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Ultraviolet filters

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The chemistry, photostability and mechanism of action of ultraviolet filters are reviewed. The worldwide regulatory status of the 55 approved ultraviolet filters and their optical properties are documented. The photostability of butyl methoxydibenzoyl methane (avobenzone) is considered and methods to stabilize it in cosmetic formulations are presented.

Introduction

The ultraviolet filter is at the heart of the sunscreen industry. Currently approved UV filters are not sufficient to fully defend us against the sun's rays. Without our acquired knowledge and advancement in this field, we are entirely vulnerable to the harmful effects of the sun. Current debates over sunscreen ingredients have not alleviated pressing concerns; skin cancer incidences are still increasing dramatically worldwide.¹ Education combined with a responsible sun care industry is required to address this epidemic rise of sun-related cancers. With a view to facilitating greater understanding of the present situation, this chapter will address the chemistry, the properties, the photo-stabilization and the regulations of ultraviolet filters worldwide.

Classification of UV filters

Ultraviolet filters can be broadly classified into two types: UV absorbers and inorganic particulates.² If you examine Table 1 you will note:

1. 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.
2. The remaining UV absorbing molecules are classified as either UVB or UVA filters or both.

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There are about 55 ultraviolet filters that are approved for use in sunscreen products globally.³ Table 1 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 ϵ ($\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$), 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 10 UV filters that are approved uniformly worldwide. They are marked with an X in Table 1 and labeled 1–6 under the category Country/region.

The chemistry of ultraviolet filters

The relationship between the chemical structures of these approved UV filters and their UV absorbing characteristics is evident as illustrated below.

1. The *para*-amino benzoates (PABA)

This basic molecule (PABA) was one of the first UV filters that appeared on the US market. It has a λ_{\max} at about 290 nm.

This molecule has an electron-releasing group (NR_2) that is substituted *para* to an electron-accepting group (COOR), which allows for the efficient electron delocalization (see Fig. 1). The energy requirements for this delocalization correspond to an ultraviolet absorption around 290 nm.

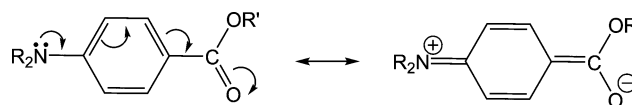


Fig. 1 The electron delocalization in a PABA molecule.

This PABA moiety is basic in many UV filters including the previously popular ethylhexyl dimethyl PABA (USAN name, Padimate-O) and the current UV filters ethyl hexyl triazone and diethyl hexyl butamido triazone (see Table 1).

2. Salicylates

Salicylates were one of the first UV filters used in sunscreens in the 1950s. They represent a very interesting group of *ortho*-disubstituted molecules with a spatial arrangement that permits internal hydrogen bonding within the molecule itself (its energy

