Sunscreen Photostability 101

Read on to find out why a sunscreen stops working and, more importantly, what can be done to correct the problem.

By Craig Bonda
The HallStar Company

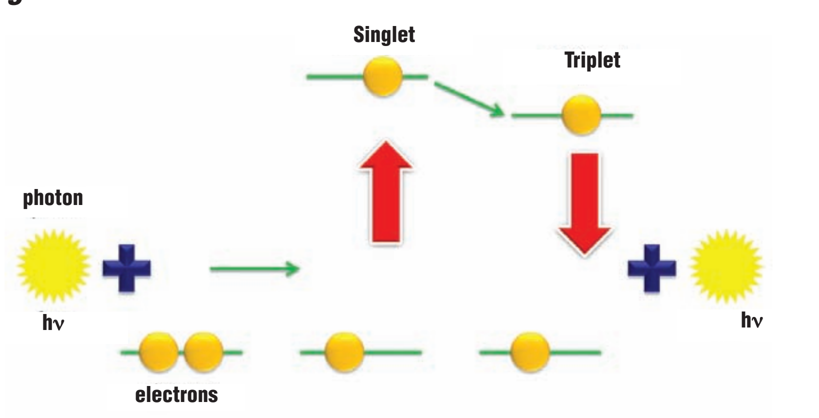
Sunscreens belong to a special class of skin care products. In the U.S., the Food and Drug Administration (FDA) requires that any product with sun protection claims must contain one or more active ingredients chosen from a list in the regulations. These ingredients include protective chemicals and ultraviolet (UV) filters, which must be listed on sunscreen labels. Before being sold to consumers, the finished product must prove its protective ability in a test conducted on human volunteers. Similar rules govern sunscreens around the world. If a product label implies in any way that the product protects you from the sun, then it is a sunscreen.

Applying a sunscreen to skin changes the way the body reacts to the sun's rays. In a way, sunscreens are like medicine you apply to your skin to keep it healthy.

The focus of this article is on one aspect of sunscreen science known as photostability, which lately has been very much in the sunscreen industry news. Why the sudden emphasis and interest? Very simply, the photostability of a sunscreen has a profound influence on its performance. But like so many things, its effect is mostly invisible to consumers. For decades, consumers have relied on the sun protection factor (SPF) rating to tell them how long they can stay in the sun without getting sunburned. Now there's credible information that even when sunburn is prevented, chronic sun exposure has other, more subtle, long term effects including premature aging of the skin which can cause a wrinkled, leathery, spotty appearance and certain types of skin cancer. That's why there's now general consensus among scientists, physicians and regulators that SPF is at best an incomplete indicator of sunscreen effectiveness, and at worst a misleading one.

That's where photostability comes in. Since the 1970s, it's been known that sunburn is caused primarily by exposure to a small portion of the sun's UV radiation known as UVB. SPF mostly indicates protection against UVB. In the early 1980s, European sunscreen makers started adding an active ingredient, known in the U.S. as avobenzone, which was supposed to improve SPF (UVB rays) and protect against UVA rays. Unfortunately the benefits were far less than predicted. The reason, it was found, was due to a lack of photostability. Ironically, the very chemicals that were supposed to protect the wearer from UV radiation were themselves harmed by UV exposure!

Fig. 1: How UV Filters Work



Protecting Sunscreens

To understand the chemical reaction that causes avobenzone to stop working, we need to look briefly at the photochemistry of UV filters. *Figure 1* details, in simple terms, how UV filters work.

Briefly, a particle of UV radiation called a photon encounters a pair of electrons in a UV filter molecule. Before the interaction begins, the molecule is in the ground state. The photon transfers its energy to the electron causing it immediately to "jump" to a higher energy orbit that is farther from the nuclear framework. The initial jump puts the molecule into the singlet excited state. The molecule may very quickly return to the ground state, possibly emitting another photon in the process. But commonly, the excited molecule decays to a less energetic excited state called a triplet excited state. There it stays for some time, getting rid of its energy as heat, before returning to the ground state.

In this way, the UV filter molecules absorb and dissipate the photon's energy so your skin doesn't have to. An SPF 30 sunscreen, if properly applied, absorbs about 97% of the UVB photons before they get to the skin.

The whole cycle, starting with absorption of the photon and ending with the return to the ground state, typically takes a molecule a few thousandths of a second to complete. If everything goes smoothly, at the cycle's end the molecule is once again available to absorb another photon. But, everything doesn't always go smoothly.

