

# SPF Boosters & Photostability Of Ultraviolet Filters

***Raw material suppliers have developed a wide range of emollients, quenchers, antioxidants and other cosmetic ingredients to improve the UV filters and boost the SPF.***

**Nadim A. Shaath, PhD.**

*Alpha Research & Development, Ltd.  
New York*

**I**T TAKES A NEAR MIRACLE to introduce a new ultraviolet filter in the U.S. Since the FDA monograph in 1978, only three new filters have been approved. Other than the few filters grandfathered via the OTC panel formed in 1973, today, the only way to pioneer a new UV filter is through one of two processes, namely, a New Drug Application (NDA) or the Time and Extent Application (TEA).<sup>1</sup> Due to the limitations of this process, suppliers were compelled to develop novel approaches to access the U.S. sun care market.

An NDA requires a commitment of many years and large sums of money, and ingredient modifications are not allowed without another expensive Amended NDA (ANDAs). The Givaudan Corporation took this route with its Parsol 1789 (Avobenzone) in the 1980s. After many years and many millions of dollars spent, Givaudan finally received an NDA culminating in Avobenzone's approval as a Category I ingredient on September 16, 1996. In 1998, zinc oxide was the second ingredient added to the monograph and on July 24, 2006 the FDA approved L'Oréal's NDA for a daily moisturizing cream that contains the EU approved UV filter Ecamsule (Mexoryl SX).

Shortly after Avobenzone was "officially" introduced in the U.S., reports of its photoinstability quickly spread.<sup>2</sup> With this fact already known in Europe, L'Oréal issued several patents for its photostabilization with Octocrylene and other ingredients.<sup>3</sup> Procter & Gamble also patented the use of Methyl Benzylidene Camphor (MBC)<sup>4</sup> and finally Roche (the succes-

sor of Givaudan) issued patents for the use of Octocrylene for molar ratios of less than 0.8.<sup>5</sup> Currently, this patent is licensed by DSM in the U.S.

In the meantime, marketers of sun care cosmetics entered the arena of high Sun Protection Factors (SPF), and successfully lobbied the FDA to remove the restriction on the maximum allowed SPF 15 and raised it to SPF 30+ in 1993 and on August 27, 2007 an SPF 50+ was proposed for the Final Monograph (FM).<sup>6</sup> To achieve higher SPF numbers in cosmetic formulations, the industry initially "loaded" the formulations with more UV actives. Intense research to improve the functionality of the filters, fueled by negative reports of inadequate sun protection in U.S. products, led to novel ways to improve the efficacy and stability of sun care products. With reports on the effect of emollients, carriers and other cosmetic ingredients on the performance of ultraviolet filters spreading<sup>7</sup> a new term was coined: SPF Boosters.

## **SPF Boosters**

Basically, SPF boosters, when first introduced into the industry, were merely emollients that efficiently dissolved ultraviolet filters that were crystalline and not liquids. In the U.S., these crystalline UV filters included the Benzophenones, PABA, Avobenzone, DEA Methoxy Cinnamate and Ensulizole. In Europe most of the new UV filters are solid in nature and include the Mexoryls, Tinosorbs, Uvinul A Plus and T-150, NeoHeliopan AP, the Benzylidene Camphors and Drometrizole. SPF boosters were then added to the formulations at a significantly higher percentage (over 5%) as they aided in the dissolution of the solid UV filters and inorganic particulates but they also—fortuitously for some—affected the UV absorbing patterns and gave better coverage which translated into improved SPF numbers. Patents for emollients that boost the SPF were issued and credited for their superior SPF boosting abilities.<sup>8</sup> Emollients and polymers

**Table I: The UV Absorbance of Selected Category I Filters<sup>13</sup>**

USAN Name	$\lambda$ MAX <sub>1(nm)</sub>	$\lambda$ MAX <sub>2(nm)</sub>	Molar Extinction Coefficient (mol <sup>-1</sup> cm <sup>-1</sup> )	
			e <sub>1</sub>	e <sub>2</sub>
Dioxybenzone	284	327	13,270	10,440
Homosalate	306		4,300	
Meradimate	336		5,600	
Octisalate	307		4,900	
Octocrylene	303		12,600	
Oxybenzone	286	324	14,380	9,180
Sulizobenzene	286	324	13,400	8,400
TEA Salicylate	298		3,000	

also boost the SPF of formulations of inorganic particulates (Zinc and Titanium Oxides) by assisting in their dispersion and rheology.