Table 1 The UV properties of the 55 worldwide approved filters

INCI NAME	Country/ region ^a	UV region	$\lambda_{\max,1}/$ nm	E_1 (1%, 1 cm)	ϵ_1/dm^3 $\text{mol}^{-1} \text{cm}^{-1}$	$\lambda_{\max,2}/$ nm	E_2 (1%, 1 cm)	ϵ_2/dm^3 $\text{mol}^{-1} \text{cm}^{-1}$
Benzophenone	3	UVA/B	284		10 300	340		8950
Benzophenone-1	5, 6	UVA/B	291	630	12 265	328	420	10 265
Benzophenone-2	3, 5, 6	UVA/B	287	580	13 700	349	410	9400
Benzophenone-3 X	1–6	UVA/B	286	630	14 380	324	400	9180
Benzophenone-4	1–5	UVA/B	286	440	13 400	324	360	8400
Benzophenone-5	1, 3, 5, 6	UVA/B	286	430		323	345	
Benzophenone-6	5, 6	UVA/B	284	490	13 500	323	390	12 950
Benzophenone-8	2, 3, 4, 6	UVA/B	284	380	13 270	327	300	10 440
Benzophenone-9	5, 6	UVA/B	284	260		331	175	
3-Benzylidene camphor	1, 6	UVB	289	890	21 360			
Benzylidene camphor sulfonic acid	1, 3, 5, 6	UVB	294	860	27 600			
Beta-2-Glucopyranoxy propyl hydroxy benzophenone	5, 6	UVA/B						
Bis-ethylhexyloxyphenol methoxyphenyl triazine	1, 3, 6	UVA/B	310	745	46 800	343	820	51 900
Butyl methoxydibenzoylmethane X	1–6	UVA	357	1110	34 140			
Camphor benzalkonium methosulfate	1, 3, 6	UVB	284	590	24 500			
Cinoxate	2, 3, 4, 5, 6	UVB	308	825	20 650			
DEA methoxycinnamate	4, 6	UVB	290	880	24 930			
Diethylamino hydroxy benzoyl hexyl benzoate	1, 3, 5, 6	UVA	354	925	35 900			
Diethylhexyl butamido triazone	1, 6	UVB	311	1460	111 700			
Digalloyl trioleate	6	UVB						
Diisopropyl methyl cinnamate	5, 6	UVB						
Dimethoxyphenyl-[1-(3,4)]-4,4-dimethyl 1,3-pentanedione	5, 6	UVA						
Disodium phenyl dibenzylimidazole tetrasulfonate	1, 3, 6	UVA	335	770	51 940			
Drometrizole	5	UVA/B	300			340		
Drometrizole trisiloxane	1, 3, 5, 6	UVA/B	303	310	16 200	341	300	15 500
Ethyl dihydroxypropyl PABA	4, 6	UVB	312		27 000			
Ethylhexyl dimethoxy benzylidene dioxoimidazoline propionate	5, 6	UVB						
Ethylhexyl dimethyl PABA X	1–6	UVB	311	990	27 300			
Ethylhexyl methoxycinnamate X	1–6	UVB	311	850	23 300			
Ethylhexyl salicylate X	1–6	UVB	305	165	4130			
Ethylhexyl triazone	1, 3, 5, 6	UVB	314	1550	119 500			
Ferulic acid	5, 6	UVB						
Glyceryl ethylhexanoate dimethoxycinnamate	5, 6	UVB						
Glyceryl PABA	4, 5, 6	UVB	297	780	18 700			
Homosalate X	1–6	UVB	306	180	4300			
Isoamyl p-methoxycinnamate	1, 3, 5, 6	UVB	308	980	24 335			
Isopentyl trimethoxycinnamate trisiloxane	5, 6	UVB						
Isopropyl benzyl salicylate	3, 5	UVB						
Isopropyl methoxycinnamate	5, 6	UVB						
Lawsone + dihydroxyacetone	— ^b	UVB						
Menthyl anthranilate	2–6	UVA	336	190	5230			
4-Methylbenzylidene camphor	1, 3, 4, 6	UVB	300	930	23 655			
Methylene bis-benzotriazolyl tetramethylbutylphenol	1, 3, 5, 6	UVA/B	305	400	26 600	360	495	33 000
Octocrylene X	1–6	UVB	303	340	12 290			
PABA X	1–6	UVB	283	640	15 300			
PEG-25 PABA	1, 3, 5	UVB	309	180				
Pentyl dimethyl PABA	5	UVB	310	310				
Phenyl benzimidazole sulfonic acid X	1–6	UVB	302	920	26 060			
Polyacrylamido methylbenzylidene camphor	1, 6	UVB	297	610	19 700			
Polysilicone-15	1, 3, 5, 6	UVB	312	180	108 000			
Salicylic acid	3	UVB	300					
TEA salicylate	2, 3, 4, 6	UVB	298	120	3000			
Terephthalylidene dicamphor sulfonic acid	1, 3, 4, 5, 6	UVA	345	750	47 100			
Titanium dioxide X	1–6	UVA/B						
Zinc oxide	2–6	UVA/B						

Note: E (% 1 cm) is the “specific extinction”, and ϵ ($\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) is the molar absorption coefficient. ^a EU (1), USA (2), Australia/New Zealand (3), Canada (4), Japan (5), S. Africa (6). For official regulations consult specific country/region agencies. ^b Approved in South Korea.

requirements produce a UV absorbance around 300 nm). See Fig. 2.

