

Chapter 9

The Chemistry of Ultraviolet Filters

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Key Points

- This chapter describes the mechanism of action for both Inorganic particulates and organic ultraviolet filters. It classifies all ultraviolet filters in commerce today and lists their physical, chemical, and spectroscopic properties as well as their regulatory status.
- Synthetic approaches for the design of the current and future UV filters are discussed, and the photostability of ultraviolet filters is addressed.
- It concludes with an analysis of the future direction in designing new, safer, and more effective ultraviolet filters.

9.1 Introduction

The chemistry of ultraviolet filters is complex, and understanding the interaction between UV light and those compounds provides insights on how sunscreen works. Possessing the knowledge for a more intelligent design and development of novel UV filters can provide efficient and stable UV protection. Although much progress has been made in the advancement of ultraviolet filters in the past five decades, progress is slow and often hampered by regulatory restrictions [1, 2]. For example, little has changed in US regulations since 1978 when the Advanced Notice for Public Record (ANPR) was issued. At the time, 21 UV filters were considered Category I Ingredients (see Table 9.1), and their use in cosmetic formulations, at the percentages approved, allowed manufacturers to claim appropriate SPF (sun protection factor) on their labels.

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Table 9.1 Twenty-one approved UV filters in 1978 in the USA

<i>UVA absorbers/reflectors</i>	%
Oxybenzone	2–6
Sulisobenzone	5–10
Dioxybenzone	3
Menthyl anthranilate	3.5–5
Red petrolatum	30–100
Titanium dioxide	2–25
<i>UVB Absorbers</i>	
Aminobenzoic acid	5–15
Amyl dimethyl PABA ^a	1–5
2-Ethoxyethyl p-methoxycinnamate	1–3
Diethanolamine p-methoxycinnamate ^a	8–10
Digalloyl trioleate ^a	2–5
Ethyl 4-bis(hydroxypropyl) aminobenzoate ^a	1–5
2-Ethylhexyl-2-cyano-3,3-diphenyl-acrylate	7–10
Ethylhexyl p-methoxycinnamate	2–7.5
2-Ethylhexyl salicylate	3–5
Glyceryl aminobenzoate ^a	2–3
Homomenthyl salicylate	4–15
Lawsone with Dihydroxyacetone ^a	0.25
Octyl dimethyl PABA	1.4–8
2-Phenylbenzimidazole-5-sulfonic acid	1–4
Triethanolamine salicylate	5–12

^aThese items have been deleted in the Final Monograph in 1999. Three additional items have been added since, namely, avobenzone (1–3 %), ecamsule (up to 10 %), and zinc oxide (2–25 %)

With the inclusion of any of those UV filters, protection from skin cancers was considered possible, and US companies could claim that “sunscreens reduce the risk of skin cancer and early skin aging when used as directed,” if the final sunscreen product has SPF >15 and critical wavelength ≥ 370 nm. Despite the increased use of sun care products since then, incidences of skin cancer have quadrupled with no sign of abatement. Are people lulled into a false sense of security when they use sunscreens? All this sun damage begs the question: do sun care products provide enough protection? The search for the ultimate UV filter goes on, and protocols for superior protection are still underway with limited success.

In this chapter, I will review the approaches for designing the current UV filters that have been approved and are available for use worldwide. Understanding how filters work can help us to determine if they offer consumers adequate protection from the sun.

9.2 Mechanism of Sunscreen Action

Electromagnetic rays interact with UV filters by either absorbing or scattering of their energy. The dispersion of inorganic particulates scatters and reflects the harmful rays. Inorganic particulates, however, also have the ability to absorb the UV radiation.

When a molecule absorbs a UV photon, the electrons in its highest occupied molecular orbital (HOMO) are promoted to its lowest unoccupied molecular orbital (LUMO) as shown in Fig. 9.1.

This singlet excited state can be deactivated by a simple vibrational relaxation back to the ground state, through fluorescence of the molecule, or by undergoing photochemical reactions. On the other hand, under certain conditions, the singlet excited state can undergo an intersystem crossing that leads to a triplet excited state as shown in Fig. 9.2.

