy among UV filters, considering the number of individuals exposed to oxybenzone, the rate is low [11].

Concerns about the estrogenic effects of oxybenzone were raised because of the results of a study using oral administration of oxybenzone in an animal model. However, it has been estimated that a human would need to apply this product daily for 35–277 years to achieve the same levels of oxybenzone to which these laboratory animals were exposed [22]. In addition, oxybenzone has been in used in the USA since 1978 without any reported

endocrinologic effects in humans. In a laboratory setting, oxybenzone has been shown to bleach coral reefs [23]. However, in the Great Barrier Reef in Australia, the greatest degree of coral reef bleaching occurred in remote areas infrequently visited by tourists. The National Oceanic and Atmospheric Administration and the Great Barrier Reef Marine Park Authority both concluded that rising water temperature is the most significant cause of coral reef bleaching [24].

Another popular topic is whether it is necessary to use sunscreen with high SPF values, as the percentage of erythemogenic UV blocked by SPF 60 (98.3%) compared with SPF 30 (96.7%) increases by only 1.6%. It should be noted that the amount of photons transmitted decreases from 3.3% at SPF 30 to 1.7% at SPF 60, a >50% decrease. With chronic sun exposure, it is photobiologically and clinically more relevant to assess the amount of UV photons transmitted [25], suggesting the long-term use of SPF sunscreens provides a better protective effect.

6 The Importance of Broad-Spectrum Protection

UV radiation of the solar spectrum consists of three components: UVA, UVB, and UVC. UVC radiation is absorbed by the ozone layer of the atmosphere; such natural protection does not exist with UVA and UVB radiation. Historically, the purpose of sunscreen was only to prevent sunburn, which is the major effect of UVB. UVA has a role in DNA damage, inducing photodermatoses and photoimmunosuppression; many of the damaging effects of UVA and resultant premature aging of the skin are only visible after many years [26]. It is now known that if a chosen sunscreen does not provide broad-spectrum UVB/UVA coverage, the user is not adequately shielded from the adverse effects of the full UV spectrum of solar radiation [2, 8]. In fact, a predominantly UVB-only sunscreen could provide the user a false sense of security of photoprotection as the user would be less likely to develop symptomatic sunburn while concomitantly increasing UVA exposure. Therefore, it is important that sunscreens have spectral homeostasis, meaning they provide uniform protection across the UVA and UVB spectrum so that UV rays from sunlight are attenuated uniformly [11].

The SPF of a sunscreen is a primary measure of the UVB, and to a lesser extent UVA2, protection offered by that product. In the USA, the UVA protection capability of sunscreens is assessed with the critical wavelength method. Sunscreen in the USA must have a critical wavelength ≥370 nm to be allowed to state "broad-spectrum" on the label. Furthermore, the FDA indicated that broad-spectrum products with SPF ≥15 are allowed to state on the label that they "decrease the risk of skin cancer and early skin aging caused by the sun." Products that fulfill the critical wavelength broad-spectrum requirement but have SPF <15 can state on the label that they work "only to prevent sunburn" [27].

Different types of UV filters are frequently combined to achieve a final product that is photostable, provides broad-spectrum protection, and has a high SPF. As an example, the superior long-wave UVA filter avobenzone is frequently combined with the UVB filters octocrylene and oxybenzone for broad-spectrum coverage and to provide photostability [28]. The FDA does not currently approve the combination of avobenzone with zinc oxide or titanium dioxide, so instead oxybenzone is often combined with these inorganic agents. Europe and other parts of the world place fewer restrictions on these combinations and a larger number of filters is available, giving manufacturers more options when producing excellent high-SPF broad-spectrum sunscreens [29].

A more recent development in photoprotection is the evaluation of appropriate protection against visible light and infrared radiation. Visible light and infrared radiation have been shown to induce 50% of free radicals generated in the skin following exposure to sunlight [30]. While UV filters in sunscreens protect against the effects of UV, they are not designed to protect against the effect of visible light and infrared radiation. Visible light is known to induce pigment darkening that lasts for weeks in individuals with darker skin types [31]. Currently, the only topical preparation that can prevent the effects of visible light is tinted sunscreens, which may not be acceptable to many individuals. Visible light is known to induce reactive oxygen species; therefore, topical or oral antioxidants hold promise in visible light photoprotection [32]. Sunscreens that contain antioxidants have been shown to suppress the infrared A-induced generation of matrix metalloproteinase-1 [33]. Clearly, more studies are needed in this area.

7 Issues of Photostability and Formulation

In addition to providing uniform broad-spectrum protection against UVA and UVB radiation, an ideal sunscreen must be photostable. Photostability can be assessed by comparing a sunscreen's absorbance before and after UV exposure. When a UV photon is absorbed by a UV absorber molecule, an excited state of the molecule is formed, and the absorbed energy must quickly dissipate into heat so that the molecule can return to its stable ground state. If the energy is not sufficiently dissipated, chemical bonds of the UV absorber can break and the UV filter can degrade [11]. Avobenzone provides the highest and broadest absorption and is the only UVA filter with such a high level of performance that is approved worldwide. However,

avobenzone is not photostable, and it undergoes rapid photodegradation when used alone or with certain other filters. Therefore, it is commonly combined with other UV filters such as bemotrizinol (not available in the USA) or octocrylene, which act to photostabilize avobenzone. In contrast, avobenzone and octinoxate are highly photo-unstable when combined, and their combination results in the destruction of both molecules, so they should not be used together [11].

Extreme temperatures (such as those found in motor vehicles) may compromise the photoprotective effects of sunscreens and lead to degradation. Jung et al. [34] exposed sunscreens to temperatures of 60 °C for 8 h and examined the physical macroscopic changes. This exposure resulted in phase separation and discoloration that did not resolve after 30 s of shaking the product. This may represent a disruption of the efficacy of sunscreens after exposure to heat. Patients should be counseled on proper storage of sunscreen, especially to avoid storing them in cars and to keep them covered or in the shade when outdoors [34].