Shortly thereafter, new cosmetic techniques positioned existing approved Category I ultraviolet filters as solubilizers and emollients of crystalline UV filters. These included Octisalate, Homosalate and Octinoxate. At this point, other ingredients that are not Category I ingredients appeared on the market as SPF boosters but also had some UV absorbance. Examples appeared in several patents, one by Hallstar for Butyl Hydroxy Benzoate (BHB)<sup>9</sup> and another by ISP for Phenylethyl Benzoate (X-TEND 226)<sup>10</sup> both with a weak UVB absorbance. Natural ingredients were included in sun care formulations for their aromatherapeutic value as well as for their natural antioxidant and SPF boosting properties.<sup>11</sup> Only a few reported that their natural ingredients had any ultraviolet absorbing potential. *Kaempferia Galanga*, for example, was patented for its SPF boosting effect.<sup>12</sup> The main ingredient in this plant is para-Methoxy Cinnamic acid and its ethyl derivative, which has a  $\lambda_{max}$  at 305 nm and an extinction coefficient of over 15,000! (Compare to the extinction coefficients of some of the Category I UV filters in the U.S. as shown in Table I).

Rohm & Haas introduced a styrene/acrylate copolymer of hollow spheres which allows for efficient scattering of UV radiation. The incident rays penetrate the film at angles, thereby increasing the path length and by Beers law, the

absorbance of the radiation, which increases the SPF value of the sunscreen film considerably.<sup>14</sup> Also, L'Oréal has a recent patent issued in 2005 for glass microspheres made from calcium aluminum borosilicate or sodium borosilicate beads. These glass microspheres enhance the efficacy of the sunscreen formulation by diffracting the incoming light and increasing the likelihood of the incident light encountering a UV molecule.<sup>15</sup>

### Photostability of UVA Filters

The other approaches to boost SPF and improve the photostability of UVA filters include:

**1. Glass Beads:** Merck (EMD) has recently introduced UV-Pearls which are encapsulated organic sunscreens via the Sol-Gel process.<sup>16</sup> The Eusolex UV Pearls (Octinoxate) boost the SPF and prevent the many disadvantages of Octinoxate. When Octinoxate is entrapped in microcapsules, there is a separation of the incompatible ingredients thereby improving the photostability of Avobenzone.

**2. Antioxidants:** Ingredients that possess antioxidant activity with the potential of quenching reactive singlet oxygen (ROS) have appeared in many sunscreen formulations.<sup>17</sup> Wondrak has identified quenchers of photoexcited state ingredients to facilitate the harmless dissipation of photoexcitation energy by inhibiting the formation of ROS.<sup>18</sup>

**3. Triplet-Triplet Quenchers:** Triplet-Triplet (T-T) Quenchers have only recently appeared in the U.S. Their inclusion in sun care formulations has opened up a new avenue for the photo stabilization of Avobenzone.<sup>19</sup>

In Europe, cosmetic companies can choose from a series of UV filters,<sup>20</sup> but the U.S., unfortunately, has very few organic UVA absorbers approved. The traditional workhorse has been Oxybenzone, which has a weak absorbance in the UVA II region (324nm) and virtually no coverage in the UVA I region (340-400nm). Two other Benzophenones (Dioxybenzone and Sulisobenzene) are rarely used and Meradimate is a weak UVA (336nm) absorber.<sup>21</sup> Thus the introduction of Avobenzone as a Category I ingredient to complement the inorganic particulates was a welcome sign