The energy in the triplet state may be dissipated in a number of ways, as shown in Fig. 9.2:

Fig. 9.1 Absorption of energy by an organic UV filter

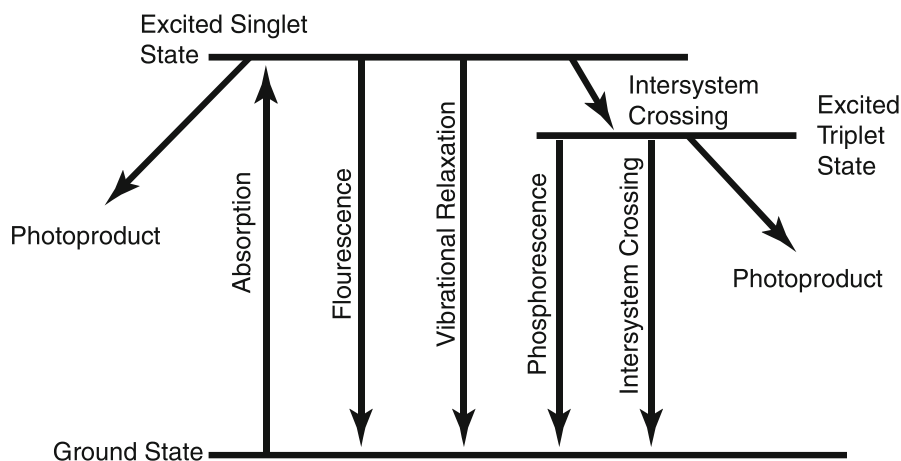
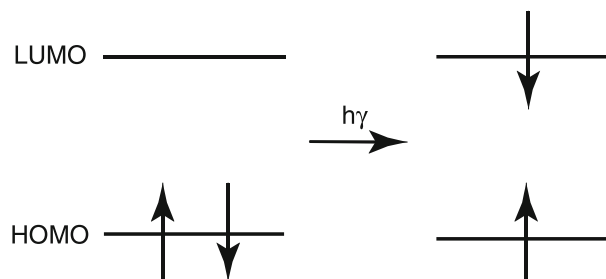
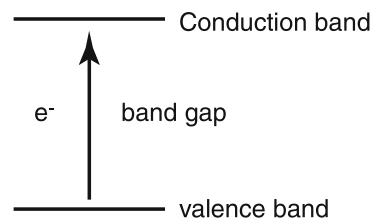


Fig. 9.2 Energy release pathways

Fig. 9.3 The band gap energy in inorganic particulates between valence and conduction bands



1. Emission of a photon (phosphorescence)
2. Energy transfer to other receptor molecules (T-T transfer)
3. Photochemical reactions

The inorganic particulates, on the other hand, either scatter or absorb the UV radiation. These particulates are semiconductors with high bandgap energy between the valence and conduction band (between 380 and 420 nm) as shown in Fig. 9.3.

The wavelength of absorption varies with the particle size of the inorganic particulates. The smaller the primary particulate size is, the higher the bandgap energy.

9.3 Classification of Ultraviolet Filters

Ultraviolet filters can be broadly classified into two types: UV absorbers and inorganic particulates. There are only two inorganic particulates approved: zinc oxide and titanium dioxide. Both ingredients are considered broad spectrum since they absorb, scatter, and reflect UVB and UVA rays depending on their particle size. The remaining UV-absorbing molecules are classified as either UVB or UVA filters or both.

There are about 55 ultraviolet filters that are approved for use in sunscreen products globally, but only 10 of them are approved uniformly for international consumption [3, 4]. Table 9.2 lists their UV absorbance maxima (λ_{max}) and their specific extinction E (1 %, 1 cm), namely, the nominal absorbance at the absorption maximum of a 1 % solution of the filter in a 1 cm optical pathway cuvette, the molar absorption coefficient C ($\text{mol}^{-1} \text{cm}^{-1}$), along with the countries or regions where they are approved. Each filter is approved or rejected according to regional requirements. Note that currently there are only ten UV filters that are approved uniformly worldwide and are marked with an ^{xxx} in Table 9.2 under category country/region.

