REVIEW ARTICLE
Global state of sunscreens

Uli Osterwalder[1], Myriam Sohn[2,3] & Bernd Herzog[3]

[1]BASF PCN GmbH, Monheim, Germany.
[2]University of Applied Sciences and Arts Northwestern Switzerland, Pharmaceutical Technology, Basel, Switzerland.
[3]BASF Grenzach GmbH, Grenzach-Whylen, Germany.

Key words:
compliance; formulation; sunscreen; SPF; UVA protection

Correspondence:
Mr Uli Osterwalder, MSc, Personal Care, BASF PCN GmbH, Rheinpromenade 1, 40789 Monheim am Rhein, Germany.
Tel: +49 174 3052300
Fax: +49 2173 4995500
e-mail: Uli.Osterwalder@basf.com

Accepted for publication:
13 January 2014

Conflicts of interest:
Authors are employees of BASF.

SUMMARY

The use of sunscreen is embedded in a hierarchy of sun protection strategies consisting primarily of sun avoidance by seeking shade and covering up with clothing. Sunscreens are, however, important means of protection; thus, understanding how they work and knowing their limitations are crucial. This review explains the role of ultraviolet (UV) filters, emollients, emulsifier systems and other components in a sunscreen, as well as trends in formulations in Europe, North America, Latin America, and Asia Pacific. Furthermore, it explains how sunscreen performance in terms of sun protection factor, UVA protection, and other metrics can be simulated. The role of sensory characteristics in assessing and improving compliance is also discussed. In the final chapter, Facts and Fiction, five of the most common myths about sun exposure and sun protection by sunscreen are debunked.

With the rise in the number of skin cancer cases diagnosed annually, negative effects of ultraviolet (UV) radiation are now well recognized and significant public education programs have been undertaken advocating photo protection, including the use of sunscreen. Just recently, the US Center For Disease Control (CDC) called for comments on 'Preventing Skin Cancer through Reduction of UV Exposure' (1). The CDC states that: 'A majority of skin cancers are caused by exposure to ultraviolet (UV) radiation from the sun or from indoor tanning devices, and are, therefore, preventable. Evidence clearly links exposure to UV radiation and a history of sunburn (indicating both intensity of UV exposure and skin sensitivity to radiation) to an increased risk of skin cancer'. The information obtained will be used for further response with regard to the public health.

This review focuses on sunscreens and explains the physics, chemistry of the UV filters, and also the trends in sunscreen formulations in Europe (EU), North America (NA), Latin America (LA), and Asia Pacific (AP). The use of sunscreen is embedded in a hierarchy of sun protection strategies consisting primarily of sun avoidance (shade) and covering up with clothing (2).

Sunscreens should protect against sunburn, skin photo, and skin cancer during the entire time of sun exposure. We assessed the status as well as open questions of current sunscreens, and discuss what still has to be improved. We identified four requirements for good UV protection (3).

First, sunscreen technology: the ideal protection profile is uniform protection across the entire UVB/UVA range (290–400 nm), similar to protection provided by sun avoidance and covering up by textiles. *In silico* experiments show

how well this can be achieved nowadays by combining UVB, broad-spectrum and UVA filters. With the help of particulate UV filters, sunscreens can protect at the border of UVA-I and up to the short visible light beyond 400 nm (3).

Second, the assessment of the sunscreen performance is crucial. The sun protection factor (SPF) is the well-established metric for sunscreen protection against erythema caused by solar-simulated sunlight, but is not sufficient if used alone to serve also as a metric for protection against photoaging and skin cancer. For these types of damage beyond sunburn, protection against UVA radiation has also to be assessed. It has now been recognized that there is no need for an extra *in vivo* UVA measurement besides the SPF, and the available *in vitro* UVA methods are well on their way to being harmonized.

Third, performance criteria and standards are also crucial for good UV protection. Assessment of UVA protection should be related to the SPF as the major claim on sunscreens, as recommended by the European commission, stating that UVA-PF/SPF ≥ 1/3. Other UVA categories such as the Boots 5-star rating with a UVA/UVB ratio > 0.9 go beyond the EU recommendation and are thus closer to uniform UVB/UVA protection, which may be regarded as an ideal sunscreen performance.

Fourth, compliance is the 'conditio sine qua non' of any good sun protection. Major deviations, besides not applying any sunscreen at all, are non-uniform application and inadequate amounts applied, which may vary between 0.5 and 2 mg/cm². Compliance is most positively influenced by the development of cosmetically elegant and pleasing formulations. As development objective, this should thus rank as high as achieving a certain protection profile or fitting into a certain standard SPF or UVA category.

Fulfilling the four requirements just discussed should lead to sunscreens becoming a more reliable means of sun protection, similar to sun avoidance and covering up by textiles. This review will touch on all four of these aspects after an introduction that explains how sunscreens work. In the final part, facts and fiction, the gathered knowledge is applied to debunk five of the most common myths about sunscreens.

The notion of the SPF – understanding sunscreens

The SPF is a simple concept based on human erythema, which is the immediate and apparent consequence of overexposure to UV radiation. The SPF stands for the attenuation of the sunburn reaction by the application of a certain sunscreen. The Australian Standard (4) gives a dynamic view that best explains how sunscreens work (Fig. 1). The accumulating sun-burning dose through the sunscreen, expressed as % of minimal erythema dose (MED, 1 MED = 100%) is plotted against the total sun exposure dose, also expressed in MED or in time (e.g. 1 MED = 10 min for skin phototype I). In Fig. 1 the dynamic behavior of SPF 1 (no sunscreen), SPF 15, and SPF 30 is shown. As an example, after 12 MED (about 2 h exposure in Australian Sun) through the SPF 15 sunscreen, 80% of the sunburn dose is reached on the skin of
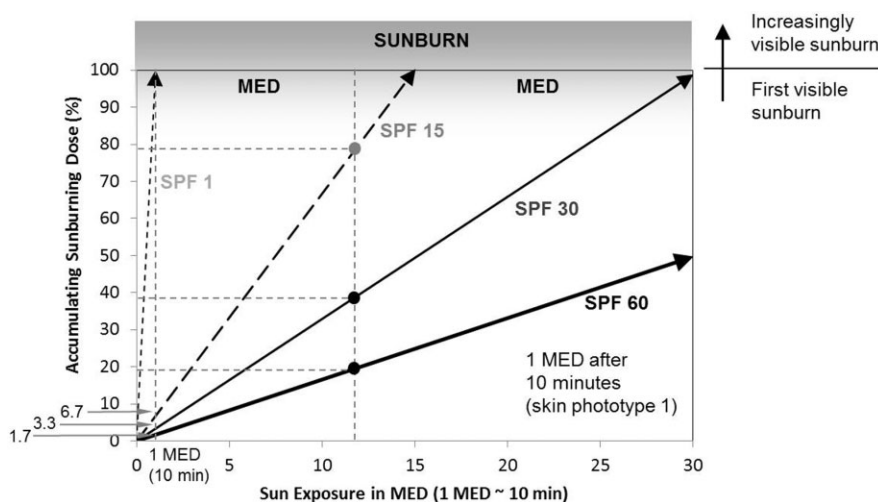

