

Photostability: The Back Story of UV Filters

Bud Brewster

Technical Editor, Cosmetics & Toiletries magazine

KEY WORDS: *organic UV filters, photostability, solvent polarity, molecular strategies*

ABSTRACT: *This chapter looks at the UV filters and discusses several strategies for increasing the photostability of organic sunscreen actives.*

Here's the story of organic UV filters. They absorb a packet of energy called a photon from incoming UV radiation and hold it briefly in an excited state before releasing it as heat or a lower-energy photon or both, and returning to the unexcited or ground state. The front story is absorption. Everybody knows that story. It's the functionality of these chemicals and their reason for being in sunscreen formulations. The back story is dissipation. That's the less familiar story of how, and if, the chemical returns to its ground state. The back story of UV filters is photostability.

"The Photostability of Organic Sunscreen Actives: A Review" is the title of a chapter in *Sunscreens: Regulations and Commercial Development*, published last year¹ as the third edition of a book on this topic in the Cosmetic Science and Technology Series (see **Defining "Sunscreen"**). Edited by Nadim A. Shaath, Ph.D., president of Alpha Research and Development Ltd. in White Plains, N.Y., USA, the book contains 48 articles by 72 authors and appears quite different in content from the 1997 second edition. Five chapters are devoted to UV filters. The one covering photostability is by Craig A. Bonda, director of R&D for personal care at CPH Innovations, an

affiliate of the C.P. Hall Company, Chicago. The industry knows this company through its sales and marketing arm, RTD*HallStar.

Bonda writes that a UV filter's fate is best understood as "a competition between the many pathways the molecule can take between its elevation to an excited state and its return to the ground state. All of the pathways result in the dissipation of excited state energy. Some of the pathways are destructive to the molecule (e.g., fragmentation, some types of isomerization, biomolecular reaction); others are nondestructive (e.g., fluorescence, phosphorescence, some types of isomerization, energy transfer to another molecule). Each pathway is associated with its own rate constant. If nondestructive pathways

Defining "Sunscreen"

If all you had was the contents page of the excellent new compilation titled *Sunscreens: Regulations and Commercial Development*, would you know what to expect in the 16 chapters whose title uses the word *sunscreen* without identifying it as either an ingredient or a formulated finished product? For that matter, if you had only the title of the book, would you expect it to be focused on consumer products or UV filters?

For example, are the following chapters about consumer products or UV filters?

- Sunscreen Evolution
- Safety Considerations for Sunscreens in the USA
- Regulation of Sunscreens in Australia
- Recreational Sunscreens
- Recent Sunscreen Market Trends

Again, are the following chapters about consumer products or UV filters?

- Regulatory Aspects of Sunscreens in Europe
- SPF Modulation: Optimizing the Efficacy of Sunscreens

In fact, the first group focuses on consumer products and the second on UV filters. This observation is not meant as a criticism. This excellent volume belongs in the formulator's library because sun protection is becoming a part of so many personal-care product forms. But the ambiguity in the use of the term *sunscreens* suggests that it has achieved a new status: multifunctionality.

predominate, then, relatively speaking, the molecule will be photostable. Conversely, if destructive pathways predominate, then the molecule will be unstable.”

This Bench & Beyond column relies heavily on Bonda’s chapter, his patents and other publications, and his response to e-mailed questions. The column also draws on publications and patents from French and Italian researchers who have developed approaches different than Bonda’s. The result is four strategies for improving the photostability of organic sunscreen actives. But first, a look at the UV filters themselves.

UV Filters

Dozens of UV filters have been approved variously for use in cosmetic products in different parts of the world, but often under different names and at different maximum percentages in formulations.^{2,3} **Table 1.1** shows the several UV filters that can be used in products marketed in the United States, Europe and Japan. They are listed by U.S. drug name and by UV filtering range. Some of the alternate names also are listed.

The UVB filters most widely used in the United States in commercial sunscreen compositions are paramethoxy-cinnamic acid esters, such as octyl methoxycinnamate (octinoxate). Other widely used UVB filters are octyl salicylate (octisalate) and benzophenone-3 (oxybenzone). The most commonly used UVA filters are the dibenzoylmethane derivatives, particularly avobenzone. Methods to photostabilize avobenzone have been a particular interest of Bonda over a string of patents, some of which are cited in this article.

