Photoprotection Insights

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Many new developments have occurred in the sunscreen market to increase both efficacy and cosmetic acceptability. Higher sun protection factor (SPF) formulations are increasingly popular as new sunscreen combinations are developed that provide better UVB protection. New methods of increasing the longevity of UVA photoprotectants provide better broad-spectrum protection. Dry touch sunscreens have even been developed that dry quickly in place on the skin, preventing rub off and a gooey heavy feel. All of these advances enable sunscreens to provide superior photoprotection. This article examines some of the major active ingredients in sunscreens. These actives have all been in the marketplace for quite some time because the US Food and Drug Administration (FDA), following the introduction of avobenzone, has approved no new ingredients. However, new uses for time-tested ingredients are resulting in the development of advanced sunscreen formulations.

Categories of Sunscreen Actives

Sunscreen actives can be classified into 2 major categories: chemical and physical. Chemical sunscreens undergo a chemical transformation (resonance delocalization) to absorb UV radiation and transform it to heat. This reaction occurs within the phenol ring, which contains an electron-releasing group in the ortho and/or para position, and is irreversible, rendering the sunscreen inactive once it has absorbed the UV radiation. Physical sunscreens, in contrast, usually are ground particulates that reflect or scatter UV radiation, absorbing relatively little of the energy. For this reason, they have longer activity on the skin surface.

Sunscreen ingredients can be divided into the following 3 groups: UVA absorbers, 320 to 360 nm (eg, benzophenones, avobenzones, anthranilates); UVB absorbers, 290 to 320 nm (eg, *para*-aminobenzoic acid [PABA] derivatives, salicylates, cinnamates); and UVB/UVA blocks, which reflect or scatter UVA and UVB (eg, titanium dioxide, zinc oxide).

Each of these sunscreen actives is discussed separately to highlight the advantages and disadvantages of each formulation. Most modern sunscreen formulations are a blend of 2 to 3 actives carefully selected to complement each other and enhance product performance. This discussion is designed to help the dermatologist understand the compatibilities of various sunscreen ingredients.

UVA Chemical Absorbers

Benzophenones

There are 3 sunscreens in the benzophenone family: oxybenzone, dioxybenzone, and sulisobenzone. Oxybenzone is used in the United States and provides weak UVA photoprotection ($<$320 nm). There have been some reports of allergic contact dermatitis to benzophenone, but they are rare. Benzophenone commonly is used as a secondary sunscreen to increase the broad-spectrum protection of the formulation. It is an oil-soluble ingredient that can add to the sticky feel of a sunscreen if used in too high a concentration. Benzophenone has found a new importance in the sunscreen industry for its ability to stabilize avobenzone, an important UVA photoprotectant.

Avobenzones

Avobenzone, also known as Parsol® 1789, was an important step forward in UVA photoprotection. Unfortunately, it is highly photounstable; 36% of avobenzone is destroyed shortly after sun exposure. It is estimated that all avobenzone is gone from a sunscreen after 5 hours or 50 J of exposure, necessitating frequent reapplication. Avobenzone also is chemically incompatible with other commonly used physical sunscreens, such as zinc oxide and titanium dioxide. However, avobenzone has assumed new importance with the introduction of a proprietary sunscreen complex known as Helioplex™ that combines avobenzone with oxybenzone and HallBrite® TQ™ to create a photostable avobenzone with long-lasting UVA photoprotectant qualities. HallBrite TQ is chemically known as 2-6-diethylhexylnaphthalate. Thus, Helioplex will provide for the United States what Mexoryl™ has provided for Europe and South America.

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Menthyl Anthranilates

Menthyl anthranilate is the only sunscreen of this family approved in the United States, where it also is known as meradimate. Its peak absorption is at 336 nm, but it is a clear, thick, sticky oil that can be used only in low concentrations in formulations for aesthetic reasons. It has a high safety profile and low allergenicity. It is very stable in formulation, without the photodegradation issues associated with avobenzone. It commonly is used as a secondary UVA photoprotectant.