Fig. 1. How a sunscreen works. Dynamic view of a sunscreen – time to erythema (according to Australian Standard). Accumulating sunburn dose (%) as a function of duration of sun exposure, with: no protection (SPF 1), SPF 15, SPF 30, and SPF 60 applied. SPF, sun protection factor; 1 MED, one minimal erythemal dose.
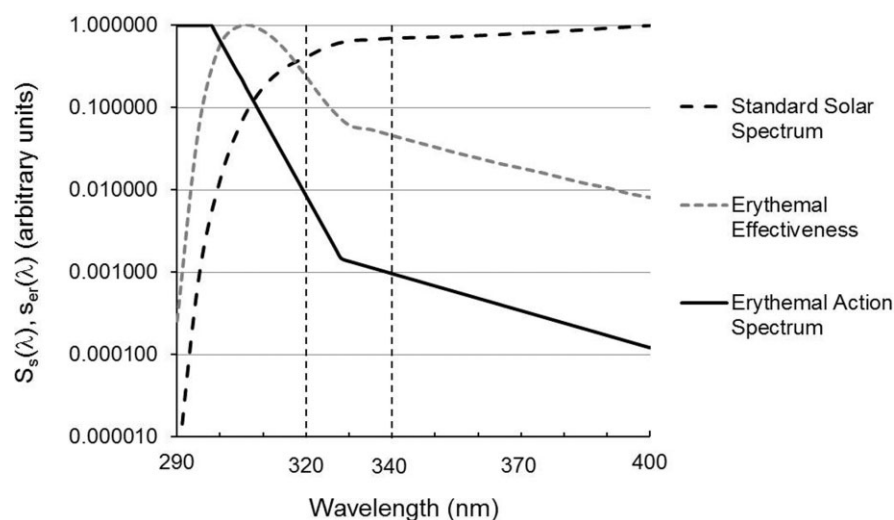
Fig. 2. Standard solar spectrum, erythema action spectrum, erythemal effectiveness spectrum (values normalized).

a skin phototype I individual, but only 40% is reached when an SPF 30 sunscreen is applied or 20% when an SPF 60 sunscreen is applied. All this is considered under the assumption that 2 mg/cm² had been applied and that the real sun corresponds to the simulated sun that has been used to establish the SPF. Although both of these assumptions are too optimistic, Fig. 1 is correct in principle; under more real-life conditions, a sunscreen with an SPF higher than 30 would have to be used to achieve the 40% sunburn dose after 2 h exposure. It is, however, safe to assume that using a sunscreen over a whole lifetime will reduce UVR exposure and thus also reduce damage and signs of aging. Diffey introduced the notion of the UV age to describe this (5).

The erythema is caused by UV radiation between 290 and 400 nm. The erythemal action spectrum is depicted in Fig. 2, showing that UVB rays are more efficient in causing erythema. On the other hand, the absolute amount of UVA-I (340–400 nm) radiation is much higher than UVA-II (320–340 nm) and UVB (290–320 nm). Therefore, UVA-I contributes substantially to erythema. Multiplication of the two curves leads to the erythemal effectiveness spectrum which spreads over the whole range of UV radiation. In fact, a hypothetical 'UVB-sunscreen' that blocks all UVB and transmits all UVA radiation would only have an SPF 11 (6). This also confirms the contribution of UVA-I to erythema.

TECHNOLOGY OF UV FILTERS AND REGULATORY

Properties of UV filters for sunscreens

The basic requirements for all UV filters that are used in sunscreens are: 1) efficacy, 2) safety, 3) registration, and 4) freedom-to-operate with respect to the status of intellectual property (7). The development of efficient molecules is the prerequisite before other aspects come into play. Efficacy means, first of all, that there is good absorbance in the spectral range of most interest for sunscreens, 290–400 nm. It also means that it is possible to incorporate the substance in sufficient amounts into cosmetic formulations. UV filters may be dissolved in the oil phase or the water phase of sunscreen formulations and thus the respective solubility must be high enough. Another possibility is to use dispersions of fine particles of the absorbing substances. In all countries, new UV filters require premarketing approval. With the help of an extensive toxicological testing program including *in vivo* tests on animals, new UV filters must be shown to be safe. So far, the European scientific opinion on safety, issued by the Scientific Committee for Consumer Safety, has been the benchmark for most countries in the world. This may change in the future due to the animal test ban for all cosmetic ingredients in Europe since March 2013.

Chemistry of organic UV absorbers

Prerequisites of organic molecules for the absorption of UV radiation, photophysical processes which may occur after the absorption of a UV photon, as well as possible photochemical reactions are discussed in detail in Herzog (8). At present, all organic UV absorbers used in sunscreens possess aromatic moieties. The substitutions at the aromatic ring are of great importance for the UV spectroscopic properties. An increase in the number of resonance structures stabilizes the excited state, thus leading to stronger absorption at longer wavelengths. For that reason, mono-substituted aromatics, both with resonance-driven electron releasing (+M) or electron

withdrawing (−M) substituents, show shifts toward longer wavelengths, also known as bathochromic shifts, and increased absorption intensities. Most efficient are di-substituted systems with a +M- and a −M-group in para-position, so-called push–pull systems. Figure 3 shows a comparison of a push–pull system, ethylhexyl dimethyl para-aminobenzoate (ED-PABA), and a UV absorber with similar groups but in ortho-position, menthyl anthranilate (MA). As expected, the absorption intensity of ED-PABA is significantly stronger than that of MA. The bathochromic shift observed with MA can be explained by the hydrogen bond that is formed between one of the hydrogen atoms of the amino-group and the oxygen of the ester bond. E11 is the specific extinction that would be shown by the extinction of a 1% (w/v) solution at an optical thickness of 1 cm. The important
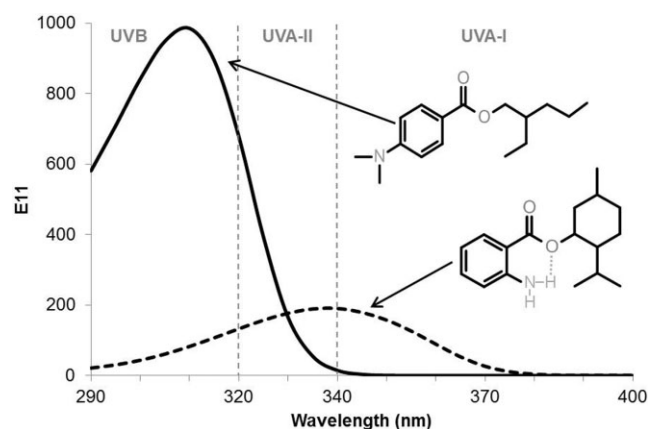
subject of photostability is covered in more depths elsewhere in this themed issue of *Photodermatology, Photoimmunology & Photomedicine*.

