

REVIEW ARTICLE**Photoprotection of Skin against Ultraviolet Radiations by Sunscreen**

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*Chemistry Department, SMDRSD College Pathankot-145001, India***Received 10 Nov 2017; Revised 03 Jan 2018; Accepted 09 Jan 2018****ABSTRACT**

Nowadays, cosmetic products represent the most important market sector for producers after food. Consumers are in regular demand of products for beauty, antiaging, wellness, skin care and sunscreen. Sunscreen help to guard skin from UV rays, either chemically or physically. UV rays are generally consists of three forms UVA, UVB and UVC, and excessive exposure of these radiation may lead to pigment changes, pre-cancerous, cancerous skin, wrinkles and skin aging, along with activating other adverse light sensitive reactions based on disease aetiology and skin prototypes. The possible pathological changes due to use of sunscreen has been reviewed during the exposure to the UV rays. It is vital to protect skin and eyes from damaging effects as the skin is an important part of our immune system. Moreover, artificial sources of UV rays should be eluded including tanning beds and sunlamps without use of sunscreen. Surfaces such as snow,sand, concrete and water can reflect up to 80% of UV radiation, when around these surfaces, even when cloud weather because it filters less than 40 % of UV radiation, sun screen should be applied. The used sunscreen products should contain SPF of at least 15 and it is advisable to have enough beta carotene and antioxidants such as vitamin C, vitamin E and Selenium when heavily exposed to sun radiation. In this review it is tried to summarize all possible issues related to sunscreens.

Keywords: Sunscreen, SPF, Pathology, UV radiation, melanin.

INTRODUCTION

Sunscreen is the one cosmetic product category which has gained extensive popularity due to its added health benefits apart from beautification^[1,2] Sunscreens as such or many other cosmetic products containing sunscreen such as skin care, hair care, lips care and eye care products are available in the market.^[3-5] Sunscreen is designed to protect us from UV radiation from the sun which has a shorter wavelength than visible light, and a lot of the energy. UV radiations are known to have a number of harmful effects on the skin. There are two types of UV radiation that can affect the skin, UVA and UVB. Both have been linked to skin cancer and a weakening of the immune system. They have also been found to be responsible for the premature aging of the skin and cataracts in the eyes. They cause the tanning of skin i.e. change in skin colour.

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Email: rummisaini@gmail.com**ULTRA-VIOLET RADIATIONS AND SKIN**

UV radiation can be divided into three categories^[6,7] One of these, UVC (with a wavelength of ~290-100nm) gets absorbed by ozone in the atmosphere before it can reach the Earth's surface so isn't of any problem. There are two other categories UVA & UVB, which can cause damage to skin when exposed.

UVB (wavelength ~290-320nm)

UVB is responsible for around 5% of the UV radiation reaching Earth, with the majority of it also being absorbed by the atmosphere. It causes our skin to produce more melanin, which results in the tanning effect on sitting in the sun. However, it can also cause sunburn and DNA damage, which can increase the risk of developing skin cancer. Sunscreen has been available as a product since around 1928, and early sunscreens were formulated to screen the skin against UVB rays.

UVA (wavelength ~320-400nm)

UVA is responsible for the largest proportion of the UV radiation from the sun that reaches the Earth's surface – approximately 95%. UVA can penetrate much deeper into the skin than UVB, down into the connective tissue. This results in wrinkling and premature ageing of the skin. UVA can also produce reactive species in the skin, and thus indirectly causing DNA damage, and contribute to an increased risk of skin cancer. It was earlier considered relatively harmless in comparison to UVB, but now the damage it can cause is beginning to be understood, sunscreens have included different chemicals to shield against this portion of the UV spectrum also.

The human skin is the largest organ of the body. Skin acts as protective barrier against the harmful effects of the environmental agents.^[8] The chronic exposure of skin to UV radiations is the main factor for various skin problems like burns, hyper pigmentation, cracks, immune suppression, wrinkles, dermatitis and most dangerous is skin cancer.^[9]

SKIN TYPE

The degree to which skin burn and the time it takes to burn on exposure to uv radiations depend on the skin type. The Food and Drug Administration (FDA) has classified the skin type on a scale from 1 to 6. The persons with 1 and 2 skin types have fair skin and have tendency to burn fast and more severely. The ones with 5 and 6 skin types, have darker skin and do not burn as easily or take longer to have burns on the skin. The people who are most probable to burn are also most vulnerable to skin cancer. It has been shown in some studies that persons having large numbers of freckles and moles have a higher risk of developing skin cancer. The people with higher-number skin types have a lower occurrence of skin cancer, but they protect their skin and eyes from overexposure to the sun, as skin cancer in people with darker skin are often detected at later stages when it is more dangerous.

