J. Soc. Cosmet. Scientists Korea
Vol. 31, No. 3, September 2005, 237-244

새로운 UV 필터에 대한 고찰

강 철 상 · 울리 오스왈더† · 번드 허조그

(주)시바화학
(2005년 6월 30일 접수, 2005년 8월 29일 채택)

Overview of New UV-filters

Chul Sang Kang, Uli Osterwalder†, and Bernd Herzog

Ciba Specialty Chemicals, Inc. Klybeckstrasse 141, CH-4056 Basel, Switzerland
(Received June 30, 2005; Accepted August 29, 2005)

요 약: 오랫동안 사용되어진 sunscreen 제품들은 "화상없이 보기 좋게 태우기"라는 목적으로 발전을 거듭해 왔다. 최근 태양 자외선이 피부암을 유발시키는 주요 원인이며, 화상과 무관한 UVA에 의해서도 피부암이 유발된다는 보고와 함께 "보기좋게 태우기"에서 "태양광선으로부터 보호"라는 목적으로 제품의 진화를 계속해 오고 있다. 최근 이러한 동향과 함께 유럽에서 수년간 유기 UV 차단제가 개발되었으며, 본 보고에서 이들에 대한 발전과정을 논의하고자 한다. 이들 UV 차단제들은 UVB는 물론 UVA를 충분히 잘 흡수할 수 있으며, 어떠한 formulation에도 잘 포함될 수 있는 성질을 가지고 있다. 또한, 이들은 부작용 없는 안전한 물질들이다. 이들 차단제들은 290 nm에서 400 nm의 넓은 범위의 UV를 차단할 수 있어 다른 차단제들과 병용할 필요성을 감소시켜 준다.

Abstract: Sunscreens have been in use for about 70 years and "tanning without burning" was propagated as their major advantage. The objective changed from "getting a tanned skin" to "getting skin protection" since UV have been proposed to a major risk of skin cancer and the risk of developing skin cancer related also to non-burning UVA. The new expectation from consumers has triggered the development of new UV absorbers and led to the approval of 7 new, organic UV absorbers in Europe over the last few years. The significant progress due to these new UV absorbers will be discussed in this report. These UV absorbers provide an efficient absorption of UV radiation (UVB and/or UVA) and easily incorporate in any kind of formulation. These are also safe, i.e. devoid of adverse effects. These new filters give the formulators new possibilities to cover the whole UV range from 290 to 400 nm, and also to use less filter due to the boosting effect of the new UVA and broadband filters.

Keywords: *sunscreen, skin protection, organic UV absorber*

1. Introduction

Sunscreens have been in use for about 70 years. "Tanning without burning" was propagated as their major advantage. This objective has been changed only some 10 ~ 20 years ago, when three things became evident: 1) The risk of developing skin cancer relates to the accumulated dose of solar radiation during a lifetime. 2) During childhood and adolescence an individual experiences usually the highest exposure to solar radiation. 3) The risks of developing skin cancer relates also to the amount of non-burning UVA. First in Australia and in the last decade also in Europe and the USA the objective changed from "getting a tanned skin" to "getting skin protection". Sunscreens should now not only protect against sunburn, which is mainly caused by UVB radiation, but also against the damaging effects of the deeper penetrating UVA radiation. With the growing awareness, special sunscreens are being designed for this new demand, and for the kids and children segments.

The new expectation from consumers and the medical

† 주 저자 (e-mail: Uli.Osterwalder@cibasc.com)

Table 1. Frequent Claims Made on Sunscreens

- SPF (Sun Protection Factor)
- Anti UVA/UVB
- Suitable for sensitive skins,
- Photostable
- Not photoallergenic
- Wider spectrum protection
- Better protection against sun burn and long term skin damage
- More water resistant
- High sand resistance
- Sunblock
- All day
- Hypoallergenic
- Non stinging
- PABA-free

community have triggered the development of new UV absorbers and led to the approval of 7 new, organic UV absorbers in Europe over the last few years. The significant progress due to these new UV absorbers will be discussed in this talk.