8 Patient Education and Compliance

Sunscreens have been shown to prevent skin cancers and photoaging, but these benefits can only be derived if patients are compliant and consistently use these products appropriately. It is important for dermatologists and other healthcare provides to counsel patients on the overall photoprotection strategy of seeking shade when outdoors, wearing photoprotective clothing, sunglasses and wide-brim hats, and applying sunscreen on exposed skin. Proper application of sunscreen would include repeat applications every 2 h when outdoors. Of note, many sources suggest sunscreen application 20 min before sun exposure to allow time to apply adequately and evenly, without rushing. However, it is known that sunscreen works instantaneously when applied to the skin and does not need to penetrate the skin to work. A generous amount of sunscreen must be applied. To achieve a desired concentration of 2 mg/cm^2 on the skin surface, the American Academy of Dermatology (AAD) recommends at least 1 oz (30 ml) of sunscreen, or about the amount one can hold in one's palm, to adequately cover the entire skin surface [35]. A revised teaspoon rule has also been described: to achieve a 2 mg/cm^2 of application, 1 teaspoon (i.e., 5 ml) should be applied to face, head, and neck; 1 teaspoon to each arm and forearm; 2 teaspoons to the front and back of the trunk; and 2 teaspoons to each thigh and leg [36]. Sun protection factor is based on the use of a sunscreen layer of 2 mg/cm^2; however, about one-quarter to one-half of this amount (0.5–1.0 mg/cm^2) is most commonly applied in real life. Faurschou and Wulf [37] showed that the relation between SPF and sunscreen quantity in vivo followed an exponential curve; thus, when individuals use only 0.5 mg/cm^2, only a fourth root of the stated SPF is actually in effect. Other studies show a linear relationship between sunscreen application amount and SPF [38]. Using a sunscreen with a higher SPF (SPF >70) can somewhat compensate for the underuse of sunscreen quantity and can provide UV protection above minimal recommended levels with lower sunscreen application amounts [38]. As stated, it is essential to educate patients to apply generous amounts of sunscreen for adequate photoprotection.

Data showed that dermatologists spend the most time of any type of physician discussing sunscreen with patients [39]. However, despite significant public education efforts by the AAD and other professional organizations, the practice of proper photoprotection by the public remains inadequate. More effort on public education, including partnership with other healthcare providers such as primary care physicians, is necessary.

AAD guidelines on selecting sunscreen include broad-spectrum coverage, SPF 30 or higher, and water resistance. A recent study analyzed 65 of the most highly rated sunscreens sold on Amazon.com. Of these products, 40% did not adhere to the AAD recommendations, mostly due to a lack of water resistance [40]. The most common cited positive factor for the use of sunscreens was cosmetic elegance. It is therefore important to keep this in mind when recommending sunscreen products to patients. The reluctance of dark-skinned patients to use sunscreen that leaves a whitish residue on the skin should be taken into consideration. Finally, an open discussion with patients regarding the known benefits versus the theoretical risks of sunscreen may help to address their concerns or misconceptions.

For patients at highest risk of photocarcinogenesis or photosensitivity, dermatologists must go above and beyond to ensure compliance with photoprotection. Utilizing more modern methods of communication with patients can result in greater rates of compliance with sunscreen application. One study sent daily text-message reminders to apply sunscreen to half of the participants for 6 weeks. At the end of the study, the 35 participants who did not receive text messages had a mean daily adherence rate of sunscreen application of 30 versus 56% for the 35 participants who did receive the text-message reminders. Of those who did receive the text-message reminders, 89% said they would recommend the text-message reminder system to others [41].

Many primary prevention programs have been implemented in schools, recreation areas such as community pools and parks, outdoor workplaces, and throughout the community. Although evidence is insufficient to recommend a specific strategy, several have been shown to

Table 3 Simple guidelines for sunscreen use

1. Use a broad-spectrum, water-resistant sunscreen with SPF 30 or greater
2. Apply a thick layer of sunscreen to all exposed skin: sunscreen filling one palm is how much you should apply when covering your entire body
3. Reapply sunscreen at least every 2 hours you are in the sun, or after sweating or going in water
4. Apply sunscreen every morning to your face, neck, and hands

improve certain photoprotective behaviors [42]. For a public health message to be successful, it must be consistent and straightforward and include instructions with which the public find it easy to comply. When promoting photoprotection, the two major motivating factors are skin cancer prevention (health based) and the cosmetic benefit of decreasing photoaging (appearance based) [43]. Simple guidelines for sunscreen use are listed in Table 3.

9 Conclusion

The use of sunscreen as a part of photoprotection, along with seeking shade and wearing sun-protective clothing, hats, and sunglasses, can be very effective in the prevention of photodamage and photocarcinogenesis from UV radiation. Sunscreen is only effective when applied regularly and in a large enough quantity (2.0 mg/cm^2, approximately 1 oz [30 ml] to cover all exposed areas); it should be broad-spectrum, photostable, cosmetically elegant, and have an SPF of 30 or greater. While several controversies regarding sunscreen exist, the data to support the regular use of sunscreen far outweigh the limited data regarding its possible side effects.

Compliance with Ethical Standards

Conflicts of interest Henry W. Lim has received research grants from Clinuvel, Estée Lauder, Ferndale, and Allergan and consulting fees from Pierre Fabre, Ferndale, Uriage, Sanofi, and Johnson & Johnson. Steve Wang has been a consultant for Ferndale and Neutrogena. Rohit Maruthi and Jennifer Brescoll Mancuso have no conflicts of interest.

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