CHEMICAL COMPOSITION OF SUNSCREENS

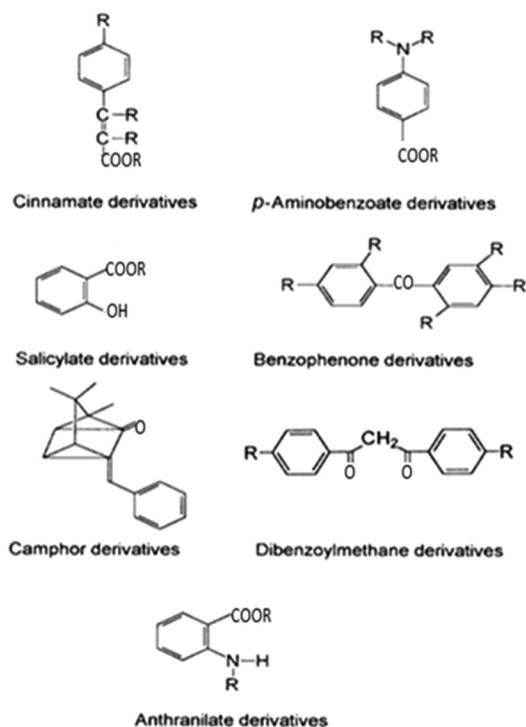
Sunscreen chemically is composed of both inorganic and organic (carbon based) compounds

to afford full protection from UV rays. The two inorganic compounds used are titanium dioxide and zinc oxide. These compounds are often described as only providing a physical, reflective barrier to UV light, but in fact they can absorb the UV radiation, and dissipate it harmlessly. The first sunscreens containing only these chemicals would have left a visible white layer on the skin.

In present day sunscreens, a combination of inorganic chemicals with organic chemicals is used. Due to their chemical structures, chemical bonds in certain organic chemicals are able to absorb photons of UV light – this energy is then dissipated harmlessly in the form of heat. Variations in structure can lead to absorption at different wavelengths; hence a mix of these organic chemicals is often used to ensure protection against the full range of UVA and UVB wavelengths.

Padimate O, Octinoxate, Octocrylene, Ensulizole, Oxybenzone, Meradimate, Avobenzone, Ecamsule along with physical blockers such as titanium oxide and zinc oxide are the most commonly used chemical compounds in sunscreens.^[10] Padimate O (octyl dimethyl) is the most powerful UV-B absorber. Octinoxate (Octyl methoxycinnamate) is the most frequently used sunscreen ingredient. It has mainly replaced PABA derivatives as the next most potent UV-B absorbers to padimate O. Octisalate (octyl salicylate) is used to enhance the UV-B protection in a sunscreen. Since they are weak UV-B absorbers so are usually used in combination with other UV filters in higher concentrations. Silicates have a good safety profile. Octocrylene may be used in combination with other UV absorbers such as avobenzone to achieve higher SPF formulas and to increase overall stability of the sunscreen. Ensulizole or phenylbenzimidazole sulphonic acid is water soluble, and is used in products formulated to be less oily such as daily use moisturizers. It is a selective UV-B filter. Oxybenzone is considered as a broad-spectrum absorber as It considerably enhance UV-B protection when used in a given formula and also absorbs UV-A. Butyl methoxydibenzoylmethane or avobenzone provides greater protection through a large portion of the UV-A range. Its photo instability can be overcome by combining avobenzone with octocrylene. Terephthalylidene dicamphor sulfonic acid or Mexoryl SX provides protection

within the near UV-A range. Mexoryl SX is water soluble, which makes sunscreen less water resistant. Due to its photo instability, it is combined with octocrylene.



These organic chemicals also explain, to an extent, why sunscreen has to be reapplied. Some of the organic chemicals used are photo stable; i.e. they won't break down when exposed to UV light. Some of them, however, will slowly break down as they absorb UV light over time – avobenzone, is one of the key examples of this. Other chemicals can be added to slowdown this breakdown, but it can be one of the reasons why it's necessary to reapply sunscreen regularly. The more apparent reasons include the fact that even sunscreens that claim to be 'water-resistant' will still eventually wash off, that is why regulation now states that sunscreens should also specify the length of time during which they remain water resistant.

You should not worry much about the chemicals present in sunscreens. All of them undergo a rigorous testing process before they are allowed to be used in sunscreens, and they all have limits on the amounts that can be used safely, to ensure that they're nowhere near the levels that could be harmful. Some are absorbed more by the skin than others, but this is accounted for in safety testing. In the US, sunscreen is categorized as an over-the-counter drug, whereas in other countries it's graded as a cosmetic.