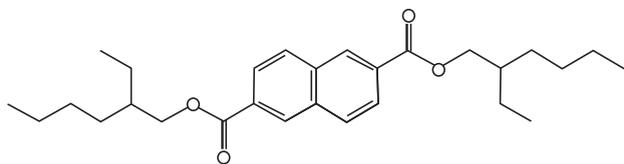
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to cosmetic formulators in the U.S. Unfortunately this ingredient suffers from severe photoinstability and was also reported to be chemically incompatible with Cinnamate UVB absorbers.<sup>22</sup> Furthermore, the FDA has placed many restrictions on its use in the U.S. The maximum allowable usage for Avobenzone is 3%, compared to 5% in Europe and up to 10% in Japan. It is also not allowed in combinations with Zinc Oxide, Titanium Dioxide, Meradimate, Padimate-O and Ensulizole. The combination of Zinc Oxide and Ensulizole with Avobenzone is under consideration for approval in the Final Monograph.<sup>6</sup>

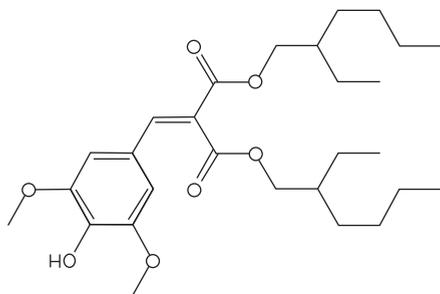
Quenchers were first introduced in Europe to circumvent the photoinstability issues of Avobenzone. L'Oréal, Procter & Gamble, Roche and others all have patents restricting the use of quencher combinations with Avobenzone. Recently a number of other quenchers were introduced into the industry, primarily in the United States, that have fancier names such as Triplet-Triplet quenchers or Excited State quenchers. These include:

**a. Corapan TQ:** A patent by Hallstar appeared in November 1999 attributing to Diethylhexyl Naphthalate (DEHN) the quenching ability to photostabilized Avobenzone.<sup>23</sup> It is currently trademarked by Symrise as Corapan TQ.<sup>24</sup> It has a UVB  $\lambda_{max}$  at 294nm with an extinction coefficient of 9000 and also possesses two UVA maximum absorbances at 332nm and 350nm with extinction coefficients of 1000 and 2000 respectively.<sup>25</sup> The excited triplet energy of Corapan TQ was estimated from the phosphorescence spectral data of similar compounds as being within 2kcal/mol of 59. Gonzenbach has reported the excited triplet energy of Avobenzone as 60 kcal/mol. Note that octinoxate is 57 kcal/mol and octocrylene is 55 to 60 kcal/mol.<sup>26</sup>

The chemical structure of Corapan TQ is shown below:



**b. Oxynex ST liquid:** Merck (EMD) has filed for a patent issued in 2007 for DESM (Diethylhexyl Syringylidene Malonate) whose structure is shown below:



DESM has a hindered phenolic functionality and is a potent antioxidant. The mechanism of photostabilization is

attributed to both its T-T and Singlet Oxygen quenching. Interestingly, DESM manages to protect combination formulations of Avobenzone and Octinoxate. It has a  $\lambda_{max}$  of 334nm with an extinction coefficient of 18,740. Its excited triplet energies were evaluated demonstrating that DESM has the ability of being a T-T quencher for Avobenzone.<sup>27</sup>

**c. Tinogard Q and Cibafast:** CIBA has recently introduced, from their industrial application division, a number of ingredients that are Excited State Quenchers (ESQ) of Avobenzone.<sup>28</sup> They reduce the potential for degradation reactions by minimizing the lifetime of excited states and inhibiting side reactions of excited state intermediates. They include:

**Tinogard Q:** Tris (Tetramethyl Hydroxy Piperidinol) citrate is highly effective and is the only Ciba ESQ ingredient that is a T-T Quencher without possessing a UV absorbance.

**Cibafast H liquid:** Sodium Benzotriazolyl Phenol Sulfonate and Buteth-3 and tributyl citrate is an anionic photostabilizer with UVA/UVB absorption.

**Tinogard TS:** Benzotriazole Dodecyl p-Cresol is a nonionic photostabilizer with UVA/UVB absorption.

**Tinogard HS:** Sodium Benzotriazole Butyl Phenol Sulfonate is an anionic photostabilizer but is also an effective UVA/UVB absorber.

