A Brief History of Sunscreens

An emulsion of benzyl salicylate and benzyl cinnamate, developed in the United States in 1928, was the first sunscreen in the world. 1930s marked the emergence of a phenyl salicylate in Australia. Quinine oleate and quinine bisulfate were available by 1935 in the United States. In 1943, p-aminobenzoic acid (PABA) was patented. Red petrolatum was used by the United States military as a sunblock during World War II. The initial compounds were primarily ultraviolet B radiation (UVB) blockers as it was to blame for the most observable effect, sunburn.[1]

Are Sunscreens Important?

Sunscreens form an essential component of a dermatologist’s arsenal. At present, the use of sunscreens is not limited only to photoprotection of those with photosensitive dermatoses, but the usage is also extended to specific photoprotection after ablative procedures and daily photoprotection to reduce photoaging. The use of sunscreens is enhanced by other photoprotective measures such as wearing a wide-brimmed hat, carrying an umbrella, wearing protective clothing, or walking in the shade. As such, it is important for a dermatologist to not overlook this vital aspect of patient care and keep themselves updated on sunscreens.

What Are the Effects of Ultraviolet Light on the Skin?

Ultraviolet radiation (UVR) is divided into three types as follows: ultraviolet A radiation (UVA), UVB, and ultraviolet C radiation (UVC). Sea-level solar UV radiation is approximately 95%–98% UVA and 2%–5% UVB. UVC is completely absorbed by stratospheric ozone that also attenuates UVB.[2,3]

UVA (320–400 nm) is responsible for the majority of the effects encountered in dermatological practice such as photoaging, tanning, photodermatoses (including polymorphous light eruption), and photocarcinogenesis. UVA penetrates deeper than UVB as it is not directly absorbed by biological targets. Due to this, it is capable of producing reactive oxygen species in the connective tissue thereby altering it and it also produces profound immunosuppression.

UVB (290–320 nm) is responsible for the most severe damage. Acute exposure to UVB leads to sunburn while a more chronic, long-term exposure has been implicated in the formation of cancer. UVB, while not penetrating as deep as UVA, exerts its impact by directly acting on DNA and proteins of the cells. The highest UVB content occurs when the sun is directly overhead, with the shortest path (e.g., noon, at the equator, at high altitude).[4]

What Are Physical and Chemical Sunscreens?

Sunscreens are divided into physical (inorganic) and chemical (organic) sunscreens based on their mechanism of action. Physical sunscreens, such as titanium dioxide, zinc oxide, calamine, iron oxide, kaolin, red petrolatum, ichthammol and talc, work by physically blocking the UVR scattering or reflecting the rays.[1]

Chemical sunscreens work by absorbing high-energy UVR and releasing them as low-energy rays, thus preventing them from reaching, and damaging, the skin. Hence, on exposure to UV light, the sunscreen undergoes a photostable reaction (except avobenzone), allowing it to retain the UV-absorbing potency without significant photodegradation.

What is the Rationale of Prescribing a Particular Sunscreen?

In children, I prefer to use physical sunscreens, such as micronized zinc or titanium dioxide, as they reflect most of the UVR and are poorly absorbed by the skin.
Of the 6 most common photoallergens, chemical sunscreens contain 5. Thus, in patients who have a prior history of photoallergy or may have factors predisposing them to photoallergic contact dermatitis, a physical sunscreen is preferred. Furthermore, patients allergic to benzophenone, a common component of UV-B blocking sunscreens, are seen often. They, too, are candidates for physical sunscreens.

In patients prone to acne, a chemical sunscreen is preferred. Caution must be exercised in checking the base of the sunscreen as well. A few times, the active ingredients may be noncomedogenic but the base may be greasy and therefore comedogenic.

I, personally, prefer a broad-spectrum sunscreen which is as close to 380–400 nm wavelength as possible. As for sun protection factor (SPF), I generally stay away from SPF 15 and go for SPF 30 or above. Sunscreens tend to be expensive, and thus, the amount used every day is far lesser than the recommended 2 mg/cm², and thus, counseling is an integral part of such a prescription.