Inorganic particulate UV filters

Any inorganic material that absorbs in the UV range could potentially be used in sunscreens. Figure 4 shows the absorption curves of a few inorganic materials compared with barium oxide: talc (magnesium silicate), titanium dioxide (TiO_2), zinc oxide (ZnO), and various iron oxides (9). Barium sulfate and talcum powder are not UV absorbers; they simply scatter light and thus are poor sunscreen ingredients. TiO_2 and ZnO show good absorption in the UV range and none in the visible range, which qualifies them to be used in sunscreens (colorless). The iron oxides are colored materials absorbing in the visible and some UV wavelengths. Due to their color, the iron oxides are not suited for use in sunscreens.

TiO_2 and ZnO are the only inorganic materials which so far are allowed for the use as UV filters in sunscreens (for details see Table 1). In order to be efficacious and nonwhitening on the skin, the particles of these rather insoluble substances have to be very small, typically in the size range around 100 nm or below. Thus, the grades of these inorganic oxides employed in sunscreens attenuate UV mainly by absorption, superimposed by some scattering (10). Being small particulate crystals, these materials are semiconductors with high band gap energy between the valence and the conduction band. The band gap of the bulk crystals is in the range of an energy corresponding to wavelengths between 380 and 420 nm. In the case of TiO_2, it alters with the size of the primary particles, that is, the
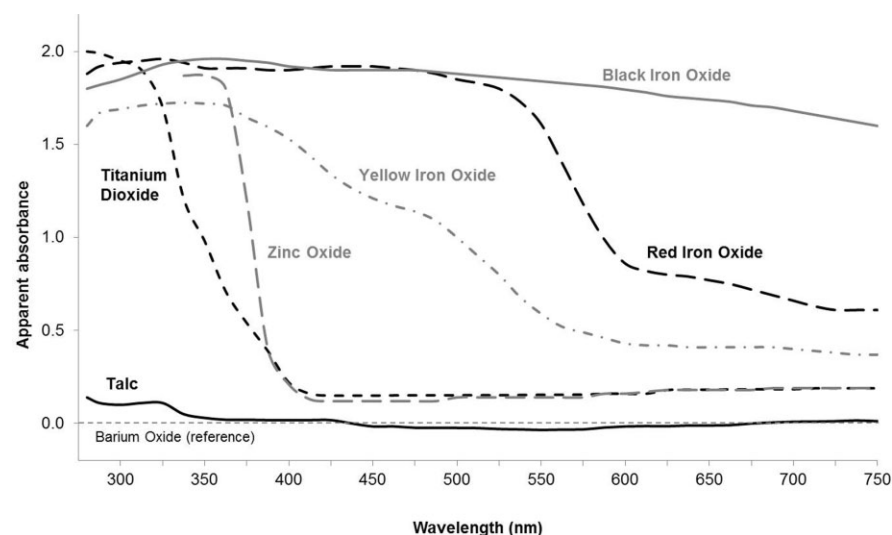
Fig. 3. UV spectra of ethylhexyldimethyl p-amino benzoate and menthyl anthranilate (E11 = specific extinction). UV, ultraviolet.

Fig. 4. Absorption of inorganic UV filters (reference barium oxide, dashed line).

Table 1. Common UV filters approved in Australia (AUS), Europe (EU), Japan (JP), and United States (USA)

	INCI (International Nomenclature of Cosmetic ingredients)	COLIPA (Cosmetics Europe)	USAN (United States Adopted Names)	Trademark	INCI abbreviation	Form	Concentration limits in sunscreen (%)			
							AUS	EU	JP	USA
Broad-Spectrum and UVAI (340–400 nm)	Bis-ethylhexyloxyphenol methoxyphenyl triazine	S 81	Bemotrizinol	Tinosorb® S	BEMT	p	10	10	3	*
	Butyl methoxydibenzoylmethane	S 66	Avobenzone	Parsol® 1789	BMBM	p	5	5	10	3
	Diethylamino hydroxybenzoyl hexyl benzoate	S 83	–	Uvinul® A Plus	DHHB	p	10	10	10	–
	Disodium phenyl dibenzimidazole tetrasulfonate	S 80	Bisdisulizole Disodium	Neo Heliopan® AP	DPDT	p	10	10	–	–
	Drometrizole trisiloxane	S 73	Drometrizole Trisiloxane	Mexoryl® XL	DTS	p	15	15	–	–
	Menthyl anthranilate	–	Meradimate	–	MA	p	5	–	–	5
	Methylene bis-benzotriazolyl tetramethylbutylphenol	S 79	Bisoctrizole	Tinosorb® M (active)	MBBT	d	10	10	10	*
	Terephthalylidene dicamphor sulfonic acid	S 71	Ecamsule	Mexoryl® SX	TDSA	p	10	10	10	*,†
UVB (290–320 nm) and UVAII (320–340 nm)	Zinc oxide	S 76	Zinc Oxide	Z-Cote® HP1	ZnO	p, d	no limit	‡	no limit	25
	4-Methylbenzylidene camphor	S 60	Enzacamene	Eusolex® 6300	MBC	p	4	4	–	*
	Benzophenone-3	S 38	Oxybenzone	–	BP3	p	10	10	5	6
	Benzophenone-4	S 40	Sulisobenzone	Uvinul® MS40	BP4	p	10	5	10	10
	Polysilicone-15	S 74	–	Parsol® SLX	PS15	l	10	10	10	–
	Diethylhexyl butamido triazone	S 78	Iscotrizinol	Uvasorb® HEB	DBT	p	–	10	–	*
	Ethylhexyl dimethyl PABA	S 08	Padimate O	Eusolex® 6007	EHDP	l	8	8§	10	8
	Ethylhexyl methoxycinnamate	S 28	Octinoxate	Uvinul® MC 80	EHMC	l	10	10	20	7.5
	Ethylhexyl salicylate	S 13	Octisalate	Neo Heliopan® OS	EHS	l	5	5	10	5
	Ethylhexyl triazone	S 69	Octyltriazone	Uvinul® T150	EHT	p	5	5	3	*
	Homomenthyl salicylate	S 12	Homosalate	Eusolex® HMS	HMS	l	15	10	10	15
	Isoamyl p-methoxycinnamate	S 27	Amiloxate	Neo Heliopan® E1000	IMC	l	10	10	–	*
	Octocrylene	S 32	Octocrylene	Uvinul® N539 T	OCR	l	10	10	10	10
	Phenylbenzimidazole sulfonic acid	S 45	Ensulizole	Eusolex® 232	PBSA	p	4	8	3	4
	Titanium dioxide	S 75	Titanium Dioxide	Eusolex® T2000	TiO$_2$	p, d	25	25	no limit	25
	Tris biphenyl triazine	S 84	–	Tinosorb® A2B	TBPT	d	¶	¶	¶	¶