The Photochemistry of Photostability

The photochemistry of photostability has been described by Bonda in the Shaath book and elsewhere,⁴ so here it will suffice to say there are multiple routes by which a UV filter molecule can dissipate its energy and return from the excited state to the ground state. Some routes—such as fragmentation, biomolecular reaction and certain isomerizations—destroy the molecule. Others—such as fluorescence, phosphorescence, certain isomerizations, and energy transfer

Table 1.1 Universal UV filters for sunscreen products and their maximum usage levels (%) by region (NL = No Limit)

U.S. Drug name	Other name	U.S. (%)	Japan (%)	EU (%)
<u>UVB Absorbers</u>				
Octinoxate	INCI Ethylhexyl methoxycinnamate	7.5		
	Old US Octyl methoxycinnamate			
	Japan 2-Ethylhexyl 4-methoxycinnamate		20	
	EU Octyl methoxycinnamate			10
Homosalate	INCI Homosalate	15		
	Japan Homomethyl salicylate		10	
	EU Homosalate			10
Octisalate	INCI Ethylhexyl salicylate	5		
	Old US Octyl salicylate			
	Japan Octyl salicylate		10	
	EU 2-Ethylhexyl salicylate			5
Octocrylene	INCI Octocrylene	10		
	Japan Octocrylene		10	
	EU 2-cyano-3,3,diphenyl acrylic acid, 2-ethylhexyl ester			10
Ensulizone	INCI Phenylbenzimidazole sulfonic acid	4		
	Japan Phenylbenzimidazole sulfonic acid		3	
	EU 2-Phenylbenzimidazole-5-sulphonic acid and its potassium, sodium and triethanolamine salts			8
<u>UVA Absorbers</u>				
Oxybenzone	INCI Benzophenone-3	6		
	Japan Oxybenzone		5	
	EU Oxybenzone			10
Avobenzone	INCI Butyl methoxydibenzoyl methane	3		
	Japan 4-tert-Butyl-4'-methoxydibenzolymethane		10	
	EU 1-(4-tert-Butylphenyl)-3-(4-methoxyphenyl)propane-1,3-dione			5
<u>Physical blockers</u>				
Zinc oxide		25	NL	NL
Titanium oxide		25	25	NL

to another molecule—preserve the molecule. Routes of the latter type are the photochemistry of photostability because the molecule survives and is ready to receive another photon.

While the molecule is in the triplet excited state, it behaves as a diradical, which means many chemical reactions are possible. Of particular importance to the sunscreen formulator are reactions between like or different UV filter molecules, those between UV filter molecules and sunscreen excipients, and isomerization or fragmentations of the UV filter molecules, any one of which may alter or destroy the UV absorption capacity of the sunscreen formulation, according to Bonda.⁵

The discussion turns now to several strategies for increasing the photostability of UV filters. They will be described here in terms of specific filters for simplicity, but please note that the source document describing these concepts probably talked in terms of families of filters. Thus, Bonda's U.S. Patent 6,962,692 discusses dibenzoylmethane derivatives, but this column will talk about only one of them, avobenzone.

Solvent Polarity

Several Bonda patents⁶⁻⁸ describe methods to optimize photostability by adjusting the polarity of the solvent system. This method is based on electron transfer theory, which holds that when a molecule absorbs or releases an electron, the rapid expansion and contraction of a molecule's electron cloud causes dislocation and rearrangement of the solvent molecules in the immediate vicinity. The energy required for the solvent molecules to accommodate these changes in dimension and charge distribution has a direct relationship to the rate at which electron transfer takes place.

Bonda's U.S. Patent 6,770,270 describes a method to prepare a sunscreen formulation by controlling the polarity of the solvent system to control the rate of photodecay of the filter system. It calls for these steps:

1. Select a UV filter or filter system.
2. Select a variety of solvent systems.

3. Prepare parallel mixtures of the filter system at constant concentration in the various solvent systems.
4. Determine a rate constant of photodecay of each of the mixtures at a selected wavelength.
5. Determine the polarity of each of the mixtures.
6. Select the final solvent system based on its polarity.
7. Mix the filter system and the solvent system.

Bonda's own studies documented a parabolic relationship between the dielectric constant of the oil phase and the photostability of several avobenzone-containing sunscreen formulations.

Polarity of the solvent system plays a role in a Playtex patent from March 2006 in which Dueva and SaNogueira claim a method to optimize the polarity, photostability and other characteristics of sunscreen formulations by using optimizing agents selected from the group consisting of diol, alcohol, glycol, polyhydric alcohol and their derivatives or combinations.⁹

Formulation Strategies

The ideal formulation strategy removes ingredients known to be deleterious to UV filter photostability and includes ingredients that are known to improve photostability. For example, the combination of octinoxate and avobenzone is well known to be photo-unstable, according to Bonda. On the other hand, the combination of octocrylene and avobenzone improves the photostability of avobenzone.

Among other ingredients known to improve the photostability of avobenzone are the following:

- Diethylhexyl 2,6-naphthalate. This ingredient, invented by Bonda and disclosed in U.S. Patent 5,993,789 and others, is now marketed as Corapan TQ from Symrise. Bonda and Steinberg reported that this ingredient improves the performance of every sunscreen, regardless of the UV filter combination.¹⁰
- Polymers and compounds containing a diphenylmethylenes or a 9H-fluorene moiety.¹¹ A related patent uses the same idea but