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Chemical and physical UV filters

Abstract

Introduction. The European Code Against Cancer recommends protection from overexposure to ultraviolet (UV) light to reduce the risk of developing skin cancers. The most harmful sub-range of UV is UVB.

Aim. The aim of the study was to collect information on the available means of protection against solar radiation, in particular UV filters, and the mechanism of their action.

Material and methods. Together 24 publications and 2 legal acts on UV filters were analyzed.

Results. Chemical filters are aromatic molecules, the carboxyl group of which under the influence of energy from absorbed radiation undergoes isomerization. The substances classified as chemical filters are para-aminobenzoic acid (PABA), p-methoxycinnamic acid derivatives and octocrylene. Physical or mineral filters include substances of mineral origin. Two types of products are used: colored pigments with a particle size of 200-300 nm and „micronized” zinc oxide or titanium oxide pigments with a particle size of 20 to 80 nm. This group includes titanium oxide, zinc oxide, iron oxides and mica-titanium oxide system.

Conclusions. Chemical and physical UV filters differ in the way they work and range of possible side effects. Most often the sunscreens available on the market contain chemical UV filters or a mixture of chemical and physical ones.

Keywords: ultraviolet, sun protective factors, chemical filters, physical filters.

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INTRODUCTION

The European Code Against Cancer states that the best protection against the sun during the summer is to stay out of its reach. It is especially important to protect against the sun's rays from 11am to 3pm, when exposure to UV radiation is the greatest. It is recommended to stay in the shade, wear sunglasses, wear densely woven cotton and even a specialized fabric that protects against UV rays. The best prevention of exposed skin on face and ears is the use of cosmetics containing sunscreen [1]. In Europe sunscreen products (or sun protective factors SPF) are classified as cosmetic products with more stringent registration criteria [2]. In the United States, all broad-spectrum SPF products are referred to as “sunscreen drugs products”, i.e. they are classified as over-the-counter medicinal products [3]. This status requires the manufacturer to provide more documentation on the effectiveness and safety, additionally to submit test results confirming that the filters used in the product are not absorbed through the skin. Stricter requirements from the United States mean that the number of photoprotective preparations available on the American market is smaller compared to other countries [4]. The use of sunscreens is the basic preventive measure against the harmful effects of ultraviolet radiation, which may leave a trace in the form of photoaging of the organism, burns, eye damage, cancer, photoallergic dermatitis and phototoxic changes.

Natural light reaching the Earth from the Sun contains a stream of electromagnetic waves and elementary particles, defined as solar radiation [5]. It can be divided into ultraviolet, visible and infrared radiation. The visible part has a wavelength in the range of 400-800 nm and accounts for about 36% of the emitted radiation, and the infrared part of the wavelength 800-5000 nm is the largest part of solar radiation. UV radiation has a wavelength of 280-400 nm [6]. The ultraviolet radiation has been additionally divided into three sub-ranges of different wavelengths: UVA (315-380nm), UVB (280-315nm) and UVC (100-280nm). The entire UVC band is absorbed by molecular oxygen and the ozone layer. Ozone only partially absorbs the UVB and the depleting ozone amount in the atmosphere, it increases the amount of the B sub-range reaching the Earth. The least absorbed radiation by atmospheric gases is UVA. Due to the above, the main ranges of UV radiation reaching the Earth's surface are UVA and UVB [7]. Even though a small amount of UVC radiation reaches the Earth's surface through the ozone layer, it very quickly causes skin erythema and DNA damage. It is irritating to the conjunctiva and the cornea of the eye. The artificial UVC fraction is used in germicidal lamps to sterilize devices and rooms [8].

The most harmful range of UV is UVB, because it has high energy and due to its penetration into the epidermis, it causes sunburns and skin pigmentation. It is also responsible for the irritation of the conjunctiva and the cornea of the eye. As a

result of the action of UVB radiation, an immediate reaction produces free radicals that contribute to the denaturation of cell membranes. Therefore, frequent exposure to this radiation has an impact on the formation of cataracts, weakening of immunity and the occurrence of neoplasms [8].

