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Novel Emerging Sunscreen Technologies

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Because of increases in the number of skin cancers diagnosed annually, adverse effects of ultraviolet (UV) radiation are being recognized, and major public education programs have been undertaken concerning photoprotection, including the use of sunscreen. In daily life, UV exposure is unavoidable; therefore sunscreen should be used regularly. Development in sunscreen manufacturing has grown tremendously in the last decade. Sunscreen active ingredients now are incorporated into cosmetics products to minimize photoaging changes. With the advances in technologies, many new UV filters have been developed recently. These have improved efficacy and safety. This article reviews these new filters, along with regulatory issues in the United States.

The introduction of new sunscreen actives does not occur frequently. Compared with the United States, there are more new filters available in Europe. In fact, eight new organic UV filters have been approved in Europe within the past 14 years:

1. Diethylhexyl butamido triazone (DBT)
2. Benzylidene malonate polysiloxane (BMP)
3. Terephthalylidene dicamphor sulphonic acid (TDSA)
4. Disodium phenyl dibenzimidazole tetrasulfonate (DPDT)
5. Diethylamino hydroxybenzoyl hexyl benzoate (DHHB)
6. Drometrizole trisiloxane (DTS)
7. Methylene-bis-benzotriazolyl tetramethylbutylphenol (MBBT)
8. Bis-ethylhexyloxyphenol methoxyphenyl triazine (BEMT)

The absorption spectra of these filters are shown in Fig. 1. TDSA, MBBT, and BEMT are at the various stages of the approval process from the US Food and Drug Administration (FDA). [1]

Ultraviolet-B filters

Table 1 lists new active ingredients previously approved for sunscreens in Europe or other countries but not yet available in the United States. They are described in greater details in the following paragraphs.

Ethylhexyl triazone

Ethylhexyl triazone (EHT) is a UVB filter. In Europe, EHT has been available for some time; in fact, in 1996, it was listed as one of the top 10 most frequently used filters in Germany [2]. EHT obtained the status of "eligible to enter the sunscreen monograph" through the FDA Time and Extent Application (TEA) process in 2003 [3]. It is now eligible to continue in the process to be added to the over-the-counter (OTC) monograph of active ingredients approved for sunscreen in the United States, upon

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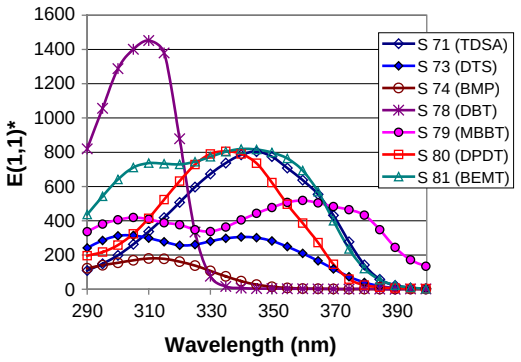

Fig. 1. Absorption spectrum of the new UV filters.

satisfactory presentation of data on safety and effectiveness to the FDA [3].

The structure of EHT is comprised of the chromophore of para-amino benzoic acid (PABA) linking it to a triazine ring. The peak absorption spectrum of EHT is 314 nm (Fig. 2). Even though solubility is limited, EHT can be incorporated in sunscreen formulations in substantial amounts [1].

Diethylhexyl butamido triazone

DBT is a very efficient UVB filter. It can be regarded as an improved version of EHT, which was considered to be the most efficient UVB filter before the introduction of DBT. Besides the slight improvement in efficacy, the solubility is increased compared with EHT [4]. The structure and absorption spectrum of DBT are shown in Fig. 3.

Benzylidene malonate polysiloxane

BMP is a new UVB filter that has a structure of benzylidene malonate chromophore attached to a specific point on a polysiloxane chain (Fig. 4) [5]. The molecular weight is about 6000 Da. Because of the large molecular weight, it does not penetrate the skin surface, thus providing improvement in safety. Because the fraction of UV-absorbing moieties in the overall mass of the molecule is small, however, the efficiency in term of $E1,1$ is quite low [1]. $E1,1$ is the extinction efficiency, and it refers to the theoretical extinction of a 1% solution of the substance measured at an optical path length of 1 cm. BMP can be combined with nanopigments such as micronized titanium dioxide (TiO_2) or zinc oxide (ZnO) for broad-spectrum UV protection. It also photostabilizes avobenzone; therefore, the combined product is photostable and provides broad UV protection.

Ultraviolet-A filters

Terephthalylidene dicamphor sulphonic acid

TDSA is a broad UV absorber, absorbing UV radiation between 290 and 390 nm with a peak at 345 nm (Fig. 5). It first was shown to be effective against the effect of chronic UVA irradiation in animal study in 1992 [6]. Unlike other UVA filters, such as avobenzone, which is a photo-unstable filter, and benzophenone, which has poor UVA absorption, TDSA provides broad UVA absorption with photostable properties [7].

Table 1
New ultraviolet absorbers that are not yet approved in the United States

Type	Sunscreen active COLIPA no./INCI name	Trade name (supplier)	Spectrum max (nm) (oil/water soluble)	Molecular mass (Da)	Approval (status)
UVB	S69 EHT	Uvinul T 150 (BASF)	314 (oil)	823	Europe, USA (TEA[a])
	S78 DBT	Uvasorb HEB (3V Sigma)	312 (oil)	766	Europe
	S74 BMP	Parsol SLX (Roche/DSM)	312 (oil)	6000	Europe
UVA	S71 TDSA	Mexoryl SX (L'Oréal)	345 (water)	607	Europe, Japan, USA (NDA)
	S80 DPDT	Neo Heliopan AP (Symrise)	334 (water)	675	Europe
	DHHB	Uvinul A Plus (BASF)	354 (oil)	398	Europe
UVB and UVA	S73 DTS	Mexoryl XL (L'Oréal)	303, 341 (oil)	501	Europe, Japan
	S79 MBBT	Tinosorb M (Ciba SC)	305, 360 (water dispersible)	659	Europe, Australia, USA (TEA[a])
	S81 BEMT	Tinosorb S (Ciba SC)	310, 343 (oil)	629	Europe, USA (TEA[a])

Abbreviations: COLIPA, European Cosmetic, Toiletry, and Perfumery Assocation; INCI, International Nomenclature Cosmetic Ingredient.

[a] With foreign marketing data.