*Time and Extent Application (TEA), Proposed Rule on FDA approval expected not before 2014.
†Approved in certain formulations up to 3% via New Drug Application (NDA) Route.
‡Not yet approved in EU, positive opinion by Scientific Committee on Consumer Safety (SCCS).
§Not being supported in the EU and may be delisted.
¶Not yet approved in EU or anywhere else (but positive Safety Opinion on 1,3,5-Triazine, 2,4,6-tris[1,1'-biphenyl]-4-yl-, SCCS Sept/Dec. 2011).
Cosmetics Europe (formerly COLIPA): http://www.cosmeticseurope.eu/, order number shows chronology of UV filter development.
Trademarks: Tinosorb®, trademark of BASF SE, Ludwigshafen Germany; Parsol®, trademark of DSM, Kaiseraugst, Switzerland; Uvasorb®, trademark of 3V Sigma, Bergamo, Italy; Uvinul®, trademark of BASF SE, Ludwigshafen Germany; Neo Heliopan®, trademark of Symrise AG, Holzminden Germany; Mexoryl®, trademark of L'Oréal, Paris France; Z-Cote®, trademark of BASF SE, Ludwigshafen Germany; Eusolex®, trademark of Merck, Darmstadt Germany.
p, powder; l, liquid; d, dispersion.

smaller the primary particles, the higher the band gap energy (10). UV radiation is absorbed by elevating an electron from the valence to the conduction band. Light at or below this wavelength will have enough energy to excite electrons from the valence band to the conduction band. Any photon with a wavelength longer than the band gap will not be absorbed by the sunscreen. The resulting electron hole can be refilled by electrons from the surrounding materials, thus leading to oxidation reactions, also known as photocatalytic effect. To prevent this effect, TiO_2 for sunscreen applications is coated with Al_2O_3 or SiO_2. Further, in most grades for sunscreens the rutile crystal modification is employed, which shows a lower tendency for photocatalysis than anatase type. The inorganic particles as such are water- dispersible, but may be rendered oil dispersible by adding organic coatings.

Fig. 5. MBBT in dioxane (dotted line), particulate MBBT in aqueous dispersion. MBBT, methylene bis-benzotriazolyl tetramethyl-butylphenol; UV, ultraviolet.

Organic particulate UV filters

Limited solubility of organic UV filters in the water phase or, predominantly, in the oil phase of sunscreen formulations may cause severe formulation difficulties (7). For this reason, the concept of particulate organic UV filters was developed, circumventing the problem of limited solubility. UV filters that are nearly insoluble in oil and in water can be prepared in the form of small particles in an aqueous phase, employing milling processes. The first example for this approach was realized with methylene bis-benzotriazolyl tetramethyl-butylphenol (MBBT) (11). The pure substance is a solid (T_m = 195°C), the particle size of the powder ranging between 40 and 150 µm. First, aqueous slurry containing 50% (w/w) of the active agent and 7.5% (w/w) of decyl glucoside as dispersing agent is prepared. After a wet-milling procedure, an average particle size of 0.16 µm is obtained. It was shown that the specific extinction of the particulate UV absorber increases with decreasing particle size (12). Thus, the small particle size is necessary to obtain an efficient product. The specific extinction comes close to the specific extinction of the UV absorber in solution.

The UV absorbance spectrum of particulate MBBT has a different shape than that of MBBT dissolved in dioxane (Fig. 5). The most distinctive features of the particle spectrum are the shift of the UVA maximum to 360 nm and an additional shoulder around 380 nm caused by intermolecular interactions of the π-electrons inside the particles. Due to the shoulder at 380 nm, this filter covers a very broad range of the UV radiation. Similar to small inorganic particle UV filters, the contribution to protection by scattering or reflectance is 5% or less (13).
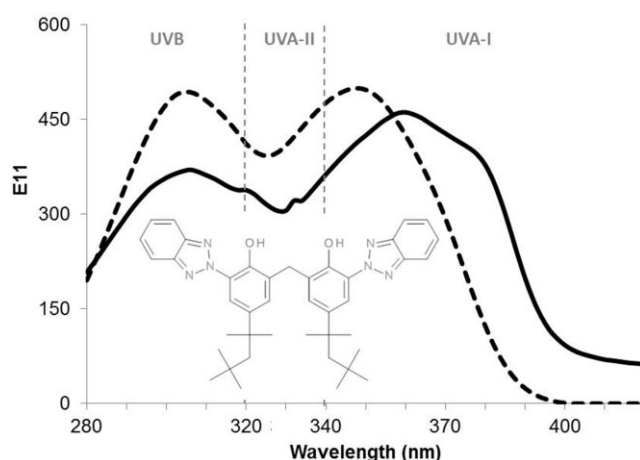
Safety and regulatory

The safety of UV filters for sunscreens has to be shown in an extensive program of toxicological studies, such as acute oral toxicity, chronic toxicity, dermal toxicity, embryo-fetal toxicity, photo-irritation, percutaneous absorption, carcinogenicity, photo-carcinogenicity, pharmacokinetics, and metabolism. UV filters for sunscreens are regulated globally as either, over-the-counter (OTC) drugs, quasi-drugs, or cosmetics (14). All countries have a positive list of UV filters, including maximum concentration allowed in sunscreens. In most countries, including Europe and Japan, UV absorbers are regulated as cosmetics; in the United States and Canada as OTC drugs; and in Australia as therapeutic drugs. The worldwide regulatory status of the UV filters is given in Table 1, containing all relevant UV filters. The number of available UV filters differs from region to region. The US sunscreen monograph lists the least number of UV filters. Currently, a total of eight UV filters that are approved in all other regions are awaiting approval in the United States via the so-called Time and Extent Application (TEA) (15). The following eight UV filters have passed the first stage of eligibility for the monograph by demonstrating a minimum of 5 years of marketing experience in at least five countries outside the United States, but it cannot be foreseen when they might be approved by the Food and Drug Administration (FDA) for use in US sunscreens (year of TEA submission/eligibility):