Additional photoprotection can be offered by antioxidants. Antioxidants that are used in sunscreens and cosmetic products are Vitamins (A, C, and E) and polyphenols. Topical Vitamin C usage has shown to protect UV-related damage. Topical application of alpha-tocopherol has demonstrated a number of effects including reduction in erythema, photoaging, photocarcinogenesis, and immunosuppression.[5]

Additional photoprotection can be offered by antioxidants. Antioxidants that are used in sunscreens and cosmetic products are Vitamins (A, C, and E) and polyphenols. Topical Vitamin C usage has shown to protect UV-related damage. Topical application of alpha-tocopherol has demonstrated a number of effects including reduction in erythema, photoaging, photocarcinogenesis, and immunosuppression.[5]

**What Are Sunscreens Classified Based on Their Spectrum?**

Organic sunscreens can further be divided, based on their primary absorption spectrum, into UVA blockers and UVB blockers. Some sunscreens have the properties of blocking both UVA and UVB radiation and are called broad-spectrum sunscreens.[2]

1. **UVA filters**
   a. Benzophenones (UVB and UVA2 absorbers) – oxybenzone, sulisobenzene, dioxybenzone
   b. Avobenzone or Parsol 1789 (UVA1 absorber)
   c. Meradimate (UVA2 absorber).

2. **UVB filters**
   a. PABA derivatives – padimate O
   b. Cinnamates – octinoxate and cinoxate
   c. Salicylates – octisalate, homosalate, trolamine salicylate
   d. Octocrylene
   e. Ensulizole.

**What Is the Concept of Broad-Spectrum Sunscreens?**

Broad-spectrum sunscreens contain both UVA and UVB filters. These are Ecamsule (Mexoryl SX), Siltriazole (Mexoryl XL), Bemotrizinol (Tinosorb S), and Bisocitrizole (Tinosorb M).[1,2]

Ecamsule is the only one which is the US Food and Drug Administration (FDA) approved, but the rest of the filters are being used in other countries, such as the European Union and Canada.

Ecamsule is primarily a UVA filter, while Tinosorb M is the first of a new class of UV filters that combine the properties of both UV conventional filters (organic and inorganic) – it scatters, reflects, and absorbs UV light.

Mexoryl XL belongs to the class of hydroxybenzotriazole molecules. It has broad-spectrum coverage and is photostable. Bemotrizinol has a broad spectrum of coverage from 280 to 380 nm and is photostable. Bisocitrizole is a broad-spectrum sunscreen, which decreases UVA more than UVB transmission. It has two absorption peaks, at 303 and 360 nm. The molecule size is large, minimizing the opportunity for systemic absorption or endocrine-like effects. It acts as a hybrid between organic and inorganic filters, combining the micronized particle technology of inorganic UV filters with an organic molecule and together, these properties serve to absorb, scatter, and reflect UVR.

Many UVA blockers such as benzophenones also have some UVB blocking properties and can be considered as broad-spectrum sunscreens.

**What About Systemic Sunscreens?**

The reapplications of a sunscreen combined with the need to apply 2 mg/cm² of the product to ensure proper photoprotection are not always feasible. With this in mind, systemic sunscreens were developed.[1,6,7]

I tends to prescribe beta-carotene 0.5–1 mg/kg which comes up to 30–40 mg in total.

Other alternatives are antimalarials, ascorbic acid, α-tocopherols (i.e., Vitamins A, C, and E), retinol, selenium, green tea polyphenols, PABA, antihistamines, aspirin, indomethacin, and corticosteroids. Antioxidants are less potent than sunscreens in preventing sunburn.

Polypodium leucotomos (PL), a South American species of fern, is a natural mixture of phytochemicals having powerful antioxidant and photoprotective properties. These include acids such as ferulic, caffeic, vanillic, p-coumaric, 3,4-dihydroxybenzoic, 4-hydroxybenzoic, 4-hydroxycinnamic, 4-hydroxycinnamoyl-quinic, and chlorogenic.

The commercially available PL capsules contain 240 mg of the extract and often additionally contain Vitamins C, E, and lycopene. The capsules have to be taken 30 min before sun exposure. With regular sun exposure, two capsules to be taken daily – one in morning and one mid-day, while for intense sun exposure, four capsules have to be taken – two in morning and two mid-day, 3 h after first dose. However, commercial capsules of PL contain gluten so should not be consumed by gluten-sensitive people.

In a status report on clinical efficacy and safety of PL, it was concluded that PL is well tolerated at all doses administered.
(120–1080 mg/day) and associated with a negligible risk of side effects. While laboratory studies did not report any adverse effect, mild-to-moderate gastrointestinal complaints and pruritus were reported only in 2% human cases. No significant drug interactions have been reported. However, data on long-term safety and safety in children, pregnant, and lactating women are lacking.

What is Sun Protection Factor?