WORKING OF SUNSCREEN

Sunscreens work in two main ways; the non chemical sunscreens such as Titanium Dioxide and Zinc Oxide would reflect UV light and block out sunlight. It is less likely to cause problems in some people with sensitive skin. Micro fine Titanium Dioxide is cosmetically more acceptable than older preparations, though in high concentrations it can still give the skin a milky quality. Chemical barrier sunscreen can absorb UV light (e.g. UVB and/or UVA); they contain chemicals such as cinnamates, benzophenones and dibenzoylmethanes (salicylates). Chemical sunscreens are not able to be seen once they have been applied to the skin and do not give a milky appearance. Sunscreen may be chemical or physical agents that protect the skin from sunburn and erythema by absorbing or blocking UV rays and available often in the form of a cream or lotion topical preparations. In addition to their photo protective qualities, these substances also help in preventing windburns and skin damage from wind driven micro particles of dirt and grime.^[1] Physical blockers may be direct physical photo blockers, and most are prominent metal compounds (iron, chromium, zinc, titanium, etc) that occur naturally, while some compounds are manmade such as bismuth. There are important photo protective blockers such as Titanium Dioxide the white pigment powder which is widely used in cosmetics. The purpose of large particle titanium is to give opacity to the products containing it and to lighten (or whiten) their colour. Opaque titanium dioxide highly reflects and strongly scatters all UV and visible rays. It also reflects much of the skin damaging Infra-Red (IR) radiations, and keeping the skin cooler, reducing damage due to heat and its subsequent photo aging. To achieve cosmetic elegance and efficacy, micro coating of the Titanium Dioxide is common. To look good, even application to the skin is essential. Large particle Titanium Dioxide products produce a very white, opaque appearance on the skin when applied. Recent studies have focused interest on the creation of more oxide materials like titanium in nanostructure due to their outstanding electronic, chemical and mechanical properties which make them fabricated with unique characteristics. Zinc Oxide has been known and used topically for centuries as a skin protectant and wound healing

adjuvant and is recognized as a mild antimicrobial agent. More than 50 years ago, Zinc Oxide was indicated as a block for UVB/UVA light.^[12] It also reflects IR from the skin, and its ability to protect in the long UVA range (300 - 400 nm) is much higher than Titanium Dioxide. Zinc Oxide absorbs, rather than scatters, most of UVA, while Titanium Dioxide primarily scatters these wavelengths. Thus, formulated in combination with Titanium Dioxide, ultrafine Zinc Oxide closes the possible gaps in the UVA range. Zinc Oxide works as complement to Titanium Dioxide protection and extends photo protection to the skin where Titanium Dioxide is insufficient. The optimal particle size range for UV blocking Zinc Oxide without blocking visible wavelengths is approximately 80 to 150 nm. Iron Oxides are most commonly seen in two areas, one as rust on exposed iron and other in cosmetics to give the coverup desired colour. Although it is not approved by the FDA as an active ingredient in sunscreens, many companies use them in their sunscreen products. Cosmetic Iron Oxides are manmade to very high purity, desired colour and particle size. Iron Oxide pigments for cosmetic use are micronized powders. These cosmetic pigments, if incorporated at adequate concentration and when properly dispersed in well designed way, not only add colour to the lotion (or cream, powder, etc.), but could contribute substantial protection of the skin from multiple wavelengths of sun light. Physical blockers may be indirect physical blocker aids, examples of these particles can be natural talc or mica, with flat and oval appearance in shape. They are very small particles, though they are much larger than direct physical blockers. A portion of very small physical blocker particles will coat the larger flat talc (mica, etc.). Being flat and smooth, the coated talc will easily slide over each other, overlapping themselves and effectively increasing protective coverage on the skin. The Chemical Absorbers/Organic filters chemical sunscreens (or Organic Filters) are usually soluble in oils or water. These filter either/or UVB and UVA irradiation to varying effectiveness. No organic filter completely blocks the UVB and/or UVA rays from the skin. Furthermore, the actual protection offered by all sun protective products relates directly to their level of concentration, the film thickness applied to the skin, as well as the careful, total coverage of the exposed skin sites,