Consider, for example, the *para*-hydroxy benzoate with a λ_{\max} at 260 nm where no internal hydrogen bonding is possible *versus* the salicylate (*ortho*) at 300 nm where the internal hydrogen bonding lowers the energy requirements significantly (and consequently raises the absorption maximum) as shown in Fig. 3.

This internal hydrogen bonding of *ortho*-disubstituted molecules lowers the energy requirements and increases the wavelength of the UV absorbance (the relationship between energy and wavelength is inversely proportional). This has been successfully used in the design of many new UV filters that have appeared on the market. Many molecules undergo hydrogen bonding between *ortho*-disubstituted or spatially close substituents to lower the energy

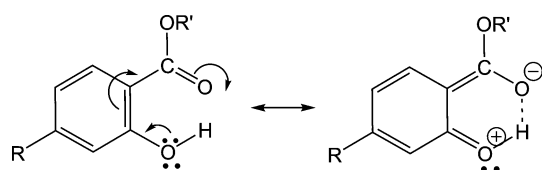


Fig. 2 The electron delocalization in a salicylate molecule.

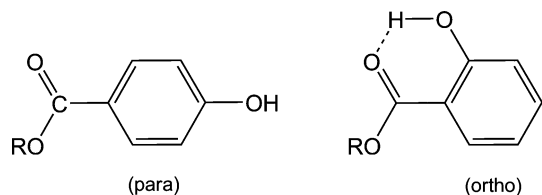


Fig. 3 *para* and *ortho*-disubstituted molecules.

requirements resulting in an increase in their absorption maximum wavelengths. This includes the salicylates, anthranilates, benzophenones, diethylamino hydroxybenzoyl hexyl benzoate, drometrisole, methylene-bis-benzotriazolyl tetra methyl butyl phenol and bis-ethyl hexyloxyphenol methoxyphenyl triazine. For a review of their chemical structures consult references 2–4.

3. Cinnamates

These molecules have similar structures where the aromatic molecule is disubstituted with both an electron releasing group (OCH_3) and an electron accepting group (the ester group that it is further conjugated with a double bond). This permits the extended delocalization of electrons enabling these molecules to absorb in the region of 310 nm as shown in Fig. 4.

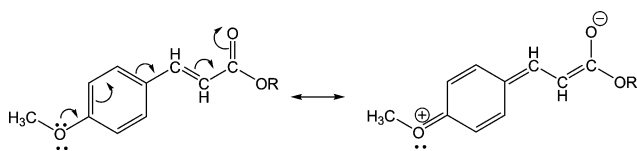


Fig. 4 The electron delocalization in a cinnamate molecule.

The cinnamates, however, are subject to a photo-isomerization between their *cis* (*Z*) and *trans* (*E*) isomers. The *E* isomer predominates and has a λ_{max} of 310 nm with a molar absorption coefficient of $19\,500\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$. Under the influence of sunlight the *E* and *Z* isomers equilibrate to a roughly equal ratio. The *Z* isomer has a λ_{max} of 312 nm with a substantially lower molar absorption coefficient of $10\,000\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$. This results in a decrease in the efficiency of the cinnamates as UV absorbers.⁵

4. Benzophenones

Resonance delocalization in the benzophenones is aided by the presence of an electron releasing group in either the *ortho* or *para* position or both, as shown in Fig. 5, which results in two λ_{max} at 286 nm (UVB) and 324 nm (UVA).