1) Amiloxate (2002)
2) Enzacamene (2002)
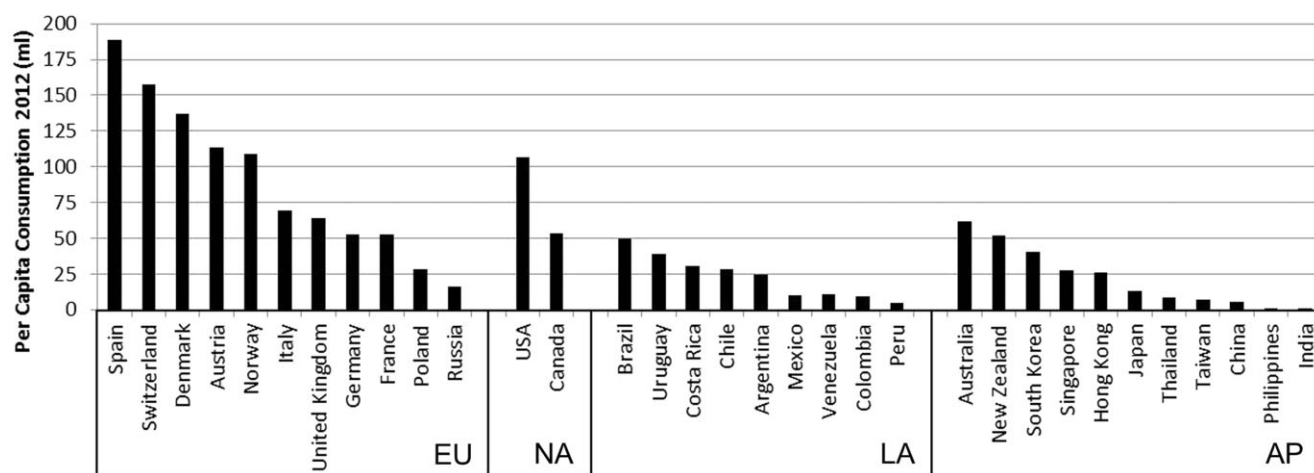3) Octyl Triazone (2002)
4) Bemotrizinol (2005)

Fig. 6. Per capita consumption of sunscreens in selected countries (2012). EU, Europe; NA, North America; LA, Latin America; AP, Asia Pacific.

5) Bisoctrizole (2005)
6) Iscotrizinol (2005)
7) Ecamsule (2007)
8) Drometrizole Trisiloxane (2009)

The PASS coalition (16) is monitoring the TEA status and is supporting legislative initiatives to help the FDA fix the problem.

FORMULATION AND COMPLIANCE

The suncare market constitutes approximately 3% of the overall personal care market in terms of retail value. From the three segments (sun protection, after sun, and self-tanning) composing the sun care market, the sun protection is by far the most important one, with almost €7.0 billion forecasted for 2014, according to EUROMONITOR (17). The market size is almost equally distributed over the four regions: EU (32%), AP (25%), LA (22%), and NA (22%). Worldwide growth has been an average of 7% per year over the last 5 years, but very unevenly distributed over the four regions: EU = 2.1%, AP = 7.2%, LA = 18.8%, and NA = 5.0%.

Worldwide, the average per capita consumption of sunscreen is about 20 ml per year (2012). As expected, there are big differences between the regions and indeed, from country to country due to geographic location, skin type, culture, attitude towards the sun, and economic situation. Figure 6 illustrates the per capita consumption of sunscreens for selected countries in each region in 2012. The average regional consumptions are EU = 52 ml, AP = 4 ml, LA = 29 ml, and NA = 101 ml. The countries with the highest per capita consumption in 2012 were per country/region: Spain (EU, 189 ml), United States (NA,

106 ml), Brazil (LA, 49 ml), and South Korea (AP, 40 ml). Based on these figures, it is easy to imagine that sun protection by sunscreen still has a high potential for development in all regions.

Market trends based on launched products 2012/2013

The high requirements in terms of performance such as high SPF value, UVA protection, water resistance, and photostability, in conjunction with high consumer expectations concerning sensory properties, require raw material suppliers and formulators to be innovative and creative in developing new raw materials and novel formulation types. Innovations in terms of sensory properties or application formats were introduced over last decade to attract consumers and improve compliance.

Sunscreen formats

Figure 7 illustrates the distribution of the sunscreen format types launched last year in the main regions, EU, NA, LA, and AP, as extracted from the MINTEL Global New Products Database (GNPD) (18). Among the high diversity of formats available on the market, the standard types, lotions, and creams/gel-creams still remain the preferred form with approximately 60% of the most recently introduced market products irrespective of the region. However, notable differences appeared around the globe in preferences for different types of products.

In Europe, emulsion sprays remain very popular; although, other forms such as sticks, oils, mousses, and
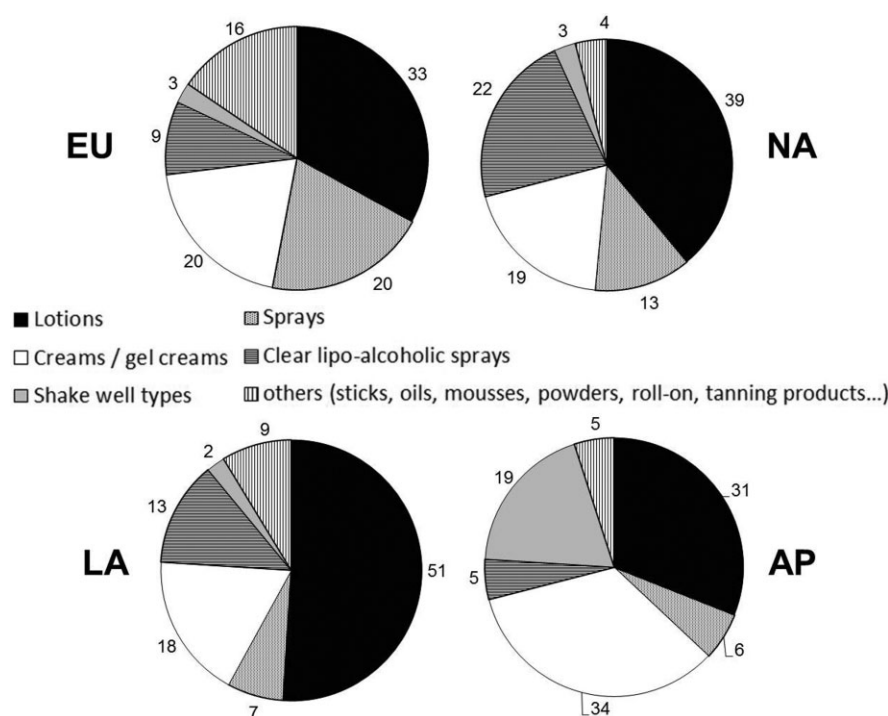
Fig. 7. Distribution of the sunscreen format types launched last year in the main regions: Europe (EU), North America (NA), Latin America (LA), and Asia Pacific (AP).

powders represent almost 16% of the launched products in contrast to the three other regions where these formats remain marginal.