SPF or SPF is defined as the ratio of the time of UV exposure necessary to produce minimally detectable erythema in sunscreen-protected skin to that time for unprotected skin. In simpler words, the number after SPF represents how many more times the skin is protected against UVR using sunscreen. Thus, for example, if unprotected skin’s minimal erythema dose (MED) is 10 min, skin with SPF 30 sunscreen applied to it will have a MED of 300 min.[8]

Table 1 lists the percentage absorption of UVB according to their SPF.[8,9]

Table 1: Percentage absorption of UVB according to their SPF

| SPF | UVB absorption (%) |
|-----|--------------------|
| 2   | 50                 |
| 4   | 75                 |
| 8   | 87.5               |
| 15  | 93.3               |
| 20  | 95                 |
| 30  | 96.7               |
| 45  | 97.8               |
| 50  | 98                 |

SPF: Sun protection factor, UVB: Ultraviolet B

Table 1: Percentage absorption of UVB according to their SPF

Apart from SPF, however, substantivity is also an important aspect of a sunscreen’s efficacy. Substantivity is the ability of a sunscreen to remain effective under the stress of prolonged exercise, sweating, and swimming. The following have been suggested to help clarify substantivity while labeling:

1. Water resistant: protects up to 40 min of water exposure (two 20 min activity intervals)
2. Very water resistant: protects for up to 80 min of water exposure (four 20 min activity intervals).

Interestingly, the FDA permits products labeled as water resistant or very water resistant to be grouped together under the same term “sweat resistant.”

To Whom Should Sunscreen Use be Advised?

Sunscreens were primarily developed to combat sunburn, but the use of sunscreens has now increased to include photoprotection against various dermatological conditions, nonmelanoma skin cancers (NMSCs), and photoaging. With the advent of myriad dermatological procedures such as chemical peels and LASERs, which damage the stratum corneum and thereby impair the photoprotection offered by it, sunscreens provide an essential form of defense.[1,8]

Childhood is when the greatest sun exposure occurs and childhood sunburns are involved in increasing risk for malignant melanoma and NMSC and thus should be avoided diligently.

Indications for sunscreen are listed in Table 2.

How Should we Advise Application of a Sunscreen?

Sunscreen is to be applied over all sun-exposed areas in a concentration of 2 mg/cm² and be allowed to dry completely before sun exposure. It should be reapplied every 2 h and after swimming, vigorous activity, excessive perspiration, or toweling.[9]

“Teaspoon rule” is an easy way to apply the recommended amount of sunscreen.

1. 3 mL (slightly more than half a teaspoon)
   a. for each arm
   b. for the face and neck.
2. 6 mL (slightly more than a teaspoon)
   a. for each leg
   b. for the chest
   c. for the back.

Sunscreens and the Indian Skin

Indian skin, which falls under Fitzpatrick types 4 and 5, does not burn and is more prone to tanning. Tanning, which is caused more by UVA than UVB radiation, may be prevented to an extent and provided a broad-spectrum sunscreen is used. However, fairer individuals, falling under Fitzpatrick type 1–3, may be prescribed sunscreens. Alternatively, those with photosensitive or photoaggravated disorders, disorders of pigmentation, at a higher altitude or postablative procedures must be prescribed sunscreens. Another thing to consider is that India, being a tropical country, the perspiration is much higher and sunscreens may easily be wiped of washed off. Thus, cost also plays an important factor.[11]

Sunscreens and Cosmeceuticals

At present, there are moisturizers available with SPF in them. I find this to be a rather faulty concept. Moisturizers are typically reapplied every 10–12 h. However, the average sunscreen will need to be reapplied every 3–4 h for maximum efficacy, especially with increased sweating as is characteristic of the tropical countries such as India.

Using moisturizers like sunscreen together can be encouraged in patients in need of both; however, the patient must be advised to apply the moisturizer first. Applying sunscreen first may increase the dryness of the skin. Furthermore, application of the moisturizer will bridge any gaps in the stratum corneum and thus reduce any irritation.
Aminobenzoic acid is an ingredient in sunscreens and can cause contact dermatitis. Studies have shown that the amount of titanium dioxide found in sunscreens is minimal, with penetration into the viable skin tissue being less than 1% of the applied total amount. The use of nanotechnology has transformed the domain of sunscreens, raising concerns about possible side effects, contraindications, and controversies.