The characteristics required for a sunscreen reflects well in the claims with which cosmetic manufactures propagate their products as summarized in Table 1.

2. The Main Subject

2.1. Requirements of UV Absorbers for Sun Protecting Products

The claims listed above relate directly or indirectly to the characteristics required of a new UV absorbers molecule:

1) Molecules have to provide an efficient absorption of UV radiation (UVB and/or UVA)

2) They have to easily incorporate in any kind of formulation

3) Molecules have to be safe, i.e. devoid of adverse effects

Indeed, many sunscreens and day creams fulfill such requirements. They have an SPF up to 60, and use filter systems with UVB and UVA protection, some in combination with microfine inorganic pigment for SPF boosting. They are very efficient and come in various types of formulations. Yet there are still a few points to be improved especially in older filter systems: namely the degree of UVA protection, the photostablility and the skin penetration. In turn improvements have been achieved either by modifying current filter systems or by designing new absorbing molecules from scratch.

2.2. Widely Used UV Absorbers

The two "workhorses" in UVB and UVA protection, ethylhexyl methoxycinnamate and butyl methoxydibenzoylmethane, dominate the ranking of market shares in Germany and Europe respectively (Table 2). Ironically it is exactly this combination that makes a filter system most photo-instable. The microfine inorganic pigments account for about 20% of the total value.

2.3. New Developments Around Conventional UV Absorbers

The photo stability problem of the widely used UVA filter butyl methoxydibenzoylmethane can be overcome by stabilizing it by other UV filters such as Octocrylene or 4-methylbenzylidene camphor, or non-UV-filters such as diethylhexyl 2,6 naphthalate (DEHN).

A method to boost the efficacy of current filter systems is the incorporation of non-absorbing particles that refract the UV radiation and thus lead to a longer pathway through the sunscreen film on the skin (e.g. Sun-Spheres®).

The microfine inorganic pigments TiO_2 and ZnO have been improved considerably to allow the easier incorporation into formulations and to become cosmetically better accepted, but some limitations still remain.

The efficacy and safety aspect of UV absorbers has also been addressed by reducing skin penetration via encapsulation UV absorbers (e.g. ethylhexyl methoxycinnamate in UV pearls®).

2.4. New UV Absorbers

In spite of all these activities around conventional UV absorbers, there is still a need to find and develop new UV absorbers. The requirements in terms of efficacy and safety are comparable with the development of a new drug, and the research and development takes several years until a substance can finally be approved in Europe. In other important sunscreen countries such as Australia, Japan and USA, UV absorbers are indeed regulated as drugs, and registration takes considerably longer.

There is a comprehensive patent literature describing

Table 2. Most Frequently Filters According to Top Ten List 1996 in Germany

Current UV absorbers (Germany, 1996)				Filter type		Market share (Europe 1998)
1)	Colipa #		INCI name	UVB	UVA	Value %
1	S 28	EHMC	Ethylhexyl methoxycinnamate	×		26
2	S 66	BMBM	Butyl methoxydibenzoylmethane		×	25
3	S 60	MBC	4-Methylbenzylidene camphor	×		7
4	S 75	TiO_2	Titanium dioxide	×		15
5	S 38	BP3	Benzophenone 3	×	(×)	15
6	S 27	IMC	Isoamyl p-methoxicinnamate	×		
7	S 45	PBSA	Phenylbenzimidazole sulphonic acid	×		
8	S 13	OS	Octyl salicylate	×		
9	S 69	OT	Octyl triazone	×		
10	S 76	ZnO	Zinc oxide	(×)	×	5

1) Ranking, Finkel P., Parfumerie und Kosmetik, 80(3), 10-16 (1999)