Meet DEXSTER

To help understand all the things that can happen—good and bad—between those excited states and the ground state, I created DEXSTER *(Figure 2)*, a graphical depiction of the processes by which a photonically excited molecule dissipates its excited state energy either by returning to the ground state or by being destroyed in the process. DEXSTER is an acronym for Deactivation of EXcited STates by Emissions and Radiationless pathways.

Think of the disc-like circular structures (in blue, purple, and yellow) as reservoirs (photochemists call them manifolds) that contain all the UV filter molecules in their various states: ground state, singlet excited state and triplet excited state. The ground state reservoir contains all the UV filter molecules you just applied to your skin before going out in the sun.

When sunscreens are exposed to sunlight, the energy in UV radiation "pumps" some of the molecules from the ground state reservoir to the singlet excited state reservoir.

The green pipes connecting the reservoirs—three each from the singlet and triplet excited state reservoirs to the ground state reservoir and one between the singlet and triplet excited state reservoirs—represent the physical processes that drain the excited state energy, much as the plumbing drains water in your house. Each pipe has its own physics and chemistry, and you'll probably be relieved to know that we're not getting into that in this article. As you can see, the pipes are labeled, and you can find a key to the labels and a bit of information about them in the footnote below.

During the process of absorbing the photon and draining the energy, a few sunscreen molecules may be altered in ways that permanently prevent them from absorbing another photon. These altered molecules are now "out of action." As the number of altered molecules increases, the number of sunscreen molecules protecting skin decreases. As a result, the sunscreen becomes less protective. It is also important to note that photochemical reactions in sunscreens proceed almost exclusively from the triplet excited state reservoir.

Keeping Sunscreens at Work

When we talk about photostability, we're really talking about the degree of reduction in the population of working sunscreen molecules—more working molecules means more photostability. The opposite is also true—fewer working molecules means less photostability. By the way, the opposite of photostability is photolability.

Loss of photostability doesn't happen all at once. Instead, the decline follows a pattern called an exponential decay curve. *Figure 3* is an example of the

Fig. 2: Get to Know DEXSTER

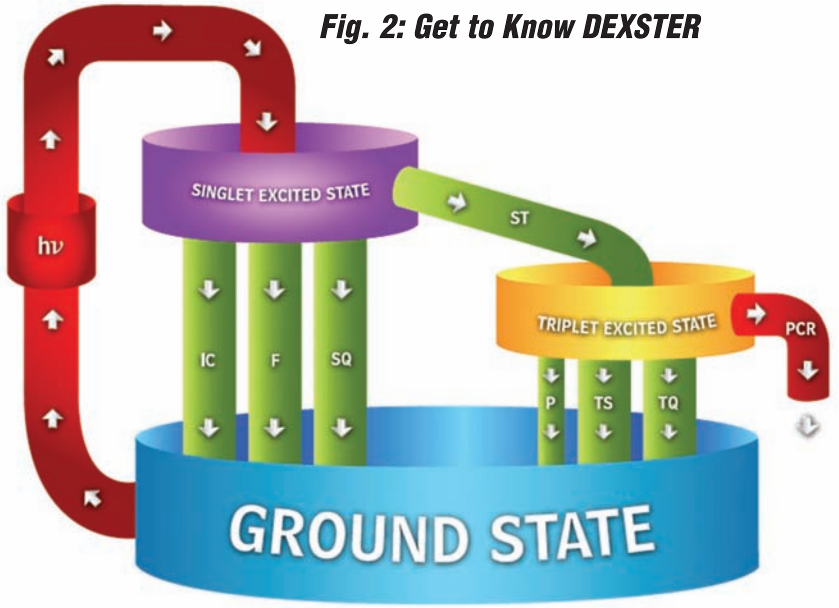
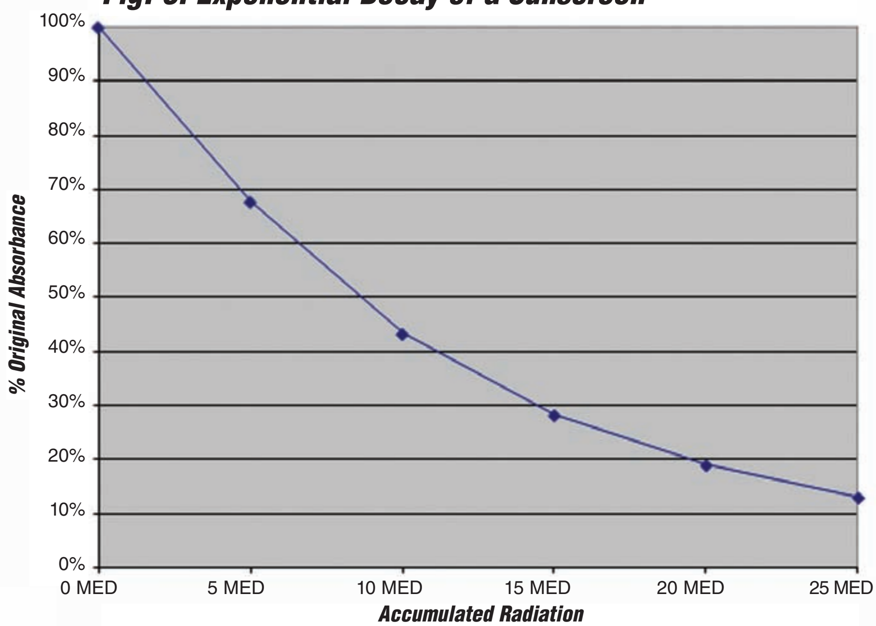