Note that the benzophenones are aromatic ketones unlike most other UV filters that possess an ester or amide linkage. These linkages assist in their metabolism and deactivation in biological tissue if absorbed. Recently, a number of negative reports on the benzophenones have surfaced, which may have an impact on

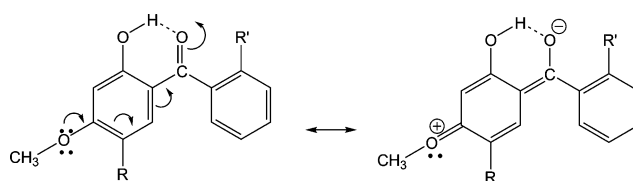


Fig. 5 The electron delocalization in a benzophenone molecule.

their use in commercial applications.⁶ Today, many organizations, including COLIPA in the EU, require that cosmetic companies list the presence of benzophenone-3 (USAN name, oxybenzone) prominently on their products. See Table 1 for a listing of all the benzophenone derivatives approved globally for use as UV filters.

5. Dibenzoyl methanes

These molecules have exceptionally high molar absorption coefficients and absorb mainly in the UVA region. The molecule undergoes a keto–enol tautomerism as shown in Fig. 6.

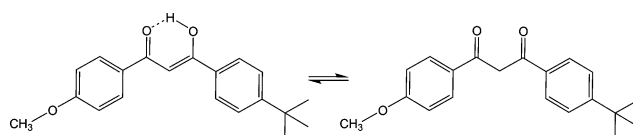


Fig. 6 The keto–enol tautomerism of butyl methoxy dibenzoylmethane.

Butyl methoxy dibenzoyl methane (USAN name, avobenzene) is currently one of the most popular UVA absorbing molecules in the industry with a λ_{max} of 357 nm. Unfortunately this molecule is photo-unstable and combinations with many other UV filters are restricted.⁷

6. Camphor derivatives

Several bicyclic molecules are approved for use worldwide. 4-methyl benzylidene camphor (USAN name, enzacamene) is currently being considered for use in the USA through the Time and Extent Application (TEA) process.⁸ They generally have high molar absorption coefficients and owe their photo-stability to the reversible photoisomerization shown in Fig. 7.

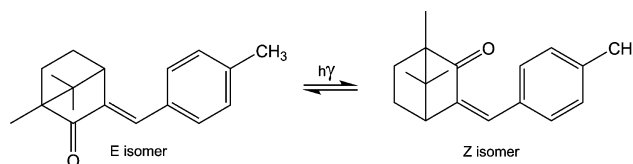


Fig. 7 Photoisomerization of camphor derivatives.

7. Dalton 500 molecules

A series of molecules have recently been designed in Europe with high molecular weights (over 500 daltons) to diminish their penetration into the skin.⁹ These molecules possess multiple chromophores that yield high extinction coefficients and also broad-spectrum protection.⁴ They are, unfortunately, not yet approved in the USA and they include:

- i. Ethylhexyl triazone (UVB, MW 823);

- ii. Benzylidene malonate polysiloxane (polysilicone-15) (UVB, MW ~6000);
- iii. Terephthalylidene dicamphor sulfonic acid (UVA, MW 607);
- iv. Disodium phenyl dibenzimidazole tetrasulfonate (UVA, MW 675);
- v. Drometrizole trisiloxane (UVA/UVB, MW 501);
- vi. Methylene bis-benzotriazolyltetramethylbutyl phenol (UVA/UVB, MW 659);
- vii. Bis-ethylhexyloxyphenol methoxyphenyl triazine (UVA/UVB, MW 629).

8. 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 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, dispersion and suspension of the particles with oils, solubilizers and emollients.¹⁰ 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 unnatural.

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, more importantly, the regulatory status of the particulate and the final cosmetic formulation.

The mechanism of UV absorption

The electromagnetic rays interact with UV filters by either absorption or scattering of their energy. The dispersion of inorganic particulates scatters and reflects the harmful rays. Inorganic particulates, however, 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 molecule orbital (LUMO) as shown in Fig. 8.