### Possible Side Effects, Contraindications, and Controversies

**Nanotechnology**

The use of nanotechnology has transformed the domain of sunscreens. However, the penetration of nanoparticles is limited by their molecular size. Lademann et al. investigated the penetration of titanium dioxide microparticles into the horny layer and the hair follicle orifice in human skin. They found that the amount of titanium dioxide found in any given follicle was <1% of the applied total amount of sunscreen. Thus, penetration of microparticles into the viable skin tissue was not detected. The larger surface area of the nanoparticles can provide an interface for catalytic reactions, producing free radicals and damage to proteins, lipids, and DNA. Nanoparticles can also form complexes with proteins, escaping immunological surveillance. The nanoparticle-protein complexes can act as haptens, inducing autoimmune diseases. Further studies are required to determine the safety of nanosized particle sunscreens.

**Allergens and irritants**

Sunscreens containing aminobenzoic acid and its esters (PABA), cinnamates and oxybenzone can cause contact dermatitis or photosensitivity reactions. Aminobenzoic acid is chemically similar to other drugs that cause photosensitivity reactions. Thus, individuals with a predisposition the same should not use a sunscreen containing aminobenzoic acid or one of its derivatives (aminobenzoate, menthyl anthranilate, or padimate A or O) due to cross-reactivity. A sunscreen containing oxybenzone or cinoxate should be recommended for these individuals instead. Miscellaneous compounds such as fragrances, lanolin, alcohol, and preservatives may also cause skin and eye irritation or sensitization.

**Carcinogenic**

A new nitrosamine known as N-nitroso-N-methyl-PABA, 2-ethylhexyl ester was found in certain sunscreens containing padimate-O. Nitrosamines themselves can be carcinogenic, but it is uncertain whether this is present in sufficient quantities in sunscreens to be of concern.

**Sunscreen and infants**

Skin under the age of 6 months may have different absorptive characteristics than that of adults and the biological systems that metabolize and excrete drugs absorbed through the skin may not be fully developed in children. Hence, it is recommended that sunscreens containing aminobenzoic acid should be avoided in children younger than 6 months of age and that no sunscreens should be used on children during the first 6 months of life.

**Vitamin D production**

UVB radiation is responsible for >90% of Vitamin D production in the skin. It is said that a few minutes’ exposure of the face, arms, and hands to noonday summer sunlight two or three times a week is sufficient for Vitamin D synthesis. There have been concerns that widespread use of sunscreens, particularly those with high SPF, may lead to a significant decrease in Vitamin D production. However, there is evidence that although sunscreens can significantly reduce the production of Vitamin D under very strictly controlled conditions, their normal usage does not generally result in Vitamin D insufficiency. In fact, Vitamin D and calcium levels have been found to be relatively normal in xeroderma pigmentosum patients, in spite of strict photoprotection.

**Hormonal effects**

Some sunscreens (oxybenzone, avobenzone, octinoxate, and padimate O) have been tested for their estrogenic/antiandrogenic properties in animal studies. However,
the endocrine effects of these agents remain controversial, warranting further human studies.

**Emerging Trends in Sunscreens**

**Nanoparticles**
Conventionally used physical blockers such as titanium dioxide and zinc oxide are thick formulations and hence not cosmetically acceptable. Newer sunscreens containing nanosized products of titanium dioxide and zinc oxide have been developed, replacing the older formulations. These ultrafine particles blend with the skin, making the sunscreen cosmetically acceptable.[2,5,26]

**Sunsheres**
Sunsheres are styrene/acrylate copolymers that do not absorb UV irradiation but enhance the effectiveness of the active sunscreen ingredients. The sunshere polymer beads are filled with water, which migrates out of the particle, leaving behind tiny air-filled spheres, which have a lower refractive index (1.0) than the dried sunscreen film (1.4–1.5). As a result, scattering of UV radiation occurs, increasing the probability of contact with the active UV filters in the sunscreen. Sunsheres are also available in a powder form and can boost SPF by 50%–70% making it possible to reduce the concentration of active ingredients.

**Microencapsulation**
Active sunscreen ingredients are entrapped within a silica shell. Thus, allergic or irritant reactions to the active ingredient can be minimized, and incompatible sunscreen ingredients can be safely combined, without loss of efficacy.