Adverse effects of exposure to sunlight include edema and erythema caused by the release of capillary-dilating inflammatory mediators, histamine, serotonin and prostaglandins [8]. The UVA radiation is responsible for the immediate darkening of the skin with dark complexion, which is an unstable reaction that disappears after a few hours. A permanent tan reaction is visible after about 2-3 days and lasts for 2-3 months. It develops mainly due to the action of UVB. High doses of UV radiation and long-term single exposure to solar radiation may lead to severe sunburn [9].

Another negative change caused by solar radiation is photoaging of the skin, i.e. skin aging under the influence of exogenous environmental factors, including ultraviolet radiation. The fractions responsible for the photoaging phenomenon are UVA and UVB. Excessive and prolonged exposure to UV radiation and artificial irradiation in a solarium is manifested by unfavorable changes in the appearance, structure and function of the skin [10]. The main symptoms of aging caused by external factors are: hypertrophic changes, dryness and roughness of the skin, actinic keratosis, deep wrinkles, telangiectasia, discoloration, lentil spots, changes in elasticity, skin laxity, sebaceous gland hyperplasia (large blackheads, yellow-brown discoloration of the skin) [11]. In skin affected by photoaging, an increase in the number of fibroblasts, macrophages and mast cells can be observed, and a decrease in Langerhans cells that have a positive effect on the immune system. Deep furrows, nodules and lumps are the result of elastosis i.e. the accumulation of atrophic elastin-like material in the papillary layer of the dermis [12]. The severity of the above-mentioned changes depends largely on the frequency and duration of exposure to the sunshine, but also on the occurrence of sunburn and the type of skin phototype [11].

Malignant skin neoplasms are the delayed effects of ultraviolet radiation on human skin. The excessive production of free radicals due to frequent exposure to UVA and UVB is responsible for the carcinogenesis process [13]. Photocarcinogenesis is a long and multi-stage process, as a result of which, there is a disability and mutation of cellular DNA, mainly within the p53 antioncogene. Under the influence of UV, the cis isoform of urocanic acid is formed in the stratum corneum, which has a strong suppressor effect, which may work together in the development of skin cancer in people chronically exposed to ultraviolet radiation [14]. The most common malignant neoplasm of the skin is basal cell carcinoma involving face, neck and upper limbs, i.e. places mainly exposed to sunlight [15]. The most dangerous form of skin cancer is malignant melanoma, accounting for 2-5% of scalp and neck cancers, and 75% of skin cancer deaths. The risk of developing it increases with age [16]. Risk factors contributing to the development of skin cancer include excessive exposure to UV rays and sunburn of the skin, especially those affected in childhood and early adolescence. People with fair skin, blue or green eyes and fair hair have a strong predisposition to develop skin cancer [17].

AIM

The aim of the study was to collect information on the available means of protection against solar radiation, in particular UV filters, and the mechanism of their action.

MATERIAL AND METHODS

Together 24 publications and 2 legal acts on UV filters were analyzed.

RESULTS AND DISCUSSION

In order to prevent the negative effects of ultraviolet radiation, photoprotection should be used. Sun protection should start from the first months of life and last throughout life. The basic measures for this purpose are suitable protective clothing (tightly woven fabric), hats, face shields- 'facekini' (face-masks with openings for eyes, mouth and nose), sunglasses, goggles, umbrellas and sun screens. An important element is to avoid exposure to the sun during peak hours of radiation. One should also avoid the frequent use of tanning beds.

Sun protection should be taken into account not only on the beach, but also in the mountains. With increasing altitude, the intensity of UV radiation increases for every 1000 m by approximately 15% [13].

A sun protection product is any preparation (cream, oil, gel or aerosol) intended to come into contact with the human skin only for the purpose of absorbing, dispersing or reflecting radiation, giving the effect of protection against UV radiation [2]. The basic ingredients of such preparations are filters. They are divided into 3 groups: physical (mineral) filters, chemical (organic) filters and compounds that trap free radicals. Physical filters reflect radiation from the entire wavelength, and chemical filters absorb some of the radiation [6].

