

Review Article

Broad Spectrum UVA & UVB Photoprotectants: An Overview

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DOI:10.18579/jpcrk/2017/16/2/116429

Received on: 20/02/2017

Revised on: 19/04/2017

Accepted on: 04/05/2017

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ABSTRACT

Purpose: Due to the high exposure of our skin to sunlight which mainly comprises of ultraviolet radiation, a harmful effect is manifested on the skin and the integumentary system. Sunscreens are formulated which safeguards the epidermis of the skin from harmful UV radiations by reflecting, absorbing or by dispersion phenomena. This review focuses on the beneficial aspects of sunscreen and also presents a detail exposition about its formulation aspects and evaluation.

Approach: The review introduces sunscreens and its traditional, chronological usage of sunscreen. The formulation and development of sunscreen emphasis on various UVA and UVB photo protectants used and its evaluation parameters is studied.

Findings: Sunscreens are found to show the photo-protecting properties by absorption or by reflecting mechanism, which has a shielding effect towards the skin against harmful radiations.

Conclusion: Sunscreens protects the skin absorbing or reflecting ultraviolet radiations. The application of sunscreens is an efficient method of protecting skin against UV radiations. Hence a sunscreen plays a vital role in protecting the skin from external harmful radiations.

Keywords: SPF, Sunscreen, UVA, UVB radiations.

INTRODUCTION

Sunscreen is a formulation which prevents the skin from sunburns, skin cancer, and other conditions caused by excessive exposure to the sun. The mechanism of sunscreens have two different modes which is by absorbing or reflecting ultraviolet radiations¹. Light is the major environmental component to which skin is exposed daily and the white light comprises of UV radiations. There are three types of UV rays UV-A (320-400 nm), UV-B (280-320 nm), UV-C (200-280 nm). Exposure to UV-A radiation results in the damage of elastic and collagen fibres of connective tissues, which causes premature ageing (photo-ageing), while UV-B radiation brings about acute inflammation (sun burn) and intensification of photo-ageing. In addition to these changes, UV-B radiations are also reported to bring about immune-suppression which reduces normal immunological defence mechanisms of the skin, therefore chances of development of malignant tumour increases^{2,3}. The application of sunscreens has an significant role in protecting skin against UV radiations. Hence it has become a necessity to develop a validated topical sunscreen product which will provide protection against both UV radiations and hence, many topical formulations like sunscreen cream, lotion, spray, gel are prepared². The efficacy of sunscreens is characterized by the sun protection factor (SPF). The SPF is a

factor to indicate the degree of protection provided by a sun care product like sunscreen. SPF is defined as the ratio of the minimal erythema dose (MED) of solar radiation measured in the presence and in the absence of a sunscreen agent⁴. Sunscreen formulations incorporate a wide variety of chemicals like derivatives of 3-benzylidenecamphor, 4-aminobenzoic acid, cinnamic acid, salicylic acid, benzophenone and 21 phenylbenzimidazole, avobenzene and zinc oxide which have particular absorbance and are effective over various areas of UV spectrum. In order to get a broad spectrum UV protection, more than one active sunscreen ingredients are added in the sunscreen product. Due to these facts, sunscreens substances are widely being used in everyday products such as moisturizers, creams, lotions, shampoos and other hair and skin preparations. The regular use of these products may help to diminish the chance of the harmful effects of ultraviolet radiation. However, it is necessary that a very efficient sunscreen substance is used in the cosmetic formulation⁵.

HISTORY OF SUNSCREEN

The ideology of using sunscreen started in early civilizations, which included variety of plant products, which were used to protect the skin from sun damage. For example, ancient Greeks used olive oil to protect the skin from sun damage, and ancient Egyptians used extracts of rice, jasmine and lupine plants whose products are still in use for skin care products. Zinc oxide paste has also been reported to be a popular product for skin protection for thousands of years⁶.

But when it comes to the invention of actual sunscreen, at least four different inventors have been attributed as being the first to invent the product.

Franz Greiter

Franz Greiter a chemist developed the first sunscreen in 1938. This sunscreen was called Gletscher Crème or Glacier Cream which had a sun protection factor (SPF) of 2. In later days, the formula of Glacier Cream was picked up by a company called Piz Buin, named after the place Greiter which was sunburned and inspired to invent sunscreen⁶.

Benjamin Green

The first popular sunscreen products were invented for the United States military by Florida airman and pharmacist Benjamin Green in the year 1944. The hazards of sun overexposure were observed in the soldiers of the Pacific tropics at the height of World War II.

Green's patented sunscreen was called Red Vet Pet (for red veterinary petrolatum). This patented product was a disagreeable red, sticky substance similar to petroleum jelly. Later, it was bought by Coppertone who enhanced and commercialized the substance and sold it as "Coppertone Girl" and "Bain de Soleil" brands, in the early 1950s^{7,8}.