**Financial support and sponsorship**
Nil.

**Conflicts of interest**
There are no conflicts of interest.

**References**

1. Lowe NJ. An overview of ultraviolet radiation, sunscreens, and photo-induced dermatoses. Dermatol Clin 2006;24:9-17.
2. Kaimal S, Abraham A. Sunscreens. Indian J Dermatol Venereol Leprol 2011;77:238-43.
3. Forestier S. Rationale for sunscreen development. J Am Acad Dermatol 2008;58:S133-8.
4. Lim H. Photoprotection and sun-protective agents. In: Wolff K, Goldsmith L, Katz S, Gilchrest B, Paller A, Leffell D, editors. Fitzpatrick’s Dermatology in General Medicine. 7th ed. New York: McGraw-Hill; 2008. p. 2137-41.
5. Rai R, Shannuga SC, Srinivas C. Update on photoprotection. Indian J Dermatol 2012;57:335-42.
6. Sonthalia S. Polypodium leucotomos: The latest ‘oral sunscreen’ on the block. Pigment Int 2015;2:104-7.
7. Avenel-Audran M. Sunscreen products: Finding the allergen. Eur J Dermatol 2010;20:161-6.
8. Levy S. Sunscreens. In: Wolverton S, editor. Comprehensive Dermatologic Drug Therapy. 3rd ed. Philadelphia: Saunders; 2012. p. 551-61.
9. Poh Agin P. Water resistance and extended wear sunscreens. Dermatol Clin 2006;24:75-9.
10. Schneider J. The teaspoon rule of applying sunscreen. Arch Dermatol 2002;138:838-9.
11. Taneja A, Mittal A, Benuwal R. Do we really need sunscreens? Indian J Dermatol Venereol Leprol 2017;83:7-8.
12. DraeLos ZD. Sunscreens and hair photoprotection. Dermatol Clin 2006;24:81-4.
13. Rai R, Srinivas CR. Photoprotection. Indian J Dermatol Venereol Leprol 2007;73:73-9.
14. Lademann J, Weigmann H, Rickmeyer C, Barthelmes H, Schaefer H, Mueller G, et al. Penetration of titanium dioxide microparticles in a sunscreen formulation into the horny layer and the follicular orifice. Skin Pharmacol Appl Skin Physiol 1999;12:247-56.
15. Donaldson K, Stone V, Tran CL, Kreyling W, Borm PJ. Nanotoxicology. Occup Environ Med 2004;61:727-8.
16. Borm PJ, Kreyling W. Toxicological hazards of inhaled nanoparticles – potential implications for drug delivery. J Nanosci Nanotechnol 2004;4:521-31.
17. Dromgoole SH, Maibach HI. Sunscreening agent intolerance: Contact and photococontact sensitization and contact urticaria. J Am Acad Dermatol 1990;22:1068-78.
18. Dromgoole S, Maibach H. Contact sensitization and photococontact sensitization of sunscreening agents. In: Lowe N, Shaath N, editors. Sunscreens: Development, Evaluation and Regulatory Aspects. New York: Marcel Dekker; 1990. p. 313-40.
19. DeSimone EM 2nd. Sunscreen and sunscreen products. In: Handbook of nonprescription drugs. 10th ed. Feldman EG, Davidson DE, editors. American Pharmaceutical Association: Washington, DC; 1986. p. 575-87.
20. Pathak MA, Robins P. A response to concerns about sunscreens: A report from the skin cancer foundation. J Dermatol Surg Oncol (United States) 1989;15:486-7.
21. Hurwitz S. The sun and sunscreen protection: Recommendations for children. J Dermatol Surg Oncol 1988;14:657-60.
22. Young A, Walker S. Acute and chronic effects of ultraviolet radiation on the skin. In: Wolff K, Goldsmith L, Katz S, Gilchrest B, Paller A, Leffell D, editors. Fitzpatrick’s Dermatology in General Medicine. 7th ed. New York: McGraw-Hill; 2008. p. 2137-41.
23. Norval M, Wulf HC. Does chronic sunscreen use reduce Vitamin D production to insufficient levels? Br J Dermatol 2009;161:732-6.
24. Solititto RB, Kraemer KH, DiGiovanna JJ. Normal Vitamin D levels can be maintained despite rigorous photoprotection: Six years’ experience with xeroderma pigmentosum. J Am Acad Dermatol 1997;37:942-7.
25. Hxsscl CL, Bangert SD, Hebert AA, Lim HW. Current sunscreen issues: 2007 food and drug administration sunscreen labeling recommendations and combination sunscreen/insect repellent products. J Am Acad Dermatol 2008;59:316-23.
26. Antoniou C, Kosmadaki MG, Stratigos AJ, Katsambas AD. Sunscreens – What’s important to know. J Eur Acad Dermatol Venereol 2008;22:1110-8.