#### d. Polycrylene:

Polycrylene is the trade name of Hallstar for Polyester-8 and is a low molecular weight copolymer (1400 Dalton's) of Adipic acid and Neopentyl glycol that is terminated with Cyano Diphenyl propenoic acid. It is basically an Octocrylene molecule that has the polymer attached at the acid moiety of Octocrylene. As such it has a third of the efficiency of Octocrylene at the  $\lambda_{max}$  of 303nm and a triplet excited state energy of 55 to 60 kcal/mol making it a potential T-T quencher.<sup>29</sup> Bonda has also reported on other similar molecules that are potential T-T quenchers or photostabilizers.<sup>30</sup>

### Other Technologies

I have already alluded to the successful use of Category I UV absorbers such as Octocrylene and Oxybenzone as quenchers and photostabilizers of Avobenzone. It has been demonstrated that the mode of action of the photostabilization of Avobenzone with oxybenzone is due to its singlet state quenching.<sup>30</sup> Also, other ingredients on the TEA list, such as MBC and Tinosorb S, are known to photostabilize Avobenzone. Chatelain and Gabard have reported on the photostabilization of Avobenzone and Octinoxate with Tinosorb S.<sup>31</sup> Tinosorb S (bemotrizinol) has two  $\lambda_{max}$  absorptions at 310nm and 343nm, with extinction coefficients of 42,840 and 47,500 respectively. It has extremely effective SPF and PPD values and is currently under consideration for approval in the USA under the TEA process. No T-T excited state energies are reported.<sup>32</sup> Recently, there have been reports on the use of lipospheres to photostabilize Avobenzone.<sup>33</sup>

Those planning to use any of the above-mentioned ingredients should always anticipate the patents and regulations that potentially limit their use.

## Mechanism of Action and Applications

After this brief review of the many ingredients that boost SPF and photostabilize Avobenzone introduced in the past dozen years or so, I will briefly reflect on their mechanism of action and their intended applications:

**1. Solubility, Emulsion and Formulation Issues:** To achieve a high SPF the UV filters must be dispersed properly in the oil phase. The efficacy of sunscreen emulsions depends upon a number of parameters<sup>34</sup> including:

- Selection of UV filters with a synergistic effect between inorganic and organic filters.
- Emulsion and oil phase rheology to control spreadability and film thickness.
- Particle size distribution to control film formation of the dispersed oil phase.
- The dry down time of the emulsion.
- The photostability of all ingredients.

A very important requisite for excellent emulsions is, of course, the total solubility of the filter in the formulation. This is accomplished by efficient emollients such as the ELEFAC, C<sub>12-15</sub> Alkyl Benzoate, diester Malates, etc. Any ingredient that will totally dissolve the filters, improve the solubility and film integrity, improve the dispersion of the inorganic and organic filters, assist with film forming in thickening the sunscreen film to improve spreadability and protection, will boost the SPF and would be a desirable attribute in sun care cosmetic formulations.

The addition of non-UV absorbing botanical extracts and other additives to boost SPF and allow for natural or other claims is perfectly acceptable. Also, the addition of an approved ultraviolet filter, such as Octocrylene, Octisalate, Homosalate, etc. to assist in dissolving other crystalline filters is obviously acceptable if stability, safety and patent issues are adequately addressed. Conditions that may require proper substantiation, and approvals, however, include the addition of the UV absorbing emollients and solvents such as BHB, Phenethyl Benzoate, etc. and the addition of substantial amounts of UV absorbing or reflect-

ing polymers, clays or inorganic particulates other than the approved Titanium Dioxide and Zinc Oxide.

**2. Encapsulation of Polymers:** The use of glass beads to encapsulate already approved UV filters for the protection of photolabile ingredients is ingenious. The use of microspheres and polymeric particles that do not absorb in the UV to change the refraction, birefringance, increase the path length, diffraction and improve the likelihood of the incident light encountering the UV molecule is perfectly acceptable.