and the most common chemical absorbers used in sunscreens Octyl Salicylate even is strictly UVB absorber and weak one, it offers many positive qualities, including nonirritating and no sensitizing to skin. Cosmetically, it is an easy to handle soothing oil and acts as a good solvent for other such as the benzophenones. Octyl Dimethyl PABA (Padimate O) is an oil like UVB absorber used in sunscreen and the most comfortable for this UV range, absorbing best at the maximum sunburn frequencies from 310nm to 312nm. Octyl Methoxycinnamate is an oily liquid most widely utilized in UVB, and considered as a second in efficiency to Padimate O, but offers broader protection from 300nm to 315nm in the sunburn region of UVB. It has an excellent safety record and is relatively easy to formulate, moisturizing and water insoluble, adhering persistently to the skin. Menthyl Anthranilate an old and safe absorber and it is absorbed moderately in the UVB range from about 300nm to 340nm. 5-Oxybenzone (Benzophenone-3) and Sulisobenzone (Benzophenone-4) are closely related solid (powder) absorbers. Oxybenzone is water-insoluble, while the acid form sulisobenzone can be made soluble in water when it is neutralized. While these compounds are categorized as UVA absorbers they are also UVB absorbers. They offer only moderate protection through both the UVB range and part of the UVA (320nm - 360nm) and quite stable and can enhance efficiency of stronger UVB absorbers. Avobenzone (Parsol™1789) is a solid (powder) absorber that exhibits good UVA absorption from about 330nm to 340nm and very good absorption in the UVA range up to about 370nm, where it loses effectiveness and can convert to its inactive form in the presence of sunlight.^[13] Octocrylene is a soothing and water resistant UVB/UVA absorber, and is considered a relatively weak sunscreen. It is very stable absorber and both protect and supplement other UV protection.

SPF (SUN PROTECTION FACTOR)

Most organizations recommend using sunscreen with an SPF between 15 and 50 (SPF ratings higher than 50 have not been established to be more effective than SPF 50). A sunscreen with an SPF of 15 protects against about 93 percent of UVB rays, and one with an SPF of 30 protects against 97

percent of rays, according to the Mayo Clinic. No SPF can block 100 percent of UV rays.^[14]

As some UV radiation still gets through the sunscreen and into your skin, the SPF number refers to roughly how long it will take for a person's skin to turn red. Sunscreen with an SPF of 15 will check your skin from getting red for approximately 15 times longer than usual (so if you start to burn in 10 minutes, sunscreen with SPF 15 will prevent burning for about 150 minutes, or 2.5 hours), according to the American Academy of Dermatology.^[15]

PHOTOSTABILITY OF SUNSCREEN

The ability of a molecule to remain intact with irradiation is called as its photostability. Photostability is a problem with all UV filters as these are intentionally chosen as UVR-absorbing molecules. Photolysis has been demonstrated, specifically with avobenzone in in vitro systems. This effect has also been observed with octyl methoxycinnamate and octyl dimethyl PABA, whereas oxybenzone has been found to be relatively stable.^[16]

The photostability of the molecules also depends on the nature of the solvent and the vehicle used. Also some ingredients have a stabilizing effect on others, for example octocrylene has been shown to photostabilize avobenzone. Some other ingredients may be added to the sunscreen formulation to provide it photo stability or raise its SPF level.^[17]

DOSAGE AND APPLICATION

It has been observed that efficiency of sunscreen is reduced due to under application of recommended dose or little habit of reapplication of sunscreen after sweating, swimming, wiping and or vigorous activity. The dose used in FDA sunscreen testing is 2 mg/cm² on exposed skin. So the Sunscreen should be applied in a concentration of 2 mg/cm² to all sun exposed areas and allowed to dry completely before sun exposure. It should be reapplied every 2 hours, and also after sweating, swimming, vigorous activity or exercise and or after each wipe if going in the sun. If we consider only the face, as commonly in country like India, one should

apply sunscreen roughly about 1/4 to 1/3 of a teaspoon for the average adult face.^[18-20]

SUNSCREEN REGULATIONS

Sunscreens are evaluated generally by one of following methods and should fulfil labelling conditions according to the countries guidelines.

US-FDA method

The FDA uses the method to measure in-vitro UV transmittance through a sunscreen film using the critical wavelength method. Sunscreen products which provide UVB protection should have a critical wavelength less than 320nm, whereas those providing both UVB and UVA protection should have critical wavelengths between 320 and 400nm. According to FDA regulations the sunscreen products should have a critical wavelength of at least 370nm to be labelled as providing "broad spectrum" UVA and UVB protection from sun.^[21]

India

Indian population have usually Type-4 skin pattern which burns less but tans easily. So use of sunscreen is necessary to avoid tan. According to Indian regulations the sunscreen products should have a critical wavelength of at least 70nm to be labelled as providing "broad spectrum" UVA and UVB protection.^[21] Indian regulations as amended from time to time considers sunscreens as cosmetics as per Indian Drug and Cosmetic Act (1940).