9.4 The Chemistry of Ultraviolet Filters

To illustrate the relationship between the chemical structures of all of these approved UV filters and their UV-absorbing characteristics, I will review one of the oldest UV filters in use, namely, PABA (para-aminobenzoic acid) and its derivatives. PABA has a λ_{max} of 290 nm with an extinction coefficient E_1 (1 %, 1 cm)

Table 9.2 The properties of the 55 approved UV filters worldwide

INCI name	Country/region ^a	UV/region	λ_{max} , nm	E_1 (1 %, 1 cm), nm	ϵ_2 , dm ³ mol ⁻¹ cm ⁻¹	$\lambda_{\text{max},2}$ /nm	E_2 (1 %, 1 cm)	ϵ_1 , dm ³ mol ⁻¹ cm ⁻¹
Benzophenone	AZ	UVA/B	284		10,300	340		8950
Benzophenone-1	JN, SA	UVA/B	291	630	12,265	328	420	10,265
Benzophenone-2	AZ, JN, SA	UVA/B	287	580	13,700	349	410	9400
Benzophenone-3 ^{xxx}	ALL	UVA/B	286	630	14,380	324	400	9180
Benzophenone-4	EU, US, AZ, CA, JN	UVA/B	286	440	13,400	324	360	8400
Benzophenone-5	EU, CA, JN, SA	UVA/B	286	430		323	345	
Benzophenone-6	JN, SA	UVA/B	284	490	13,500	323	390	12,950
Benzophenone-8	US, AZ, CA, SA	UVA/B	284	380	13,270	327	300	10,440
Benzophenone-9	JN, SA	UVA/B	284	260		331	175	
3-Benzylidene Camphor	EU, SA	UVB	289	890	21,360			
Benzylidene camphor sulfonic acid	EU, AZ, JN, SA	UVB	294	860	27,600			
Beta, 2-glucopyranoxy propyl hydroxy Benzophenone	JN, SA	UVA/B						
Bis-ethylhexyloxyphenol methoxyphenyl triazine	EU, AZ, SA	UVA/B	310	745	46,800	343	820	51,900
Butyl methoxydibenzoylmethane ^{xxx}	ALL	UVA	357	1110	34,140			
Camphor benzalkonium methosulfate	EU, AZ, SA	UVB	284	590	24,500			
Cinoxate	US, AZ, CA, JN, SA	UVB	308	825	20,650			
DEA methoxycinnamate	CA, SA	UVB	290	880	24,930			
Diethylamino hydroxybenzoyl hexyl benzoate	EU, AZ, JN, SA	UVA	354	925	35,900			
Diethylhexyl butamido triazone	EU, SA	UVB	311	1460	111,700			

(continued)

Table 9.2 (continued)

INCI name	Country/region ^a	UV/region	λ_{max} , nm	E_1 (1 %, 1 cm)	ϵ_2/dm^3 $\text{mol}^{-1} \text{cm}^{-1}$	$\lambda_{\text{max},2}/\text{nm}$	E_2 (1 %, 1 cm)	ϵ_1/dm^3 $\text{mol}^{-1} \text{cm}^{-1}$
Digalloyl trioleate	SA	UVB						
Diisopropyl methyl cinnamate	JN, SA	UVB						
Dimethoxyphenyl-[1-(3,4)]-4,4-dimethyl 1,3 Pentanedione	JN, SA	UVA						
Disodium phenyl dibenzimidazole tetrasulfonate	EU, AZ, SA	UVA	335	770	51,940			
Drometrizole	JN	UVA/B	300			340		
Drometrizole trisiloxane	EU, AZ, JN, SA	UVA/B	303	310	16,200	341	300	15,500
Ethyl Dihydroxypropyl PABA	CA, SA	UVB	312		27,000			
Ethylhexyl dimethoxy benzylidene dioximidazoline propionate	JN, SA	UVB						
Ethylhexyl dimethyl PABA ^{xxx}	ALL	UVB	311	990	27,300			
Ethylhexyl methoxycinnamate ^{xxx}	ALL	UVB	311	850	23,300			
Ethylhexyl salicylate ^{xxx}	ALL	UVB	305	165	4130			
Ethylhexyl triazone	EU, AZ, JN, SA	UVB	314	1550	119,500			
Ferulic acid	JN, SA	UVB						
Glyceryl ethylhexanoate dimethoxycinnamate	JN, SA	UVB						
Glyceryl PABA	CA, JN, SA	UVB	297	780	18,700			
Homosalate ^{xxx}	ALL	UVB	306	180	4300			
Isoamyl p-methoxycinnamate	EU, AZ, JN, SA	UVB	308	980	24,335			
Isopentyl trimethoxycinnamate trisiloxane	JN, SA	UVB						
Isopropyl benzyl salicylate	AZ, JN	UVB						
Isopropyl methoxycinnamate	JN, SA	UVB						
Lawsone + dihydroxyacetone	-	UVB						