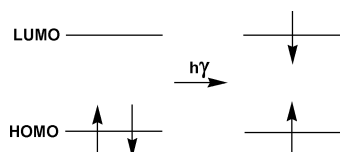


Fig. 8 Absorption of energy by an organic UV filter.

This singlet excited state can be deactivated by a simple vibrational relaxation back to the ground state or 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 which leads to a triplet excited state as shown in Fig. 9.¹¹

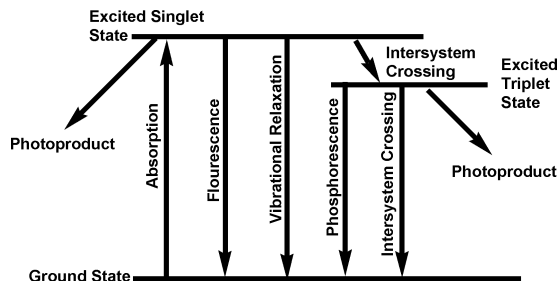


Fig. 9 Energy release pathways.

The energy in the triplet state may be dissipated in a number of ways, as shown in Fig. 9:

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 semi-conductors with high band-gap energy between the valence and conduction band (between 380 and 420 nm) as shown in Fig. 10.

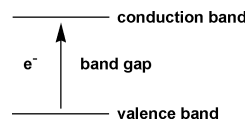


Fig. 10 The band gap energy between valence and conduction bands.

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

The photostability of UV 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.¹²

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 ineffective as a UVA or UVB filter. In addition, it has been reported to fragment when exposed to UV radiation into reactive species, as shown in Fig. 11.¹³

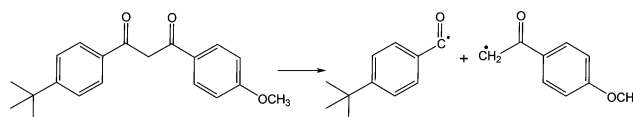


Fig. 11 The fragmentation of butyl methoxydibenzoyl methane (avobenzene).

Other studies have also shown that avobenzene (enol-form) reacts with other molecules including ethylhexyl methoxy cinnamate

(USAN name, octinoxate) to yield photo-adducts.¹⁴ Numerous attempts to photo-stabilize avobenzone have been introduced, including:

1. Glass beads

UV-Pearls, which are encapsulated organic sunscreens, have recently been introduced in the US market.¹⁵ They boost the SPF and prevent the many disadvantages of octinoxate. When octinoxate is trapped in microcapsules, there is a separation of the incompatible ingredients thereby improving the photo-stability of avobenzone. These “sunglasses” for the skin exert their UV absorbing property without the potential of skin penetration and thereby reduce the dermal uptake resulting in a low allergy potential.

2. Microspheres

Sun spheres that increase the effective SPF and UVA absorbance through the physical phenomenon of light refraction have recently appeared on the market.¹⁶ This styrene/acrylate copolymer of hollow spheres allows for efficient scattering of UV radiation. The incident rays penetrate the film at angles, thereby increasing the path length and, by Beer's law, the absorbance of the radiation, which increases the SPF value of the sunscreen film considerably.

3. ROS quenchers

Ingredients that possess antioxidant activity with the potential of quenching singlet oxygen and other reactive oxygen species (ROS) have appeared in many sunscreen formulations. A titanium dioxide lattice that is doped with manganese ions claims to have zero photo-reactivity, enhancing the performance of avobenzone through its free radical scavenging activities.¹⁷ Other actives are available that are efficient ROS quenchers.¹⁸

4. Triplet–triplet quenchers

Triplet–triplet quenchers (T–T), also termed excited-state quenchers (ESQ), have recently appeared on the market. Quenchers were first introduced in Europe to circumvent the photo-instability issues of avobenzone.¹⁹ Their inclusion in sun care cosmetic formulations has opened up a new avenue for the photo-stabilization of avobenzone.²⁰ The mechanism of T–T quenching has been extensively reviewed in the literature.¹² In the EU, cosmetic companies can choose from a series of effective UVA filters, whereas their counterparts in the United States have very few options. They rely exclusively on ESQ molecules to photo-stabilize avobenzone. These UV absorbing molecules include:

- i. Octocrylene;
- ii. 4-Methyl benzylidene camphor;
- iii. Bis-ethylhexyloxy phenol methoxyphenyl triazone;
- iv. Polysilicone-15.