Fig. 3: Exponential Decay of a Sunscreen



MED = Minimum Erythemal Dose, the amount of UV radiation needed to start sunburning

Defining DEXSTER acronyms (from the left): IC is internal conversion. F is fluorescence. SQ is singlet quenching. ST is singlet-to-triplet intersystem crossing. P is Phosphorescence. TS is triplet-to-singlet intersystem crossing. TQ is triplet quenching. PCR stands for photochemical reactions.

Fig. 4: Destructive Molecular Rearrangement

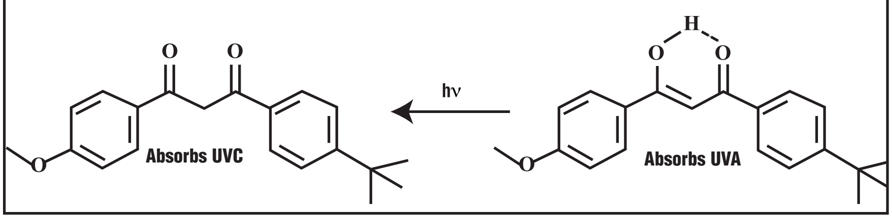


Fig. 5: Destructive Photochemical Reaction

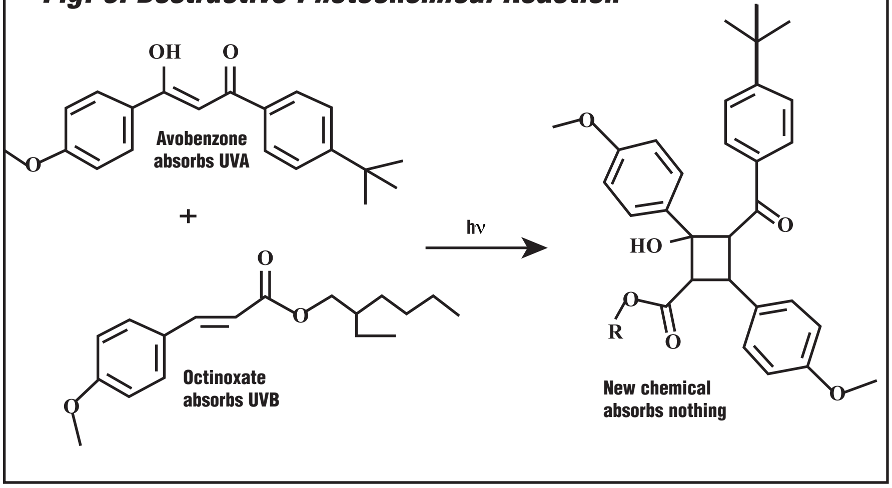
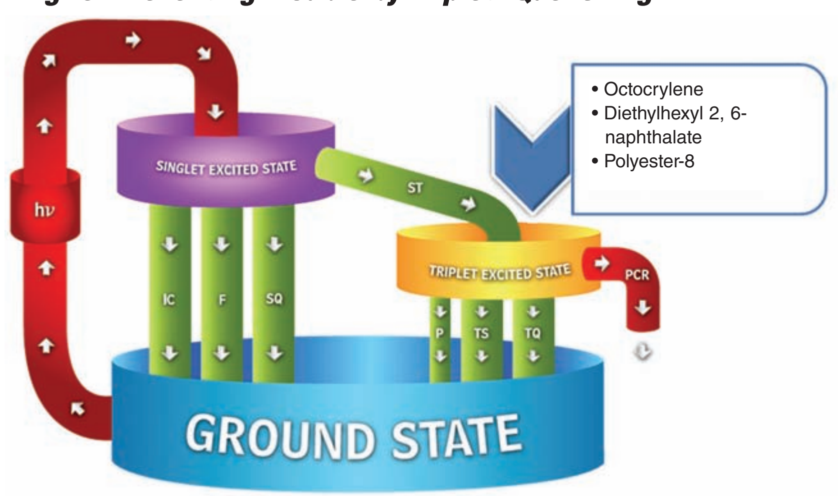


