The ABCs of SPFs: An Introduction to Sun Protection Products

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This article discusses the biological effects of sunlight, the chemistry of common UV absorbers and factors to consider when formulating and testing sun-care products.

Sunscreens are a special class of personal care products containing active ingredients that can absorb ultraviolet (UV) radiation to shield skin from the damaging effects of the sun. These products are classified as OTC drugs and are regulated by the Food and Drug Administration (FDA) in the US.

UV Light and Its Effects

Sunlight is composed of many wavelengths spread across the electromagnetic spectrum. As this solar radiation passes through Earth's atmosphere, some of these wavelengths are filtered out. The remaining radiation reaches the Earth as UV and infrared light. UV light is of particular concern because it can interact with skin cells and cause a variety of damaging effects. It consists of wavelengths grouped into the following three categories.

- UVC light ranges from 200-290 nm. This range has the lowest wavelength and consequently the highest energy because wavelength and energy are inversely related. Almost all light in this range is filtered out by the atmosphere, although a small amount is produced by arc welders and certain tanning lights.
- UVB light ranges from 280-320 nm and is called the burning or erythemal region because it penetrates through the stratum corneum (SC) and the epidermis. This type of light causes most of the skin damage that is immediately apparent, like reddening, which is known as erythema or sunburn.
- UVA light is composed of wavelengths from 320-360 nm. This range has the lowest energy, but it penetrates deeper into the skin and interacts with more skin structures. Low doses of UVA can penetrate into the dermis, where it can stimulate the production of melanin, the pigment responsible for tanning and protecting the skin from further damage.

While UVB is responsible for most sunburns, high doses of UVA can also cause reddening. Furthermore, the amount of UVA that reaches the Earth's surface is higher than the amount of UVB. Higher doses of UVA can penetrate into skin structures and cause damage to structural components, such as the elastin and collagen matrix. Chronic sun exposure, particularly to the UVA range, also results in a condition known as UV-induced photoaging, which occurs when key support matrix elements are damaged by radiation. This is a cumulative process that contributes to wrinkles, sagging and other signs of aging. The impact of photoaging can easily be seen by comparing the difference in skin on the face to an area that is not exposed to constant sunlight, such as the buttocks. While this skin is physiologically identical to the face, it appears smoother because it is exposed to less light. Studies have shown intrinsic differences between photo-aged skin and intrinsically aged skin.

In the US, products that screen out this part of the spectrum can make anti-aging claims that are extremely popular now. These products do not just guard against sunburn and skin cancers, they also protect one's youthful appearance. In addition to dermal problems, there are also data suggesting UVA is one possible agent causing certain types of cataracts.

Hair Damage

In addition to its effects on skin, UV light has also been shown to cause two types of hair damage. When hair is exposed to enough UV light, it can become discolored. Brown hair tends to fade, while blond and red hair tends to yellow. This has been attributed to photo-oxidative bleaching processes and the photo-degradation of amino acids, such as cystine, tyrosine and tryptophan. The breakdown of amino acids is also responsible for the other types of hair damage induced by UV exposure, namely the reduction in tensile strength. Due to short- and long-term effects on health and beauty, it is desirable to protect skin and hair from UV light. Of course, the most direct solution is to shield them from the sun by physically blocking them with clothing, hats or umbrellas. However, this is not always practical or desirable. To protect exposed skin and hair from the damaging effects of sunlight, scientists have developed various chemicals that can absorb or block UV radiation.

The Chemistry of UV Absorbers

Certain chemical compounds are able to interact with UV light, defusing its damaging energy. The chemical bonds in these molecules can absorb UV light and remit or reabsorb it in a harmless form. These chemicals are typically aromatic compounds that have a carbonyl group. In general, they also have an electron releasing group, such as an amine or a methoxyl group in either the ortho- or para-position on the aromatic ring. When UV light strikes one of these molecules it causes a photochemical excitation; the molecule is stimulated to a higher energy level. When the molecule returns to its original energy state, the excess absorbed energy is emitted as light with a different energy state. Most sunscreens emit energy in the infrared region and may contribute a minuscule heating effect to the skin. Others emit in the blue range of visible light. In fact, products that use these types of compounds give the skin a slight bluish cast. Each sunscreen molecule can repeat this absorption-emission cycle multiple times before it decays.

A variety of compounds have been developed that have a molecular structure capable of UV absorption. These absorbers can be formulated in appropriate vehicles that can be conveniently applied to exposed skin to protect cells from interaction with the radiation. Common UV absorbers include organic compounds, such as para-amino benzoic acid (PABA) and its esters (salicylates cinnamates, benzophenones, anthanilates, dibenzoylmethanes and camphor derivatives. In addition, inorganic sun blocking materials, such as titanium dioxide, are commonly used in sunscreen formulations.

Key Sunscreen Chemicals

PABA and its derivatives: PABA is an aromatic ring with amino and carboxylic acid groups that has been used in sunscreen products since the 1950s. PABA is an effective sunscreen, but because of the way its functional groups are positioned (the parastructure), the molecule is prone to oxidation and discoloration. It also tends to form a crystalline structure that can make the material hard to work with in cosmetic formulations. Furthermore, in recent years, concerns have been raised about the safety of the material. Scientists have attempted to overcome some of these drawbacks by esterifying PABA with other materials. For example, combining PABA with glycerin yields glyceryl PABA that is more water-soluble than the parent compound. Despite these improvements, PABA-based sunscreens have gained a negative reputation with certain consumers, and many formulators avoid using them. In fact, many products are now labeled "PABA-free."

Salicylates: Salicylates were the first sunscreen chemicals to be widely used in commercial preparations, and they continue to be popular today. Benzyl salicylate, octyl salicylate and homomenthyl salicylate are among the most popular. These molecules all contain functional groups attached to the ortho position and are able to create internal hydrogen bonds. Because they absorb UV radiation around 300-310 nm, they are ideal for use as UVB screens. Although salicylates are less-effective UV absorbers than other sunscreens, they have an excellent safety profile and can be readily incorporated into cosmetic vehicles. Due to their active groups interacting with each other, they are less likely to react with the skin or other ingredients.

Cinnamates: Cinnamates, particularly benzyl cinnamate, were used as early sunscreen compounds. They contain an extra unsaturated group conjugated to both the aromatic ring and the carboxylic acid group. This structure gives these molecules good UV absorbance in the 305 nm range. Currently, octyl methoxycinnamate is preferred because it is insoluble in water. This makes it ideal for use in waterproof products.

Benzophenones: Benzophenones are the only UV absorbers belonging to the aroma ticketone category. This unique structure allows them to absorb UV light beyond 320 nm. Unfortunately, these materials are solids that are difficult to handle and hard to incorporate into cosmetic products.

Physical blockers: Other materials, such as titanium dioxide and zinc oxide,