UVB Chemical Absorbers

PABA Derivatives

For all practical purposes, the PABA derivatives rarely are used in modern sunscreen formulations. A recent review of the marketplace showed that less than 2% of sunscreens use PABA derivatives because of allergenicity concerns. Octyl dimethyl PABA, also known as padimate O, is the most commonly used PABA derivative, with a maximal absorption at 296 nm. It has average photostability, with approximately 15.5% lost to photoexposure.

Salicylates

The salicylates are an important class of UVB photoprotectants. This class includes octyl salicylate (octisalate), homomenthyl salicylate (homosalate), and trolamine salicylate. It is the internal hydrogen bonding of the salicylates that provides for maximal UVB absorption at 300 to 310 nm. Approximately 56% of the sunscreens in the current marketplace use the salicylates as a secondary sunscreen active since they have an excellent safety record with minimal allergenicity.

Cinnamates

The cinnamates are the most popular sunscreen category currently used in true sunscreens, sunscreen-containing moisturizers, and facial foundations. Eighty-six percent of products with an SPF rating contain octyl methoxycinnamate, also known as octinoxate, which has maximal absorption at 305 nm. Octyl methoxycinnamate has excellent photostability, with only 4.5% degradation after UVB exposure.

UVA/UVB Filters

The physical UVA/UVB absorbers are titanium dioxide and zinc oxide. Titanium dioxide usually is micronized to contain particles of many sizes to provide optimal UV scattering abilities. Unfortunately, it leaves a white film on the skin and is used mainly for beachwear products. Zinc oxide usually is available in a microfine form, meaning it contains small particles of one size, making it appropriate for day wear. A newly introduced colorless zinc oxide with extremely small particles is finding its way into many cosmetics and moisturizers.

Approval of Sunscreens

There are many sunscreens available in Europe, Canada, and Asia that are not approved in the United States. Mexoryl has been used in Europe and Canada as a sunscreen active. It was originally developed to stabilize avobenzone, much like Helioplex, and is available in 2 forms: Mexoryl SX and Mexoryl XL. Mexoryl SX is a water-soluble form that is suitable for day wear sunscreen formulations. This would include sunscreen-containing moisturizers and facial foundations. Mexoryl XL is an oil-soluble form that is suitable for water-resistant sunscreen formulations, including those worn on the beach and during vigorous physical exercise. Recently, Anthelios SX containing ecamsule, which has been marketed in Europe and Canada as Mexoryl SX, was approved by the FDA. Thus, new sunscreen formulations will be available as the unapproved ingredients pass the scrutiny of the FDA.

Sunscreen Formulation

Sunscreens typically are made from combinations of these ingredients. Usually, actives with different peaks of absorbency are combined to yield a sunscreen with the broadest protection possible. Oily ingredients usually are used in low concentrations to prevent a sticky feel but may be required to achieve the desired SPF. Sunscreen formulation definitely is an art. Careful formulation only is part of the success of a sunscreen. The ability of the sunscreen to be applied in an even thin film that will not separate or migrate is important. Sunscreens combine with sebum, sweat, topical medications, and cosmetics, which can interrupt or destroy the film. Furthermore, most sunscreens are tested in a laboratory under ideal wearing conditions. For practical purposes, it can be assumed that most sunscreens perform at half of their rated SPF.

Summary

Sunscreens remain an important part of dermatology, with new developments creating longer lasting, more aesthetic photoprotection. Current sunscreen research is aimed at creating better polymers to increase the length of time the sunscreen film remains in place on the skin, despite the presence of sebum and perspiration. Polymers also can suspend particulates, such as zinc oxide and titanium dioxide, allowing the film to be invisible on the skin. Hopefully the incorporation of new approved actives in the sunscreen monograph will further broaden skin photoprotection. ■