Other Inventors

In the early 1930s, South Australian chemist H.A. Milton Blake experimented to produce a sunburn cream. The founder of L'Oreal, chemist Eugene Schueller invented the first sunscreen in 1936.

Water-resistant sunscreens were introduced in 1977, and recent development efforts is focused on making sunscreen protection both long-lasting and broad-spectrum, as well as more appealing to use.

In 1980, Coppertone developed the first UVA/UVB sunscreen⁸.

Different formulations of sunscreen

- Sunscreen creams
- Sunscreen lotions
- Sunscreen gels
- Sunscreen powders
- Sunscreen spray
- Sunscreen wipes

Composition of UV radiations.

UVA^{9,10}

UVA rays falls in the region of Ultraviolet radiations that is in the range of 400-320nm. UVA rays account for up to 95 percent of the UV radiation reaching the Earth's surface. UVA rays are less intense than UVB, UVA rays are 30 to 50 times more prevalent. These rays

are present with relatively equal intensity during all daylight hours throughout the year, and can penetrate clouds and glass.

UVA rays penetrates the skin more deeply than UVB, which play a major part in skin aging and wrinkling (photo aging). Recent studies changed the believes of scientists who believed that UVA rays did not cause major damage in areas of the epidermis (outermost skin layer) where most skin cancers occur. Studies over the past two decades, however, show that UVA damages skin cells called keratinocytes like basal and squamous cells in the basal layer of the epidermis, where most skin cancers occur. UVA, even play a major role in the development of skin cancers.

UVA is the dominant tanning ray. Tan results from injury to the skin's DNA which results in skin darkening which is an imperfect approach to prevent further DNA damage. These imperfections or mutations can lead to skin cancer.

UVB^{9,10}

UVB rays falls in the region of Ultraviolet rays that is in the range of 320-290nm. UVB rays are the head cause of skin reddening and sunburn, tends to damage the skin's more surface epidermal layers. UVB rays play a key role in the development of skin cancer and a contributory role in tanning and photo aging. Its intensity varies by season, location, and time of day. The most significant amount of UVB hits us between 10AM and 4PM from April to October. However, UVB rays can burn and damage your skin year-round, especially at high altitudes and on reflective surfaces such as snow or ice, which bounce back up to 80 percent of the rays so that they hit the skin twice. UVB rays do not considerably penetrate glass. The below table 1 lists the UVA & UVB blocking agents and fig.1 describes the general formulation of sunscreen.

Evaluation Tests for Sunscreen

1. Physical analysis¹¹

Emulsions were prepared accordingly and then the obtained emulsions were submitted to a set of organoleptic (colour, look, feel, thickness) and physical (phase separation and creaming) analysis.

2. pH determination¹²

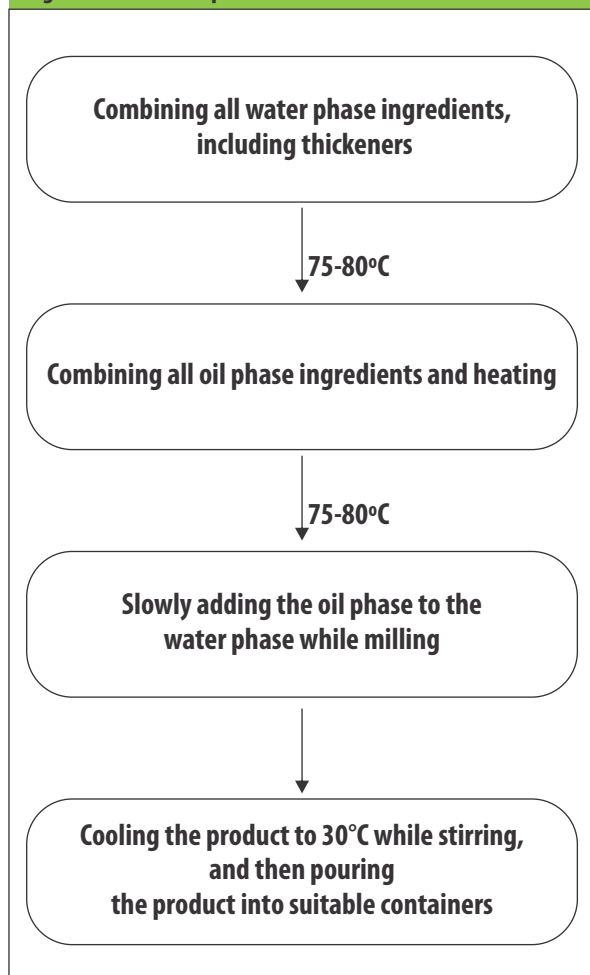
The pH values of various emulsions were stored at different conditions. It was determined using a digital pH Meter. The pH tests were repeated for several emulsions after 1 day, 3 days, 7 days, 14 days, 21 days, and 28 days of storage.