Table 3. New UV Absorbers in Europe

Order of COLIPA #				Type	
1)	INCI name	Abr	Trade Name	B	A
S 71	Terephthalidene dicamphor sulfonic acid	TDSA	MEXORYL® SX		×
S 73	Drometrizole trisiloxane	DTS	MEXORYL® XL	×	×
S 74	Benzylidene malonate polysiloxane	BMP	PARSOL® SLX	×	
S 78	Diethylhexylbutamido triazone	DBT	UVASORB® HEB	×	
S 79	Methylene-bis-benzotriazolyl tetramethylbutylphenol	MBBT	TINOSORB® M	×	×
S 80	Disodium phenyl dibenzimidazole tetrasulfonate	DPDT	NEOHELIOPAN® AP		×
S 81	Bis-ethylhexyloxyphenol methoxyphenyl triazine	BEMT	TINOSORB® S	×	×
2)	Diethylamino hydroxylbenzoyl hexyl benzoate	DHHB	UVINUL® A Plus		×
2, 3)	2,4-Bis-[4-[5-(1,1-dimethyl-propyl)benzoxazol-2-yl]phenylimino]-6-[(2-ethylexyl)imino]-1,3,5-triazine		UVASORB® K2A		×

1) COLIPA number, 2) EC-Registration in progress, 3) INCI name not issued yet

many new structures and substances that can in principle be used as sunscreen actives. Most substances that were once identified will however never make it to a commercial product. Table 3 shows the 7 organic UV absorbers that have recently been approved in Europe and 2 more that currently are in the registration process (opinion of SCCNFP issued).

2.5. Efficacy of the New UV Absorbers

The most important characteristic of a cosmetic UV absorber is its spectrum. A filter system of a modern sunscreen for adults or children should cover the whole UV spectrum from 290 to almost 400 nm. Five of the seven new filters offer the possibility to cover more of the UV-A range (Figure 1).

This spectral information allows the sunscreen formulator to make a first guess about the performance of a new filter system. The actual performance will then however also depend on the formulation of the sun protection product.

Filter S71 (TDSA) was the first photostable UVA filter. It is water-soluble, i.e. will be in the water phase of an emulsion system and can thus act synergistically together with filters in the oil-phase. S 71 is also used together with stabilized BMBM (OC, TDSA, BMBM) to give equal coverage of UVB and UVA.

Filter S73 (DTS) was the first photostable broadband filter. Siloxane groups were added to the Benzo-

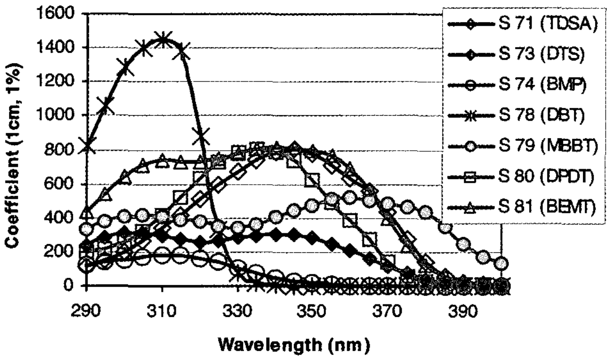

Figure 1. Absorption-spectra of the new UV absorbers (E1,1).

triazole chromophore for better water resistance. The two filters S71 and S73 are not freely available. They can only be found in L'OREAL products.

Filter S74 (BMP) is a polymer UVB filter, especially designed for day creams. Because of the additional weight of the polymer structure, efficacy suffers a little.

Filter S78 (DBT) is a very efficient UVB filter; an improvement on the formerly most efficient UVB filter EHT (S69). Besides the slightly improved efficacy it is supposed to have better solubility in most emollients used in sun protection products.

Filter S79 (MBBT) is a photostable UVA filter with strong absorption in UVB. Its unique feature is that it comes as microfine organic particles. Hence it is not only absorbing UV radiation, but also scattering and reflecting it. The microfine organic particles are dispersed in the water phase, leading to a synergistic effect together with oil-soluble filters.

Filter S80 (DPDT) is a new water-soluble UVA filter. Similarly to S71 and S79 it should show synergistic effects together with filters in the oil phase.

Filter S81 (BEMT) is a true broadband filter. It therefore allows the reduction of the number of filters in a given system. S81 is oil-soluble and photostable.