Menthyl anthranilate	US, AZ, CA, JN, SA	UVA	336	190	5230			
4-Methylbenzylidene camphor	EU, AZ, CA, SA	UVB	300	930	23,655			
Methylene bis-benzotriazolyl tetramethylbutylphenol	EU, AZ, JN, SA	UVA/B	305	400	26,600	360	495	33,000
Octocrylene ^{xxx}	ALL	UVB	303	340	12,290			
PABA ^{xxx}	ALL	UVB	283	640	15,300			
PEG-25 PABA	EU, AZ, JN	UVB	309	180				
Pentyl dimethyl PABA	JN	UVB	310	310				
Phenyl benzimidazole sulfonic acid ^{xxx}	ALL	UVB	302	920	26,060			
Polyacrylamido methylbenzylidene camphor	EU, SA	UVB	297	610	19,700			
Polysilicone-15	EU, AZ, JN, SA	UVB	312	180	108,000			
Salicylic acid	AZ	UVB	300					
TEA salicylate	US, AZ, CA, SA	UVB	298	120	3000			
Terephthalylidene dicamphor sulfonic acid	EU, AZ, CA, JN, SA	UVA	345	750	47,100			
Titanium dioxide ^{xxx}	ALL	UVA/B						
Zinc oxide	EU, US, AZ, CA, JN, SA	UVA/B						

^aEU, EU, US, AZ, CA, JN, SA, Canada, JN, Japan, SA, S. Africa. For official regulations, consult specific country/region agencies

Note: E (1 %, 1 cm) is the "specific extinction," and C ($\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) is the molar absorption coefficient

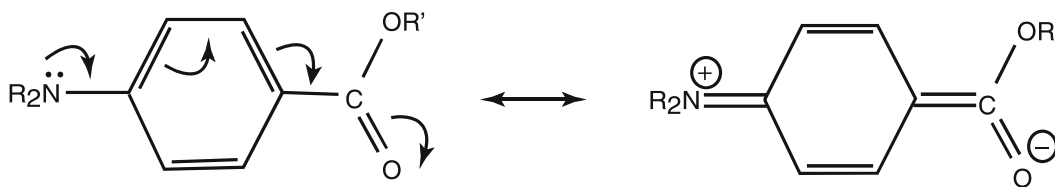


Fig 9.4 The electron delocalization in PABA molecule

of 640 or a $E_1(\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1})$ of 15,300. That characterizes this molecule as an efficient UVB filter which could yield SPF of over 8 by itself alone and in combinations can yield SPF well over 15 in cosmetic formulations. This molecule and its octyl (2-ethylhexyl) derivative, namely, padimate-O, were the workhorse molecules for producing efficient UVB protection in the USA in the past decades. These molecules have fallen out of favor recently as they tend to discolor and stain clothing and, most importantly, were implicated in a number of irritation cases by the consumer. Nevertheless, these molecules served as elegant examples of how sunscreen molecules exert their UV protection action. These molecules possess both an electron-releasing group (NR_2) and an electron-accepting group ($-\text{COOR}$), group that is situated in a para-position on the basic benzene (aromatic) molecule. This configuration allows for an efficient electron delocalization, with an energy requirement corresponding to an ultraviolet absorption of about 311 nm. Due to symmetry consideration and the ease of electron delocalization in the molecule, the absorption (as measured by its extinction coefficient) is quite high (990). Figure 9.4 illustrates that process.