'Shake well' formats are especially popular in AP, accounting for 22% of the products launched there compared with only 2% in the three other regions. These generally consist in a very fluid water-in-silicone formulation, which provides an exceptional light and silky skin feel. They contain a high amount of volatile silicones that enable a high spreading during application, a fast absorption of the product after application on skin, and a final silky skin feel. The bottle generally contains a small ball to shake the formulation before use, to ensure its macroscopic homogeneity. Several years ago, such products also entered the European market, where they were associated with pocket sun protection but now only represent about 2.5% of recently launched products. Light gel-cream formulations with aqua-like touch have become popular of late in AP and have won market share from water silicone systems.

In NA, sprays including emulsion sprays and even more lipo-alcoholic clear continuous sprays are very popular (19), and have an important market share in NA, with almost 25% of the launched products. This percentage is much lower in LA, EU, and AP, with 13%, 9%, and 5%, respectively. The packaging for this type of product is mainly based on aerosol cans. This form of application is considered very convenient and easy to use. The pres-

ence of ethanol in generally high amounts provides a nongreasy skin feeling with fast skin absorption of the product. This kind of sunscreen is also popular in Europe; there is, however, a tendency to reduce the amount of ethanol, presumably to decrease potential skin irritation. Moreover, in Europe this type of formulation is mainly packaged in normal pump spray bottles, with aerosol cans being less trendy and requiring a special labeling for flammability. Some products in the United States have indeed been withdrawn from the market due to that flammability hazard (20) when propellants are used.

Day care with UV protection

The products that we considered as skin care with UV protection were those launched products that explicitly promoted daily use. Beyond the products assigned as mere sunscreens, we observe a growing trend in the introduction of skin care products with UV protection. Face care and foundation products, especially BB creams (short for blemish balm), contribute to about 20% of the products with sun protection introduced last year in NA and EU, and about 10% in LA and AP. BB creams have achieved great success, first at their place of origin in Germany, then in Korea, and now around the globe. They aim to cover skin imperfections, keeping a natural skin look, and embrace combinations of claims such as moisturizing,
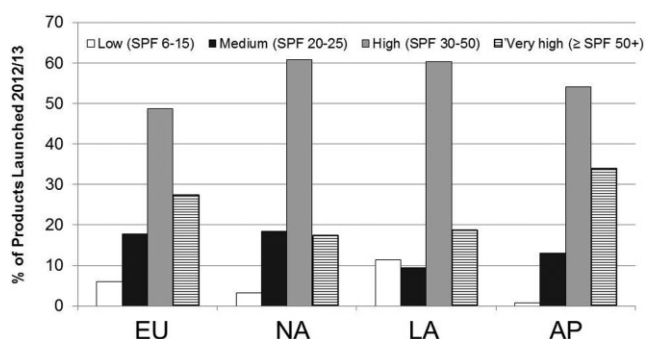
Fig. 8. Worldwide distribution of protection categories of sunscreen products launched between August 2012 and August 2013. EU, Europe; NA, North America; LA, Latin America; AP, Asia Pacific.

anti-aging, skin lightening, and UV protection. BB creams are characterized by their multifunctionality (21). From BB creams, now CC creams (short for color correction) have been emerging; these products exhibit the benefits of BB creams and are like a skin care product with natural, light coverage benefits.

Daily care with a UV filtering system should not exhibit high SPF values but rather balanced protection over the complete UV range; UVA radiation is likely to play an important role for chronic photodamages such as visible signs of premature skin aging (22, 23), photoimmuno-suppression (24), and contribution to skin cancer by generation of radical oxygen species (25). A daily use of skin care with sun protection has been shown to prevent acute UV-induced histologic damage in human skin compared with the intermittent use of sunscreen with equal or even higher SPF (26).

SPF claims

Sunscreens with SPF values of the *high protection* category (SPF 30–50) are the most launched products worldwide with 50–60% depending on the region (Fig. 8). There is a noteworthy change toward the development of sunscreens with higher and higher SPF values, which leads away from products with SPF values of the low protection category. There is a distinct difference regarding the percentage of launched products of the low protection category between Asia and LA. In Asia, where white skin is desirable by avoiding sun exposure and wearing high SPF sunscreens, products with low SPFs are almost nonexistent compared with LA, where tanning is still fashionable, which might explain the highest launch of products with lower SPFs. Interestingly, SPFs achieving values of 70 to 100 are indeed found in LA like in Asia (classified under SPF 50+ in

Fig. 8). However, there is a global trend toward capping the maximum claimed SPF value at 50+, already in application in Europe, Japan, and Australia. In NA, the current FDA proposed monograph also suggests capping the highest claimed SPF value at 50+. It makes sense to stop the race to higher and higher SPFs in view of the difficulties in measuring high SPF values accurately and reproducibly, as well as the difficulties concerning reliability and compliance. Efficacy and performance testing (e.g. SPF) is covered in more depths elsewhere in this themed issue of *Photodermatology, Photoimmunology & Photomedicine*.

Basics of a sunscreen composition

The three core components categories required in sunscreens are UV filters, emollients, and emulsifiers; secondary components are photostabilizers, film formers, boosters, and sensory enhancers, as illustrated in Fig. 9.

UV filters

The core active ingredients required to achieve UV protection are inevitably UV filters. A judicious combination of the UV filters enables the achievement of a high UV protection performance while maintaining pleasant formulation aesthetics. Targeted light skin feeling can be achieved by choosing the right filter system, as certain UV filters may impart an unwanted greasy and heavy skin feel. In addition, the tendency toward the development of sunscreens with high SPFs leads to an increased concentration of UV filters, mainly loaded in the oil phase, in association with the required emollients. It becomes a challenge to stabilize the formulations that have such a high oil phase content while simultaneously maintaining the pleasant aesthetics of the product. To overcome this issue, some filters are available for the water phase such as the soluble UVB filter PBSA, the dispersible UVB filter TBPT, and the broad-spectrum filter, as well as the alternative to the normally oil-soluble broad-spectrum filter BEMT, embedded in a water-dispersible PMMA matrix. The incorporation of these UV filters prevents overloading of the oil phase and consequently offers more flexibility to the formulator regarding sensorial adjustment. Additionally, the presence of UV filters in the two phases of an emulsion leads to an improved efficacy related to the more homogeneous film left on the skin after application and water evaporation (27, 28).