Filter S.. (DHHB) is a replacement of BMBM, i.e. a powerful oil soluble UVA filter. In contrast to BMBM it is photostable. This product has been launched but it is still in the registration process; the opinion of the SCCNFP, stating that it is safe to use up to an incorporation level of 10% has been published in October 2003.

Table 4. Efficacy of Available UVA and Broadband Filters in Terms of Fulfilling the Australian Standard on Its Own (Transmission < 10%, 320 ~ 360 nm, without Taking into Account Photostability)

Efficacy	Filter COLIPA #		Amount required
1	S 81	BEMT	1.9%
2	S 80	DPDT	2.1%
3	S 71	TDSA	2.5%
4	S 66	BMBM	2.9%
5	S 79	MBBT	3.3%
6	S 73	TDS	4.9%
7	S 76	ZnO	7 ~ 14%[1)]

1) Depends on size of microfine particles

2.6. Improved UVA Protection with New UVA/Broadband Absorbers

There are more possibilities than ever before to achieve good coverage of the UVA region. The question remains, what this exactly means in terms of actual protection of the sunscreen user. There are several *in vivo* and *in vitro* methods to assess UVA protection. Except for Japan (*in vivo* method based on persistent pigment darkening) and Australia (*in vitro* method based on transmission) there are no official standards yet. The chances for a harmonization as it has been achieved with the SPF seem to be rather remote at the moment.

The Australians took a very pragmatic approach with their UVA standard 2604, since their skin cancer problem is acute and no delay in protective measures is justified. Without waiting for all details of a scientific proof about how damaging UVA radiation may be, they defined that a sunscreen with a broad-spectrum claim must reduce the UVA part by at least 90%. So only 10% of the UVA radiation between 320 and 360 nm will reach the skin.

If we look at all the available UVA and Broadband absorbers we can determine the following ranking in terms of meeting the criterion of the Australian Standard. This ranking is just one way to show the efficacy of these filters, in reality they will of course be used in combination with UVB filters which may also contribute to fulfilling the Australian standard. Nonetheless this comparison gives the formulator a first idea about how much filter is required to meet

Table 5. Comparison of Various UVA-assessment Methods and Different Filter/Systems

Method for UVA Assessment	Combination	4% BMBM	4% ZnO	4% MBBT
SPF (*in vivo*, n=5)	alone	5 ± 2	4 ± 1	5 ± 2
PFA (Protection factor of UVA) (PPD)	alone	3.9 ± 0.4	2.8 ± 0.5	3.3 ± 0.5
Australian Std. fulfilled	alone	Yes	**No**	Yes
UVA/UVB-Ratio w/o Irr.	alone	1.45	0.79	1
UVA/UVB after 10 MED	alone	**0.22**	0.77	1.01
λ_C (nm) w/o Irradiation	alone	383	376	386
λ_C (nm) after 10 MED	alone	**366**	376	387
SPF (*in vivo*, n=5)	+ 5% EHMC [1)]	11 ± 4	13 ± 7	13 ± 4
PFA (Protection factor of UVA) (PPD)	+ 5% EHMC [1)]	5.0 ± 0.7	3.2 ± 0.3	5.1 ± 0.6
Australian Std. fulfilled	+ 5% EHMC [1)]	Yes	**No**	Yes
UVA/UVB-Ratio w/o Irr.	+ 5% EHMC [1)]	0.74	0.36	0.61
UVA/UVB after 10 MED	+ 5% EHMC [1)]	**0.54**	0.39	0.64
λ_C (nm) w/o Irradiation	+ 5% EHMC [1)]	381	366	382
λ_C (nm) after 10 MED	+ 5% EHMC [1)]	**374**	368	383

[1)] 5% ethylhexyl methoxycinnamate plus additional 5% octocrylene in the case of BMBM (for stabilization)

Formula	Composition	SPF(calc)	UVA-Transm.
F-1	7% EHMC, 3% BP-3	14	100%
F-3	5% EHMC, 3% BEMT	15.5	60%
F-5	1% EHT, 3% BEMT, 3% MBBT	14.1	25%