Of course, the creation of a polymer backbone chemically bonded to an ultraviolet filter to reduce the permeability of the UV molecules changes the characteristics of the UV filter and approvals for a totally new UV filter must be sought in a manner similar to Mexoryl XL (the trisiloxane derivative of Drometrizole), Parsol SLX (a polysiloxane derivative of Benzylidene Malonate) and Tinosorb M as an organic particulate. None of the three have been approved in the U.S. as Category I filters. Similar modifications of other UV absorbing molecules including existing low molecular weight approved UV filters is highly encouraged.

**3. Antioxidants and ROS Quenchers:** This is a very viable route and a recommended regimen for all sun care formulations. It has been demonstrated that the use of antioxidants and free radical quenchers contributes

significantly to the photostability of products. Antioxidants, however, that are also UV absorbers may require regulatory approvals as adjuvants in suncare regimens.

**4. Triplet-Triplet Quenchers, Charge Transfer and Excited State Quenchers:** These molecules must be photochemically inert. This means that they should have no absorbance in the UVB or UVA regions (290-400nm). Most quenchers reviewed in this report under this category fail the basic premise of being photochemically inert. The UV absorbance of most T-T quenchers on the market are at least twice as effective as Octisalate, Homosalate or Meradimate and are comparable to the three Benzophenones. (See Table I).

To be effective with Avobenzone, T-T quenchers will proba-

Excellent emulsions require total solubility of the filter in the formulation.



### About the Author

Dr. Nadim A. Shaath received his B.Sc. degree (Honors) in Chemistry from the University of Alexandria, Egypt in 1967 and his Ph.D. in Organic Chemistry from the University of Minnesota in 1973. He joined the Chemistry Faculty at the State University of New York at Purchase in 1975. In 1979-1980 he served as the Chairman of the Chemistry Department at SUNY-Purchase and then joined Felton Worldwide, a flavor, fragrance and sunscreen company, as Director of Research. In 1990 he was appointed CEO of Kato Worldwide.

In 2000 he founded Alpha Research & Development, Ltd., and is currently its president. Alpha R&D, Ltd. is a research, sourcing and product development company in the fields of cosmetics, sunscreens, analytical testing, fragrances, essential oils and aromatherapy. He is the author of the book entitled *The Encyclopedia of Ultraviolet Filters*, published by Allured in March 2007 and is the editor of three sunscreen books published by Marcel Dekker.

bly have to be ultraviolet absorbers. To quote Dr. Bernd Herzog from Ciba, "It is important that there is a match of the energy levels, such that the stabilizer can take over the excitation energy from the absorber. For that reason it is likely, that the stabilizer is also a UV absorber."<sup>35</sup>

The mechanism of quenching photoexcited states of skin chromophores and other organic photosensitizers is complex and effective screening of compounds is complicated.<sup>18</sup>

Other physical phenomena relating to rheology, dispersion, film integrity, thickening, increasing the path length, etc. all

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may contribute to the synergistic effects when UV filters are combined.

**5. New Ultraviolet Absorbers:** Clearly the industry should seriously pursue new UV filters that better address UVA protection, more photostable ingredients, more "broad" or "full" spectrum protection, safer, 500 plus Dalton UV ingredients with fewer side effects and decreased skin permeability, etc. All creations, of course, need to be registered, patented, governmental agency approved and, more importantly, their combinations with other UV filters, quenchers and cosmetic formulations protected. This may be cumbersome and expensive but in the long haul the only logical and profitable way.

## Conclusions

SPF boosters, quenchers and ingredients designed for improving the photostability of UVA filters have proliferated in U.S. sun care formulations. This is basically the only viable and remaining option that cosmetic chemists have in response to the demands from dermatologists, marketers and ultimately the consumer, to formulate high SPF and photostable products with substantial UVA protection. The raw material manufacturers supplying the sun care industry, stymied by the lack of regulatory approvals in the U.S. for new and improved UVB and UVA filters, have resorted to ingenious methods to produce ingredients that basically allow the cosmetic chemist to formulate with severely inadequate UVB and potentially photochemically unstable UVA filters. The rise of SPF boosters and quenchers of photolabile UVA filters must be examined and ultimately approved. ●

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