If this PABA molecule was substituted differently on the benzene ring, say, an ortho-relationship instead of the para-relationship in PABA, the molecule would behave quite differently. In fact, menthyl anthranilate, another approved UV filter in the USA that has an ortho-relationship between its amine and ester grouping, is no longer a UVB filter. It is considered a UVA filter with a UV absorption of 336 nm but with a considerably weaker extinction coefficient E_1 (1 %, 1 cm) of 190. In examining the electron delocalization process in the ortho-disubstituted amine (menthyl anthranilate or meradimate), it is quite apparent that other processes are in play in this molecule, mostly through-space hydrogen bonding that eases the energy requirements of the electron delocalization. Since energy and wavelength are inversely proportional to one another, lower-energy requirements would produce a longer wavelength absorption. The through-space extra electron delocalization in the meradimate molecule produces a desired bathochromic (to higher wavelength) to UVA protection but, unfortunately, significantly lowers the ease of delocalization since the side chain hydrogen bonding electron transfer deviates from planarity, increases the energy requirements, and results in a lower extinction coefficient.

These two simple processes, namely, aromatic electron delocalization (contributing to the UV absorption) and the ortho-through-space hydrogen bonding (contributing to the ease of delocalization), are the basis of designing most of the ultraviolet

Fig 9.5 The para (parabens) with a lower λ_{\max} vs. the ortho (salicylates) with a higher λ_{\max}

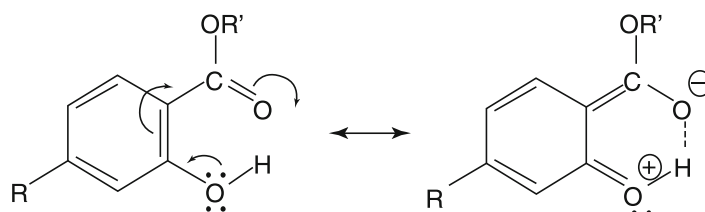
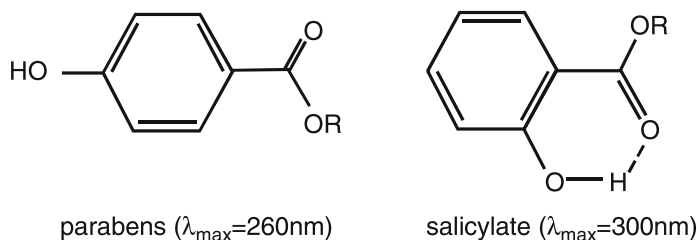


Fig 9.6 Resonance delocalization and through-space hydrogen bonding in salicylate

filters in the world today. Numerous similar examples to illustrate the forces at play in UV molecules are available. For instance, compare the parabens (para-disubstituted) to the salicylate (ortho-disubstituted molecules) in Fig 9.5.

Again, as predicted, the parabens would have a low UV absorbance of about 260 nm (that would not be considered a UVB filter) but with a considerable extinction coefficient, whereas the salicylates (homosalate or octisalate) have a higher UV absorbance of 306 nm (UVB filter) but with a lower extinction coefficient of 180 due to its ortho-through-space hydrogen bonding as shown in Fig. 9.6.

For a detailed review of the mechanism of all the other approved UV filters (cinnamates, benzophenones, dibenzoylmethanes, camphor, and triazone derivatives), consult other references [2].