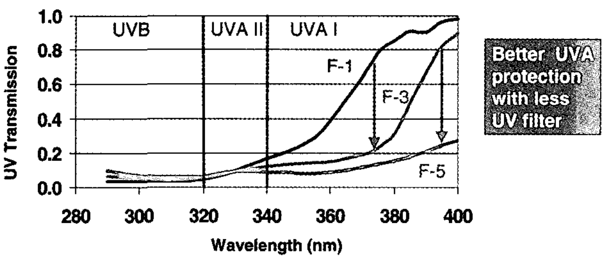

Figure 2. Different UVA transmission (320 ~ 400 nm) through sunscreen formulations with SPF around 15 (calculated with sunscreen simulator).

the Australian Standard.

Herzog *et al* compared various UVA assessment methods for two conventional (BMBM and ZnO) and a new UVA filter (MBBT). Table 5 gives an example with 4% use concentration of these filters with and without additional UVB filter. The actual performance of these filters in commercial applications would also depend on the actual formulation of the end product.

The pure UVA-absorbers can be compared on the basis of the persistent pigment darkening results of formulations containing in each case 4% of the respective filter. With BMBM a PFA (Protection factor of UVA) of 3.9, with MBBT of 3.3 and with ZnO of 2.8 is achieved suggesting a ranking in terms of the PFA (protection factor of UVA) of BMBM > MBBT > ZnO. With 4% of the respective UVA-absorber plus 5% EHMC, in the case of BMBM (stabilized with 5% OCR) a PFA (protection factor of UVA) of 4.0, with MBBT of 5.1, and with ZnO 3.2 is obtained, resulting in a ranking of MBBT > BMBM > ZnO. Formulations of BMBM photo stabilized by addition of OCR show higher PFA (protection factor of UVA) than the respective formulations without OCR. Thus, these results indirectly confirm the photo stabilizing effect of OCR towards BMBM.

Changes in UVA-protection occurring after irradiation due to photo instabilities can be observed *via* the UVA/UVB-ratio or the critical wavelength. There is a more sensitive change of the UVA/UVB-ratio compared to the critical wavelength. The UVA/UVB-ratio allows a more differentiated assessment of the relative UVA-attenuating properties.

There is a correlation between the Japanese UVA-PFs and Australian Standard results. Formulations, which meet the requirements of the Australian Standard are likely to show PFA (protection factor of UVA) larger than 3.9 ± 0.5 and vice versa.

2.7. Demonstration of Improvement on Sunscreen Simulator

To illustrate and quantify the improvement some

Table 6. Effect of UVB Absorber Together with 6% MBBT (Broadband Filter)

	UVB-Absorber (4%) (added to 6% of MBBT, S79)		SPF *in vitro* (Stand. Dev.)	UVA/UVB Ratio	Critical Wavelengt	Effect on SPF
	6% MBBT alone		9.3±1.4	0.98	385 nm	
1	+ 4% Ethylhexyl Methoxycinnamate	EHMC	23.5±7.8	0.54	382 nm	+++
2	+ 4% Octocrylene	OC	11.5±3.1	0.74	384 nm	+
3	+ 4% Isoamyl p-Methoxycinnamate	IAMC	26.1±4.7	0.41	379 nm	+++
4	+ 4% Ethylhexyl Triazone	OT	30.1±11.9	0.55	383 nm	+++
5	+ 4% 4-Methylbenzylidene Camphor	MBC	33.1±7.2	0.45	382 nm	+++
6	+ 4% Octyl Salicylate	OS	10.5±1.3	0.67	384 nm	+

Remarks:
EHMC: Strong synergistic effect of most frequently used UVB Absorber
OC: Small effect since OC is a very weak UVB absorber
IAMC: Analog OMC
OT: Excellent synergy of most efficient UVB absorber
MBC: Excellent synergy of very common UVB absorber
OS: Barely an effect
The absolute value of the UVA protection is constant (6 % MBBT), hence the UVA parameters become smaller with higher SPF values.
SPF boosting can also be achieved in combinations with TiO_2.