Emollients

Besides UV filters, emollients are key components in sunscreens. They play a triple role, which includes solubilizing,
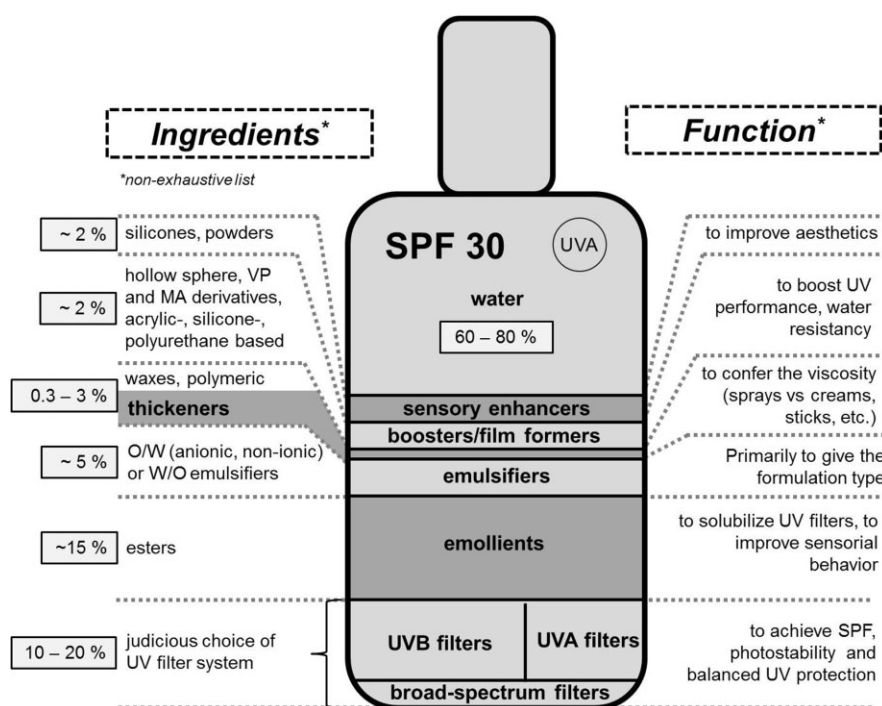
Fig. 9. The ingredients of a typical sunscreen and its functions. SPF, sun protection factor; O/W, oil-in-water; W/O, water-in-oil; UV, ultraviolet.

photostabilizing, and sensorial enhancing properties. Firstly, emollients enable solubilization of crystalline UV filters, a prerequisite for their functionality as UV absorbers, and homogeneous distribution of the UV filters in the formulation itself. Examples of effective solubilizers of UV filters are the well-used benzoate esters (29) or phenethyl benzoate (30).

Some emollients have also be shown to help in the photostabilization of photounstable UV filters, especially avobenzone (BMBM), which goes through a molecular breakdown process when subjected to UV irradiation, leading to nonabsorbing by-products (31). Some emollients show quenching efficacy with regard to the excited state of BMBM to avoid photodegradation of the molecule. Examples of such compounds include ethylhexyl methoxycrylene (32, 33), diethyhexyl 2,6-naphthalate (31), butyloctyl salicylate, tridecyl salicylate, polyester-8, diethylhexyl syringylidene malonate, benzotriazolyl dodecyl p-cresol, etc.

Nevertheless, these photostabilizing emollients generally also have an inherent UV absorption as reported elsewhere (34). The UV absorbance of these compounds can even achieve a substantial UV absorbance of a registered efficient broad spectrum filter like BEMT. These compounds are not listed on the UV filter positive list of the cosmetics regulation (35). This raises the subject of using components referred to as nonregistered UV filters (36, 37).

Furthermore, depending on their polarity, emollients have been reported modifying the wavelength of maximum absorbance and extinction of UV filters (38). However, the reported evaluations compared emollients with extreme polarity differences from ethanol and water to esters and hydrocarbons, all of which are not the most relevant UV filter solubilizers used in sunscreens.

Finally, emollients also strongly impact the skin feeling in terms of ease of spreading, greasiness, stickiness, etc. To that end, emollients such as dibutyl adipate, dicaprylyl carbonate, coco caprylate, propylheptyl caprylate, are particularly suitable for sun care formulations, because they show a good solubilizing power of crystalline UV filters and at the same time provide a light nongreasy skin feel (39).

Emulsifier system

The emulsifier system defines the emulsion type, oil-in-water (O/W), or water-in-oil (W/O) system. Generally, O/W systems are preferred for their easier spreading and lighter skin feel. The external water phase that mostly evaporates during application may also provide a fresh and pleasing sensation. Anionic emulsifiers, such as potassium cetyl phosphate, sodium cetearyl sulfate, C20–22 alkyl phosphate, are often used in sunscreens at low concentrations, and allow the incorporation and stabilization of inorganic UV filters. Furthermore, a combination of anionic and nonionic emulsifiers, including PEG-100 stearate, ceteareth types, and glyceryl stearate, allows the stabilization of high oil phase contents that are frequently required for the achievement of high SPF values. Some

glucoside-, lecithin-, phosphate-based emulsifiers combined with fatty alcohol enable the building of lamellar liquid-crystalline structures that positively impact formulation stability, skin hydration, and skin compatibility. The water resistance of O/W systems is generally lower as hydrophilic emulsifiers re-emulsify and promote a wash-off of sunscreen film on skin with water contact. Conversely, W/O systems are recognized for their contribution to improved water resistance properties as they typically do not contain any hydrophilic emulsifiers and are thus often used for sunscreens intended for children. Sunscreens for children often contain lipophilic-coated inorganic UV filters that are also easier to be dispersed and stabilized in higher amounts when formulated in W/O systems. W/O emulsifiers often used in sun care are, among others, PEG-30 dipolyhydroxystearate, polyglycreyl-2 dipolyhydroxystearate, and polyglyceryl-3 diisostearate.