9.5 New Molecules Appearing on the World Market

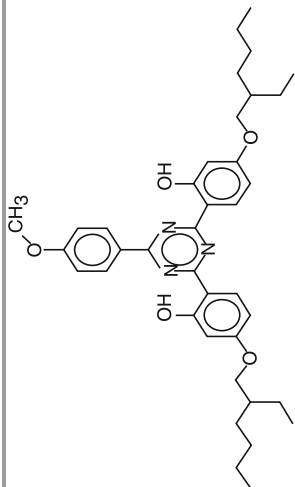
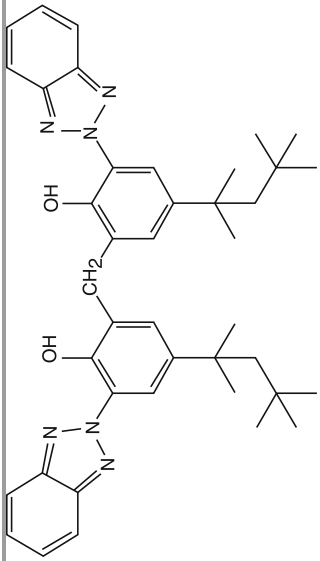
A series of molecules have recently been designed in Europe with high molecular weights (over 500 Da) to diminish their penetration into the skin. These molecules possess multiple chromophores that yield high extinction coefficients and also broad-spectrum protection [5]. They are, unfortunately, not yet approved in the USA. They are listed in Table 9.3.

In the USA, there are eight applications pending under the process termed TEA (Time and Extent Application) that, when approved, will undoubtedly enhance the UV protection of American consumers from the cancer-causing rays [6]. Two of the eight TEA ingredients, bemotrizinol and bisoctrizole, when approved for use in the USA, can be used to impart more photostable sunscreen formulations. See Table 9.4 below illustrating the properties of these two UVA ingredients.

Table 9.3 EU-approved UV filters for sunscreens designed with Dalton's of 500 or higher

Filter type	UV filter INCI name	COLIPA#	Trademark (supplier)	ϵ/dm^3 $\text{mol}^{-1} \text{cm}^{-1}$	λ max (nm)	Mol. weight (Dalton)
UVB	Benzylidene malonate polysiloxane	S74 BMP	Parsol SLX (DSM)	108,000	314	~6000
	Diethyl butamido triazone	S78 DBT	Uvasorb HEB (3V Sigma)	111,170	312	766
	Ethylhexyl triazone	S69 EHT	Uvinul T150 (BASF)	119,500	312	823
UVA	Disodium phenyl dibenzimidazole tetrasulfonate	S80 DPDT	Neo Heliopan AP (Symrise)	52,400	334	675
	Terephthalidene dicamphor sulfonic acid	S71 TDSA	Mexoryl SX (L'Oreal)	47,100	345	607
UVA/UVB	Bis-ethylhexyloxyphenol methoxyphenyltriazine	S81 BEMT	Tinosorb S (BASF/Ashland)	42,800/47,500	310/343	629
	Drometrizole trisiloxane	S73 DTS	Mexoryl XL (L'Oreal)	15,900/15,500	303/341	501
	Methylene bis-benzotriazolyl tetramethylbutylphenol	S79 MBBT	Tinosorb M (BASF)	32,000/38,000	305/360	659

Table 9.4 Specifications of bemotrizinol and bisoctrizole [7]

Commercial name:	Tinosorb S, Eusolex S,	Tinosorb M
Structural formula:		
Molecular formula:	$C_{38}H_{49}N_3O_5$	$C_{41}H_{50}N_3O_2$
Molecular weight:	627.8 g/mol	658.86 g/mol
INCI name:	Bis-ethylhexyloxyphenol methoxyphenyl triazine (BEMT)	Methylene bis-benzotriazolyl tetramethylbutylphenol (and) aqua (and) decyl glucoside (and) propylene glycol (and) xanthan gum
USAN name:	Bemotrizinol	Bisoctrizole
CAS-no:	187393-00-6	103597-45-1
Physical Appearance:	Light yellow powder	Aqueous white dispersion (50 % active)
λ_{max} :	310 and 340 nm	305 and 360 nm
E (1 %,1 cm):	819 (in ethanol, 340 nm)	480 (in water, 360 nm)
λ_c (critical wavelength)	373 nm	388 nm
UVA/UVB ratio:	0.73	1
Recommended level (%)	10 % in Australia and EU 3 % in Japan	20 % (10 % active) in Australia, EU, and Japan