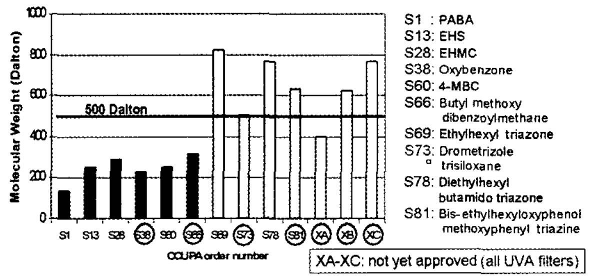

Figure 3. The 500 dalton rule-a common denominator in the development of UV absorbers (selection of oil-soluble UV filters of the last 50 years).

calculations were carried out with different formulations using the Ciba (Sunscreen Simulator [15,16] (www.ciba sc.com/personalcare). Figure 2 shows the composition of three formulations with similar SPF, i.e. similar UVB protection, but different degree of UVA protection. In spite of great differences, all these formulations could make "UVA" or "broadband" claims at the moment.

The amount of UVA radiation still reaching the skin through a layer of sunscreen is best seen from the transmission curve of that sunscreen. The transmission spectrum was calculated using a 2 step film model [15]. The area below the sunscreen with the highest UVA transmission (320 ~ 400 nm), F-1 with Benzophenone-3 has arbitrarily been set as 100%. Formula F-3 with BEMT reduces this UVA exposure through the sunscreen already to below 60%. With formula F-5, using BEMT and another new UVA filter such as Methylenebisbenzotriazolyl tetramethylbutylphenol (MBBT), the UVA exposure is reduced down to a quarter of the value achieved with the conventional formulation F-1.

2.8. Improved UVB Protection with New Broadband Absorbers

All new broadband absorbers (S73, S79, S81) will also contribute to sunburn protection, i.e. have some boosting effect on the SPF (*in vitro*). Combinations of 6% MBBT with 4% UVB filters of different performance are shown in Table 6. This kind of analysis allows the formulator to aim for the optimal composition of a sun protection product in terms of amount of UV absorber for a desired SPF and degree of UVA-protection. This again will finally also depend on the other parameters of the formulation.

2.9. Improvement in Formulation

To make good formulations is key for good sun product. The consumer will only apply a sunscreen regularly as they should, if they like it. The best UV filter system is not efficient and not sufficient if the sunscreen is not applied properly. The seven new UV absorbers widen the options of the formulator considerably to make such cosmetically appealing formulations. There are 4 new filters for the oil-phase of an emulsion (S73, S74, S78, S81) and 3 for the water phase (S71, S79, S80).

There are however other restrictions for the formulators. Two filters (S71, S73) are proprietary and can therefore not be used by everybody. In addition there are patent restrictions on the use of certain combinations of some filters, e.g. the use of S80 together with S81 is not possible due to mutual patent blockage of two sunscreen manufacturers.

2.10. Safety of the New UV Absorbers

All new UV absorbers underwent the scrutiny of the European approval process, hence they can all be considered safe. Vera Rogiers will cover this part in detail.

2.11. The 500 Dalton Rule

In the development of UV absorbers over the last decades, an interesting observation can be made. Besides the other developments such as encapsulation, polymers and microfine pigments, there was also a development in the class of the important oil-soluble UV filters towards higher molecular weight. The "500 Dalton rule" known from the development of transdermal drugs can be seen as a common denominator. The 500 Dalton rule for the skin penetration of chemical compounds and drugs states, that the development of new innovative compounds should be restricted to molecular weight of under 500 Dalton, when topical dermatological therapy or percutaneous systemic therapy or vaccination is the objective [17]. In turn we may postulate a 500 Dalton rule for the development of sunscreen actives, which says that the focus should be on the search for UV absorbers with a molecular weight above 500 Dalton, when sunscreen actives are the objective. As we see in Figure 3, the development is clearly heading in that direction. But it is also clear that the 500 Dalton rule is neither a necessary nor a sufficient condition for the safety of a new sunscreen active. In any case the safety has to be assessed separately as described in Vera Rogiers part.