Many other molecules that are not approved UV filters have recently been introduced to photo-stabilize avobenzone. All of those molecules that are labeled as excited-state quenchers (ESQ) or triplet–triplet (T–T) quenchers absorb ultraviolet radiation. Their use in commerce as inactive ingredients without approval as ultraviolet filters by the governing bodies of their respective countries or organizations is unclear. These include:

- i. Diethylhexyl naphthalate (DEHN) is reported to photostabilize avobenzone *via* a triplet–triplet quenching mechanism. It has a UVB λ_{max} at 290 nm with a molar absorption coefficient of $9000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. It also possesses two UVA λ_{max} at 332 nm and 350 nm with molar absorption coefficients of 1000 and $2000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, respectively.²¹ It fails to stabilize combination formulations of avobenzone and octinoxate.

- ii. Diethylhexyl syringylidene malonate (DESM) has a λ_{max} of 334 nm with a molar absorption coefficient of $18\,740 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. It has a hindered phenolic functionality and potent antioxidant activity. Their mechanism for photo-stabilization is attributed to two properties, namely triplet–triplet quenching and singlet oxygen quenching.²² Interestingly, it manages to protect combination formulations of avobenzone and octinoxate.

- iii. Polyester-8 is a low molecular weight (1400 daltons) copolymer 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 λ_{max} of 303 nm.²³

5. Singlet–singlet quenchers

Another mechanism attributed to the photo-stabilization of avobenzone is the singlet–singlet quenching mechanism. The example most often cited is benzophenone-3 (USAN name, oxybenzone). It stabilizes the singlet excited state of avobenzone. Recently, a new molecule, methoxycrylene, has been reported to stabilize avobenzone *via* a singlet–singlet stabilization mechanism. Such a mechanism, though unlikely due to the exceedingly short singlet lifetime of avobenzone, has been supported by fluorescence experiments.²⁴ Methoxycrylene is similar to octocrylene with an extra methoxyl substituent in the *para* position. This electron-releasing substituent increases the resonance delocalization, which leads to lower energy requirements and higher frequencies. This molecule, as a result, absorbs in the UVA region, (λ_{max} 340 nm and a molar absorption coefficient of $12\,000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$).

Conclusions

The creative integration of sound scientific research into effective sunscreen products is necessary. Clearly, the best answer for efficient UV protection is to create new and superior UV absorbing molecules that are photo-stable. Table 1 reveals that there are only 10 UV filters that are approved by all governing international bodies. This is woefully inadequate. This limits the introduction of products that are approved worldwide by multinational cosmetic companies. Other than TiO_2 and oxybenzone, avobenzone is the only other UVA-absorbing filter that is currently approved all over the world. It is, unfortunately, photo-labile and requires the use of quenchers or other ingredients and technologies to photo-stabilize it. Photo-unstable molecules, which require additional molecules to remain stable in cosmetic formulations, are not the answer. To quote Gonzenbach, “Protection from UV radiation, using a UV filter which is supposed to absorb the radiation by another UV filter, would be similar to one protecting an umbrella from getting wet by deploying a second umbrella over it. If an umbrella does not repel rain, it needs to be improved otherwise”.²⁵ New UVA

molecules that do not permeate the skin and are also photo-stable are sorely needed. Currently, a number of these molecules are available and in commerce in the EU. Many more UV filters that can be approved globally will assist in creating superior sunscreens that will combat the epidemic rise of skin cancers.

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