Chemical filters are aromatic molecules, the carboxyl group of which, under the influence of energy from absorbed radiation, undergoes isomerization [6]. Substances classified as chemical filters are para-aminobenzoic acid (PABA), p-methoxycinnamic acid derivatives and octocrylene [18]. Other substances classified as chemical filters are included in the "List of UV-filters allowed in cosmetic products" [19].

Physical filters include substances that are generally of mineral origin. Two types of products are used: colored pigments with a particle size of 200-300 µm and 'micronized' zinc oxide or titanium oxide pigments with a particle size of 20 to 80 nm. The first group includes titanium oxide, zinc oxide, iron oxides and mica-titanium oxide system. Due to the size of the particles and the dullness, they can leave a white undercoat on the surface of the skin, they are inconvenient to use. This feature is used in some makeup products [6].

In products protecting against UV radiation, in addition to the above-mentioned groups of filters, there may be natural filters. An example of a natural filter is bee putty containing compounds capable of absorbing UVA rays and UVB: caffeic acid, coumaric acid, ferulic acid, benzoic acid. Such a natural filter is included in sticks and protective lipsticks. Natural sunscreens also include anthracene derivatives – aloin from aloe extract and naphthahinone – nut extract. Due to their poor protection against UV rays, they are used primarily in tan-fixing cosmetics [18].

Sunscreen products are xenobiotics, i.e. chemicals that are not natural components of a living organism and are an exposure to it [20]. If a person does not eat and drink large amounts of them, they do not pose a threat of poisoning, which means that they depend on relatively harmless substances [21].

Each sunscreen product should have a sun protection factor on the packaging. According to the current recommendations of the European Union, the packaging of such a cosmetic should additionally contain information specifying the class of protection against UV radiation of this preparation. The sun protection factor is most often marked with the SPF (Sun Protection Factor) symbols and relates primarily to the protective effect against UVB rays. The SPF index in Europe is determined *in vivo* on 10-20 volunteers. On their backs, an adhesive tape with 1x1 cm holes is placed and the exposed surfaces are illuminated by the lamp's radiation, closing the adhesive holes after a specified time. After 24 hours, the resulting erythema is assessed and the minimum erythematous dose (MED) is determined without protection, and the MED with protection is determined in the same way. The time needed to induce erythema therefore, corresponds to the minimum erythema dose. In this way, the time is determined during which a person with a certain phenotype can be exposed to the sun without the appearance of erythema. This time is multiplied by the sun protection factor (SPF) [18].

Although the sun protection factor only applies to protection against erythematous UVB radiation, photoprotective products should also protect against UVA. Sun protection products do not guarantee complete protection as none of them absorbs all UV radiation. Therefore, their packaging should not contain a statement that they provide complete protection against the risks caused by excessive exposure to UV. The label should not ensure that the product does not need to be reapplied [2]. Even when using sunscreen, remember to avoid prolonged exposure to solar radiation. People using filters with higher UV protection factors tend to extend the time spent in the sun, which may increase the risk of melanoma [1]. It is recommended to avoid excessive UV exposure, apply sunscreen 30 minutes before exposing the skin to sunlight, and repeat the application of the cream a maximum of every 2 hours in case of swimming or other physical exertion in the fresh air. Children, adolescents and seniors should be particularly protected against UV rays. Moreover, the principles of occupational health and safety prohibit pregnant women from working in conditions of exposure to ionizing radiation and in an environment where $\frac{1}{4}$ of the maximum permissible intensity of ultraviolet radiation has been exceeded [22]. Patients are endangered by exposure to sunlight during pharmacotherapy. With the use of some groups of drugs, skin lesions may appear in places exposed to direct exposure to UV radiation – on face, neck, neck, cleavage, forearms. Drugs that cause photodermatitis are bactericides (azithromycin, co-trimoxazole), antifungal (terbinafine), antiparasitic (quinine, quinidine), psychotropic, sedative and neurological drugs (doxepin, promazine, promethazine) and antiallergic drugs. In pharmacy practice, it is also worth paying attention to the need for photoprotection in patients chronically taking commonly known painkillers (ibuprofen, diclofenac, ketoprofen), anti-diabetic drugs (glipizide, metformin), and antihypertensive and circulatory drugs (atenolol, captopril, diltiazem, enalapril) [23].