2.1 For Oil-in-Water Emulsion Creams^{13,14}

Weigh exactly 5 ± 0.01 g of the cream in a 100 ml beaker. Add 45 ml of water and disperse the cream in

Table 1: UVA and UVB blocking agents.

FDA-Approved Sunscreens	
Active Ingredient/UV Filter Name	Range Covered
	UVA1: 340-400nm
	UVA2: 320-340nm UVB: 290-320nm
Chemical Absorbers:	
Aminobenzoic acid(PABA)	UVB
Avobenzene	UVA1
Cinoxate	UVB
DioxybenzoneUVB,	UVA2
E1` camsule (Mexoryl SX)	UVA2
Ensulizole (Phenylbenzimidazole Sulfonic Acid)	UVB
Homosalate	UVB
Meradimate (Menthyl Anthranilate)	UVA2
Octocrylene	UVB
Octinoxate (Octyl Methoxycinnamate)	UVB
Octisalate (Octyl Salicylate)	UVB
Oxybenzone	UVB, UVA2
Padimate O	UVB
Sulisobenzene	UVB, UVA2
Trolamine Salicylate	UVB
Physical Filters:	
Titanium Dioxide	UVB, UVA2
Zinc Oxide	UVB,UVA2

Fig 1: Method of Preparation of sunscreen cream

it. Determine the pH of the suspension at 27°C using the pH meter.

2.2 For Water-in-Oil Emulsion Creams^{13,14}

Weigh 10 g of the cream to the nearest 0.1 g. Add 90 ml of rectified spirit previously adjusted to pH 6.5 to 7.0. Warm, if necessary to 45°C and stir thoroughly for 15 min. Filter the alcoholic layer through a filter paper and determine the pH of the filtrate at 27°C using the pH meter.

3. Test for Thermal Stability¹⁵

With the help of spatula, introduce the cream into glass bottle and tap it to settle to the bottom. Fill up to two third capacity of bottle and insert

the plug and tighten the cap. Place the filled bottle in the incubator at 45±1°C for 48 h. The sample shall be taken to have passed the test, if on removal from the incubator shows no oil separation or any other phase separation.

4. Determination of residue¹⁶

Weigh accurately about 5g of material in a weighed, clean and dry squat from weighing bottle and dry to constant mass 105±1°C. Cool in desiccators and weigh.

$$\text{Residue percent by mass} = 100 \frac{M_1}{M_2}$$

M1= mass in g of the residue

M2= mass in g of the material taken for the test.

5. SPF¹⁷

1g of each sample was weighed, transferred to a 100ml volumetric flask, diluted to volume with ethanol, followed by ultrasonication for 5min and then filtered through cotton, rejecting the ten first ml. A 5.0ml aliquot was transferred to 50 ml volumetric flask and dilute the volume with ethanol. Then a 5.0ml aliquot was transferred to a 25ml volumetric flask and the volume was made up with ethanol. The absorption spectra of samples in solution were obtained in the range of 290 to 450nm using 1 cm quartz cell, and ethanol as a blank. The absorption data were obtained in the range of 290 to 320, every 5 nm, and 3 determinations were made at each point, followed by the application of Mansur equation.

$$SPF_{\text{spectrophotometric}} = CF + \sum_{290}^{320} EE(\lambda) \cdot I(\lambda) \cdot Abs(\lambda)$$

- **EE- Erythema effect spectrum**
- **I- Solar intensity spectrum**

6. Centrifugation tests¹⁸

Centrifugal tests were performed for emulsions directly after the preparation. Tests were repeated after 1 day, 7 days, 14 days, 21 days and 28 days of storage. They were performed at 5000 rpm and 25° C for 10 min by placing 10 g of each sample in centrifugal tubes and the results were reported.

7. Stability tests^{19,20}

Stability tests is conducted for conditions for emulsions to explore the effects of these conditions on the storage of emulsions these tests were performed on samples kept at 8°C±2°C, 25°C±2°C, and 40°C±2°C. Colour phase separation and liquefaction of emulsions were absorbed at various time intervals during 28 days.

CONCLUSION

The most apparent acute benefit of currently available sunscreens is the prevention of sunburn from UVR exposure. This effect has been suggested to be both a benefit and a potential concern. The obvious benefit is the prevention of sunburn that may reduce the risk of melanoma skin cancers because severity and frequency of sunburns has been associated with non melanoma skin cancer formation. The concern has been inadequate protection of existing sunscreens and, more important, the potential for prolonged UVR exposure without acute signals (i.e. sunburn) ultimately leading to greater doses of UVA. On a practical view there is no such evidence calming that usage of sunscreen prolongs the sun exposure. However it's just been a popular assumption till date. Regardless, it should be noted that for a given acute UVR exposure, the skin damage produced in the absence of sunscreen photo protection exceeds that obtained in their presence.

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