Fig. 6: Preventing Trouble by Triplet "Quenching"



exponential decay curve of a sunscreen as measured in the author's laboratory. As you can see, as the amount of radiation increases, the sunscreen's absorbance decreases. Ideally, during exposure to sunlight, the sunscreen's absorbance won't change at all. In other words, none of the sunscreen's molecules will be altered in ways that prevent them from again absorbing another photon. It would be photostable.

Okay, now that we know what photostability is, what causes a sunscreen to lose it? Well, the simple answer is that the energy in UV radiation from the sun causes some of the sunscreen molecules to engage in chemical reactions that irrevocably change them. Because photons are involved, these reactions are called photochemical reactions. Some of these reactions are apparently minor rearrangements of a sunscreen molecule's structure. Unfortunately, even small changes make big differences in a molecule's ability to absorb more photons, or at least the ones that protect you.

Figure 4 is an example of that. The drawings represent two forms of the avobenzone molecule. The one on the left absorbs UVC radiation, the one on the right absorbs UVA radiation. UVC is filtered out by the ozone layer, so absorption does not have significant value. The useful form of the molecule is on the right. It does a great job of protecting against UVA radiation, the kind that ages the skin and is even implicated in some cancer. Problem is, when it absorbs a photon (signified by the symbol hν in the drawing), there's a chance it will revert to the form on the left, rendering it ineffective.

In *Figure 5* there's another example that shows what can happen when avobenzone is mixed with octinoxate, the most widely used UVB absorber, and both are exposed to UV radiation. In this one, an avobenzone molecule is photoreacting with an octinoxate molecule to produce a complicated new chemical in a process known to chemists as a 2+2 cycloaddition. In the process, both molecules—and their ability to protect your skin from UV radiation—are destroyed.

The Role of Photostabilizers

A lot of other things can happen too that we won't cover in this article. Suffice it to say that the less these things happen the better the sunscreen will be at protecting skin. And to help them do that better, sunscreen manufacturers have learned to use photostabilizers.

Photostabilizers are a group of chemicals with the amazing ability to take the excited state energy away from other molecules before they get into trouble, for example, before they undergo those dreaded photochemical reactions. Then the photostabilizer molecules dispose of the energy safely.

To understand this process, take a

look at *Figure 6*. Most photostabilizers in use today "drain" the triplet excited state reservoir before photochemical reactions can occur. Next time you pick up a sunscreen package, check the ingredients listed on the product's label. Chances are if the active ingredients include avobenzone, one of these three ingredients will be there too. These "triplet quenchers" work really well in many products. Where they don't work well is when the photochemical reactions are so rapid that the triplet quenchers can't drain the Triplet Excited State reservoir fast enough to prevent them.

Recently, HallStar introduced a new kind of photostabilizer, one that drains the singlet excited state reservoir. Previously, this was thought to be impossible because molecules stay in the singlet excited state for such a short period of time. For example, avobenzone stays in the singlet excited state for only 13 one-thousandths of a billionth of a second. But the new photostabilizer—SolaStay S1 (INCI: Ethylhexyl methoxycrylene)—works. It is a singlet quencher that dramatically reduces the flow of energy to the triplet excited state reservoir, as illustrated in *Figure 7*. Since it is quenching the singlet excited state molecules don't even go to the triplet excited state reservoir. They return to the ground state and get back to work.

Because it works so fast, the new photostabilizer allows sunscreen manufacturers to formulate products with combinations of active ingredients that were once considered to be too photounstable to be effective. As a result, they can use lower levels of active ingredients to achieve higher levels of protection. Look for this ingredient on sunscreen labels starting next year.

In the beginning of this article, I suggested that sunscreens are like medicine you apply to your skin to keep it healthy. To continue that analogy: as with all medicines, you want to take the minimum effective dose. When sunscreens are not photostable, the "dose" has to be increased to account for the loss of protection due to photolability. When sunscreens are photostable, you are truly taking the minimum effective dose. ●

Fig. 7: Preventing Trouble by Singlet "Quenching"