People prone to sunburn should use photoprotection measures all year round. Not only this group is obliged to use

sunscreen 365 days a year. UVA radiation, responsible for photoageing, accompanies people even on cloudy days and penetrates through the windows and car windows.

The desired level of sun protection indicated on the protective filter can be achieved by applying 2 mg/cm² of the product to the body of an adult, i.e. about 6 tablespoons of emulsion (36 g). Consumers tend to apply less of these products, leading to a disproportionate reduction in protection.

The physical and chemical filters contained in sunscreen products do not differ much in their mechanism of action. Since 1940, there has been a misconception that mineral filters work by reflecting radiation. A 2015 study at the University of Florida using a spectrophotometer (model OL755) measured reflection and transmission. This study proved that only 4-5% of the effect of physical (inorganic) filters is the reflection or scattering of ultraviolet radiation from the skin surface. The remainder of the UV protection is provided by the absorbance of the UV photons and the conversion of radiation into heat similar to that in the case of chemical filters [24].

Chemical filters, due to their chemical structure, can lead to photosensitivity. Such a reaction can be triggered by some chemical sun filters: oxybenzone or benzophenone, and to a lesser extent cinnamic acid derivatives, butylmethyl-dibenzoylmethane, there are photoallergic cases caused by octocrylene [6]. Photoprotective products containing photosensitizing substances are not recommended for patients taking medications with phototoxic and photosensitizing properties. The lower sensitizing effect of physical filters is important in preparations intended for children and for skin prone to irritation and atopy. The radiation-absorbing properties of chemical filters contribute to the release of free oxygen radicals that degrade collagen, elastin and DNA of skin cells [25]. Another difference between the two types of filters is the ability to absorb both UV bands. Not all chemical filters have this ability, and each physical filter is characterized by absorption of UVA and UVB [26].

Mineral filters provide protection against UV radiation over a wide wavelength range without being absorbed into the systemic circulation. Chemical filters, being oil and / or water-soluble, are absorbed through the skin, making them easily accessible to the systemic circulation. The disadvantage of physical filters is that they leave a white film on the skin that is difficult to spread. Most often, when analyzing the information on protective products against UV radiation, we find that they contain chemical UV filters or a mixture of chemical and physical filters.

CONCLUSIONS

Chemical and physical UV filters differ in the way they work and range of possible side effects. Most often the sunscreens available on the market contain chemical UV filters or a mixture of chemical and physical ones.

TABLE 1. UV filters belonging to chemical (organic) filters [19].

Chemical UV filters	
• PABA,	• Drometrizole Trisiloxane,
• Camphor Benzalkonium Methosulfate,	• Diethylhexyl Butamido Triazone,
• Homosalate,	• 4-Methylbenzylidene Camphor,
• Benzophenone-3,	• 3-Benzylidene Camphor
• Phenylbenzimidazole Sulfonic Acid,	• Ethylhexyl dimethyl PABA,
• Terephthalylidene Dicamphor Sulfonic Acid,	• Benzophenone-4, Benzophenone-5,
• Butyl Methoxydibenzoylmethane,	• Methylene Bis-Benzotriazolyl Tetramethylbutylphenol,
• Benzylidene Camphor Sulfonic Acid,	• Disodium Phenyl Dibenzimidazole Tetrasulfonate,
• Octocrylene,	• Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine,
• Polyacrylamidomethyl Benzylidene Camphor,	• Polysilicone-15,
• Ethylhexyl Methoxycinnamate,	• Diethyloamino Hydroxybenzoyl Hexyl Benzoate
• PEG-25 PABA,	
• Isoamyl p-Methoxycinnamate,	
• Ethylhexyl Triazone	

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