3. Conclusion

Triggered by new requirements towards better UV protection, seven new UV absorbers have been developed and approved in Europe over the last few years. These new filters give the formulators new possibilities to cover the whole UV range from 290 to 400 nm, and also to use less filter due to the boosting effect of the new UVA and broadband filters.

References

1. World health organization, international agency for research on cancer, Sunscreens, IARC Handbooks of Cancer Prevention, 5, Lyon, France (2001).
2. R. M. MacKie, Primary and secondary prevention of malignant melanoma, KARGER, Basel, Switzerland (1996).
3. S. Tavenrath, So wundervoll sonnengebraunt: kleine Kulturgeschichte des Sonnenbadens, JONAS, Marburg, Germany (2000).
4. J. Ferguson, M. Brown, D. Alert, S. Bielfeldt, J. Brown, A. Chardon, C. Hourseau, C. Mazilier, J. Cuthbert, K. D'Arcy-Burt, J. Jolley, M. Murdoch, P. Finkel, P. Masson, F. Merot, A. McLennon, J. Poret, and S. Siladji, Collaborative development of a sun protection factor test method: a proposed European Standard, *Int. J. Cosmet. Sci.,* **18**, 203 (1996).
5. COLIPA sun protection factor test method, ref. 94/289, Oct. 1994, The european cosmetic toiletry and perfumery association - COLIPA, Rue du Congres, 5, B-1000 Bruxelles (1994).
6. Japan Cosmetic Industry Association (JCIA): Standard SPF test method (1991).
7. Diffey, B. L. A method for broad-spectrum classification of sunscreens, *Int. J. Cosmet. Sci.*, **16**, 47 (1994).
8. AS/NZS (2604) Australian/New Zealand Standard. AS/NZS (1998).
9. A. Chardon, D. Moyal, and C. Hourseau, Persistent pigment-darkening response as a method for evaluation of ultraviolet A protection assays. Sunscreens: development, evaluation, and regulatory aspects, ed. N. J. Lowe, N. A. Shaath, and M. A. Pathak, 559, 2nd Ed., Marcel Dekker, New York (1997).
10. U. Osterwalder, H. Luther, and B. Herzog, Sun protection beyond the sun protection factor - new efficient and photostable UVA filters, SOFW - Jour-

nal, **127**, 45 (2001).

11. H. Gers-Barlag, E. Klette, R. Bimczok, C. Springob, P. Finkel, T. Rudolph, H. U. Gonzenbach, P. h. Schneider, D. Kockott, U. Heinrich, H. Tronnier, R. Bernklau, W. Johncock, R. Langner, H. J. Driller, and H. Westenfelder, *In vitro* testing to assess the UVA protection performance of sun care products, Int. *J. Cosm. Sci.*, **23**, 3 (2001).
12. B. Diffey, When should sunscreen be reapplied, *J Am. Acad. Dermatol.*, **45**(6), 882 (2001).
13. B. Herzog, S. Mongiat, C. Deshayes, M. Neuhaus, K. Sommer, and A. Mantler, *In vivo* and *in vitro* assessment of UVA-protection by sunscreen formulations containing eitherbutyl methoxy dibenzoyl methane, methylene bis-benzotriazolyl tetramethylbutylphenol, or microfine ZnO, Oral presentation at 22nd IFSCC, Edinburgh, 23 September (2002).
14. G. Nohynek and H. Schaefer, How safe are organic filters in is there a sunscreen paradox, 24th BADECOS Symposium, 29 Brussels, Belgium (2001).
15. B. Herzog, Prediction of sun protection factors by calculation of transmissions with a calibrated step film model, *J. Cosmet. Sci.*, **53**(1), 11 (2002).
16. The Ciba sunscreen simulator, www.cibasc.com/personalcare (2005).
17. J. D. Bos, Meinardi MM: The 500 Dalton rule for the skin penetration of chemical compounds and drugs, *Exp. Dermatol.*, **9**(3) 165 (2000).