9.6 Inorganic Particulates

These ingredients are chemicals that reflect, scatter, and absorb the UV radiation. They include titanium dioxide and zinc oxide. They are available in micronized and nanosized forms that enhance sun protection without imparting the traditional opaqueness that was aesthetically unappealing in cosmetic formulations. These metal oxides are reactive and insoluble in cosmetic formulations without chemical treatment. This treatment includes coating of the metal core and dispersion and suspension of the particles with oils, solubilizers, and emollients [8, 9]. Many users falsely believe that “natural” claims are admissible if only inorganic particulates are used in sunscreen products. Unfortunately, most of these chemical treatments render the inorganic particulates synthetic and unnatural.

There has been a shift to zinc oxide from titanium dioxide recently, mostly due to its broad-spectrum and higher UVA protection. It is also popular since it has a lower refractive index of 1.9–2.0 compared to titanium dioxide’s 2.5–2.7, which leads to superior transparency. Recently, ZnO was also approved in Europe. In the USA, combinations of ZnO and TiO₂ with avobenzone are still not allowed.

Titanium is the ninth most common element on the Earth’s crust. In nature, it exists only in combinations with other elements such as iron and oxygen. Three titanium ores are of commercial importance: ilmenite, rutile, and anatase. Ilmenite is a composite of oxides of iron and titanium. Rutile and anatase are also never pure and contain various amounts of metal including those that may pose health hazards to humans. Therefore, commercial TiO₂ is always synthetic [8]. Rutile and anatase have different crystalline structure and different physical and chemical properties. Of the three forms of TiO₂, rutile is the most thermally stable.

Zinc ranks 24th in abundance on the Earth’s crust but never occurs free in nature. It is widespread around the world with important deposits located in North America and Australia. ZnO is produced by oxidizing vapors of Zn in burners. Pure ZnO is typically a white or yellow-white powder.

The optical behavior of ZnO and TiO₂ consists mainly of scattering or absorbing the light. The scattering from molecules and very tiny particles is predominantly Rayleigh scattering. When the particle size is at the same magnitude as the wavelength, Mie scattering predominates. The absorption, on the other hand, is a function of the number of atoms that interact with the light in its pathway. Light with a wavelength below 420 nm has enough energy to excite electrons in the valence band and can be absorbed by the inorganic particulate (see Fig. 9.3). Since the bandgap wavelength of ZnO is longer than that of TiO₂, ZnO absorbs a broader-spectrum range of UV light than TiO₂. TiO₂ is not considered an efficient UVA absorber; rather, it is an efficient UVB absorber. The attenuation of UVA by TiO₂, therefore, mainly takes place via scattering.

When using inorganic particulates, the following parameters need to be carefully evaluated:

- (i) The type of metal
- (ii) The particle size
- (iii) The coating

- (iv) The oil
- (v) The dispersant
- (vi) The loading
- (vii) The absorption coefficient

Each of the above parameters may influence the behavior, the concentration, the solubility, the potential interactions, and, most importantly, the regulatory status of the particulate and the final cosmetic formulation.

9.7 The Photostability of UVA Absorbers

As described earlier, the exposure of UV-absorbing molecules to solar radiation may lead to photochemical reactions that can compromise both the physical attributes of the UV filters (color, appearance, etc.) and their chemical properties leading to undesirable reactions and by-products [10].

Avobenzene is one of the most important UVA filters in commerce today. Unfortunately, this molecule is photounstable. In its enol form, it exhibits an excellent UVA absorption at 357 nm, but in its diketo form, its absorption is in the UVC region and thereby is ineffective as a UVA or UVB filter. See Fig. 9.7.

Other studies have also shown that avobenzene (enol form) reacts with other molecules including ethylhexyl methoxycinnamate (USAN name, octinoxate) to yield photo-adducts [11]. It has also been reported that upon exposure to UV radiation, avobenzene tends to fragment into reactive species as shown in Fig. 9.8.