ADVERSE EFFECTS OF SUNSCREEN

In some people, sunscreen protection can cause adverse reactions that cause them to choose not to protect their skin. In a longitudinal study of 603 subjects applying sunscreen daily, 19 percent developed adverse reactions and the majority of reactions were irritant in nature. The most common irritation complaint is burning of the eye area when applying the sunscreen. Contact dermatitis is a longer lasting irritation that can be categorized as an irritant or allergic contact dermatitis. Para-amino benzoic acid (PABA), PABA esters, benzophenones, fragrances, and preservatives account for most of the

reactions^[22,23] Individuals with sensitive skin can better use sunscreens containing inorganic particulates (titanium dioxide and zinc oxide) because these ingredients do not cause irritation or sensitization. Acne is another common complaint caused predominantly by the vehicle rather than the ingredients within the sunscreen. Gels or sprays with less oil may reduce this adverse effect. Oxybenzone containing sunscreens should not be used on children because of its disruptive property to hormones. Sunscreens, particularly those with high SPF, may lead to a significant decrease in vitamin D production. Regular sunscreen use may reduce UV-dependent cutaneous synthesis of vitamin D. Clinical trials under conditions of usage, have shown that persons prescribed to cautiously apply sunscreens still receive enough sunlight to maintain normal vitamin D levels. Sufficient vitamin D levels can be obtained from incidental sun exposure, diet, and supplements.^[24] For persons taking rigorous photo protection, daily consumption of 600 IU of vitamin D through diet or supplements is recommended.

Application of sunscreen may result in blockage of skin pores which can cause acne and rosacea like adverse effects. Use of sunscreens for kids should be done with high precautions. Sunscreen products are quite expensive so their regular use year round cannot be afforded by everyone.^[25,26]

NATURAL CHEMICALS AS SUNSCREENS

Natural chemicals like polyphenols, carotenoids, anthocyanidins, vitamins, fixed and volatile oils available from vegetables, fruits, medicinal plant parts, algae and lichens have been found to be more effective than synthetic chemicals used in sunscreens. It is because of their long term useful effects especially against free radical generated skin damages (wrinkles) along with UV-rays blocking.^[27-29] They possess strong antioxidant activity. Aloe vera juice and fixed oils have moisturizing and cooling effect, volatile oils have antimicrobial activity, polyphenols like curcumin have wound healing and anti-inflammatory effect, tannins and resveratrol show anticancer activity, anthocyanidins, carotenoids, vitamins have anti ageing or cell rejuvenating type of activities too.

^[30-32] All these characteristics of these natural chemicals make them choice ingredients in cosmetics including sunscreens.

CLOTHING

An inexpensive and excellent form of sun protection is with clothing. The clothing with tight weave is more effective. With wet clothing, protection from sun decreases considerably. Dark coloured clothes protect better than light coloured ones. A crude test of clothing for protection from sun is to hold it up in visible light and observe the penetration. Lesser the penetration of sunlight through the fabric, better the protection. The FDA defines clothing with a SPF rating as a medical device. Hat is the most vital article of clothing. A hat with 4-inch wide circumferential brim is needed to cover the entire face and neck.^[33]

CONCLUSION

Although there are many positive effects of UVR, the negative effects can potentially be life threatening. Encouraging photo protection is currently the best preventative measure to maintain homeostasis within the skin. It is important to educate people on how to pick an appropriate sunscreen as this will increase compliance. New FDA regulations recommend using broad-spectrum sunscreens with an SPF of at least 15, applying sunscreen 15 minutes before sun exposure, and reapplying no less than every two hours. Sunscreens are popularly used in the form of lotions, creams, gels, sprays, sticks and oils. These days photo-protective chemicals are also added in hair care (e.g. shampoo), skin care (e.g. moisturisers, foundations and concealers), lip care (e.g. lipsticks, lip balms) and even in eye care (e.g. eye creams) products with more than 30 SPF.⁵⁷⁻⁵⁸ Consumers these days are in demand of all-in-one sunscreen which should be non-toxic, non-allergic, water or sweat proof, moisturizing, cooling, antioxidant and UV-A as well as UV-B protective with high SPF values along with skin radiating, anti-acne and anti-ageing properties.⁵⁶ Dermatologists should also encourage their patients to limit time in

the sun especially between 10am and 2pm. If a person must be out in the sun, he or she should wear protective clothing, such as hats, long-sleeved shirts, pants, and eye protection with UV protecting goggles.

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