Approaches to improve the photostability of the UVA filters included the use of glass beads and microspheres and the use of ROS quenchers, triplet-triplet (T-T) and singlet-singlet (S-S) quenchers [10]. These quenchers, also termed excited-state quenchers (ESQ), have recently appeared on the US market to circumvent the photo-instability issues of avobenzene. The mechanism of T-T quenching has been extensively reviewed in the literature [12]. These UV-absorbing quenching

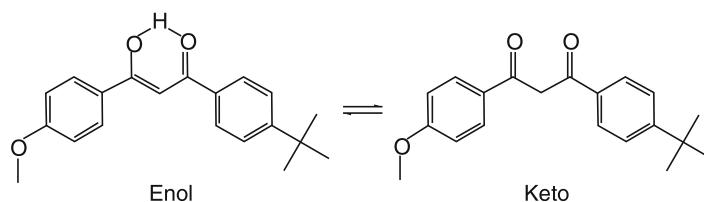


Fig 9.7 The keto-enol tautomerism of avobenzene

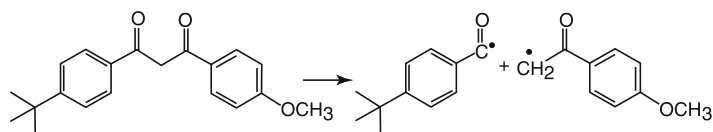


Fig. 9.8 The fragmentation of butyl methoxydibenzoylmethane (avobenzene)

molecules include octocrylene, 4 methyl benzylidene camphor, methoxycrylene, polyester 8, diethylhexyl naphthalate (DEHN), and diethylhexyl syringylidene malonate (DESM).

9.8 Future Direction

This illustration of the mechanism of UV action of the molecules we have today to combat the rising incidence of skin cancer reveals a deficiency in our arsenal for UV protection. The design of filters in the last century relied on small absorbing molecules that tend to penetrate the skin and potentially may interact with substrates in the body. In addition, the USA clearly has inadequate ingredients to protect consumers properly from the UVA radiation. The workhorse of the so-called UVA chemical absorbers, avobenzone, is photounstable and needs to be supported with quenchers and other ingredients to remain active as a UVA filter. In addition, protection from the infrared rays is not addressed. Whenever the subject of skin damage from the nonionizing infrared rays has come up in the past, it was summarily dismissed. IR rays were thought to be benign because of their relatively low energies and frequencies. They are the source of most of the “heat” produced from the sun. Recent evidence, however, has shown that the IR rays, particularly the IRA rays (750–1400 nm) penetrate much deeper into the skin, induce significant free radicals in the dermis and diminish the skin’s antioxidant capacity [13]. IRA radiation has been reported to upregulate an enzyme that destroys the collagen fibers (the matrix metalloproteinase-1 (MMP-1) expression) [14]. Others recently reported that the ultraviolet filters used in today’s sun care regimens prevent no more than 55 % of the damaging free radicals from the sun’s UV radiation but none of the IRA-induced free radicals [15]. It is estimated that 65 % of the energy generated by the IRA radiation reaches the skin’s dermal layers, the tissue responsible for the skin’s structure with its fibers, elastin, and collagen. IRA biological effects cause the loss of elasticity and reduced firmness thus leading to the formation of wrinkles and the aging of the skin [16–19].

9.9 Conclusions

Protection from the burning (erythema) UVB rays is a basic requirement. Protection from the UVA rays is paramount and so is protection from the damaging heat rays and the longer wavelength radiation of the infrared [20, 21]. In my opinion, our ingredients are woefully inadequate, especially the currently US-approved filters. We can no longer ignore the facts: sunscreen ingredients in cosmetics are not adequately preventing cancer incidence in the USA. We have lulled ourselves into a false sense of security. A cream or a lotion alone cannot, at this date, guard you entirely from the effects of the powerful sun. Heed all practical advice: wear

protective clothing, seek shade, avoid noon sun exposure, and do use adequate and properly applied sunscreens. Until advanced ingredients are developed and approved, use all available measures to mitigate the effects of the total spectrum of the solar radiation.

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