Rheology modifiers

The final product properties for viscosity and spreadability are strongly influenced by rheology modifieres. In W/O systems, thickeners that are introduced in the external oil phase include fumed silica, organophilic clays, and most frequently waxes such as fatty alcohols, fatty acids, glycerides, and ester waxes. Waxes are not shear thinning compared with fumed silica. O/W systems might contain starch-, cellulose-, hydrophilic clay-based viscosity enhancers. However, generally the thickening system contains synthetic polymeric compounds based on acrylates that are dispersed and neutralized in the external water phase. Furthermore, hydrophobically modified polymers of acrylic acid, sulfonic acid, or acrylamide, generally preneutralized, show additional benefits such as emulsifying properties or water resistance improving properties. Synthetic polymers show a shear-thinning behavior; the thickened water phase generally breaks on skin during cream application that leads to an ease of spreading of the product. Care must be taken in the choice of the synthetic polymer thickener and of the inorganic UV filter grade, if both are present in a formulation, because synthetic polymers generally show poor compatibility with inorganic UV filters. Additionally, the introduction of natural gums, such as xanthan gum, mostly has a stabilizing rather than thickening effect.

Boosting ingredients

Additional help increasing the performance of a sunscreen is provided either by boosting the efficacy of the UV absorber system or by improving the film-forming property on skin. Hollow particles consisting of styrene/acrylates copolymer act by increasing the optical pathlength of radiation due to their scattering properties, thereby augmenting the probability of UV light meeting a UV absorber molecule before reaching the skin surface (40). The same principle is valid for particulate filters such as MBBT and TBPT that on top of their absorbing efficacy also scatter UV light.

Film formers, in contrast, boost UV performance by improving sunscreen film-forming properties during application, which thus results in a more uniform distribution of the UV actives on skin or by increasing water resistance properties. Various classes of film formers include hydrophobic or water dispersible ingredients. A nonexhaustive list of film formers promoted for sun care application are vinylpyrrolidone derivatives such as VP/hexadecane copolymer, VP/eicosene copolymer, tricontanyl PVP, and 'aqua (and) hydrolyzed wheat protein/PVP crosspolymer'. Acrylic polymer-based film formers may be acrylates/octylacrylamide copolymer (41), 'polyacrylate 15 (and) polyacrylate 17' (42), C8-22 alkyl acrylate/methacrylic acid crosspolymer. Other water-dispersible polymers include polyester-5 or polyurethane-based ingredients. Film formers based on maleic derivatives may be C30-38 olefin/Isopropyl maleate/MA copolymer (43), octadecene/MA copoylmer (and) methyl acetyl ricinoleate (and) di-methylheptyl adipate. Silicone water resistance agents may include alkylmethylsiloxane, silicone elastomers (44), and dimethicone polyacrylate.

Sensory enhancers

Finally, sensory enhancers may be added to create an aesthetically appealing formulation. Sensory enhancers mainly are powders or silicones fluids/silicone powders to improve spreading, reduce tack and greasiness. Depending on their particle size and particle shape, powders might adsorb oil, ease spreadability, provide matte and powdered finish, reduce tackiness, or impart velvety touch. Commonly used powders are nylon-based compounds (45), corn starch derivatives, polymethylsilsesquioxanes, polymethylmethacrylate silica, HDI/trimethylol hexyllactone crosspolymer (and) silica, boron nitride (46).

Regarding silicone compounds, different classes might be used to modify skin feeling. Volatile cyclic or short linear chain silicones (eyclopentasiloxane,ethyltrisiloxane, etc.) are able to enhance spreadability of the formulation (47). Silicone gums provide velvety feel, and silicone elastomer dispersions tend to exhibit a silky and powdery touch, absorb greasiness, and mask stickiness.
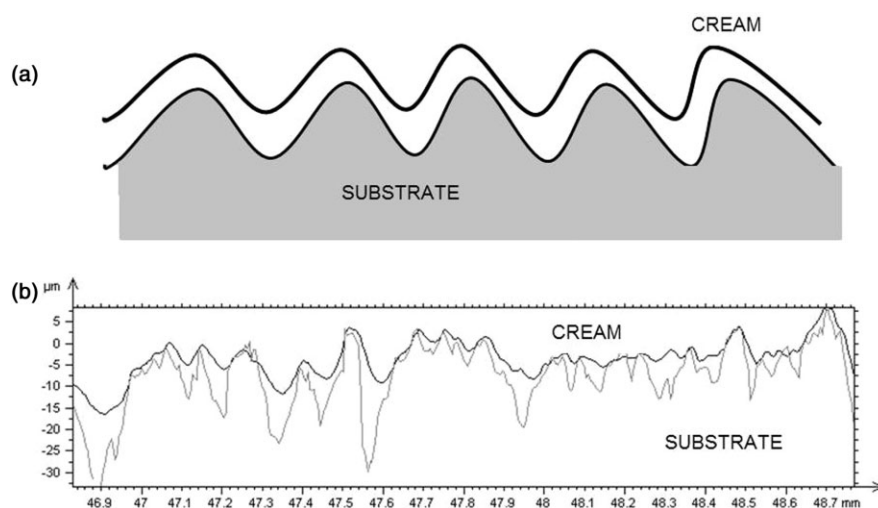
Fig. 10. Sunscreen distribution on a substrates surface: (a) ideal distribution, (b) real distribution.

Sunscreen film on skin

The UV filter system, the proper dispersion, and the solubilization of the UV filters in the emulsion and finally the uniform distribution of the UV-absorbing molecules on skin are key factors for achieving optimum performance. The sunscreen film after application should be as uniform as possible, ideally an identical cream thickness over the whole covered body surface. The sunscreen film is composed of a multitude of different thicknesses (48). During application, creams usually have tendency to fill the valleys, leaving the peaks only slightly covered with a thinner film.

Achievement of a uniform film thickness as drawn in Fig. 10a is unlikely. In the example of a real film distribution as shown in Fig. 10b, the sunscreen filled the valleys in particular but let the peaks almost unprotected (49). This enormous variation in the thickness of the sunscreen film has a strong negative impact on the product efficacy. However, the degree of the film inhomogeneity depends on the formulation, especially on the emulsion type, viscosity, rheological profile, and presence of film-forming ingredients (50).

Simulation of UV protection performance by sunscreens

Based on the UV filter composition and assumptions about the irregular film on the skin, the performance of a sunscreen can be simulated. Equation (1) establishes the relationship between the SPF on one side and erythemal action spectrum, irradiance spectrum of the UV source, and transmittance of the sunscreen on the other side. Whereas irradiance data $S_s(\lambda)$ and erythemal action spectrum $s_{er}(\lambda)$ data can be obtained from literature, the trans-

mittance $T(\lambda)$ has to be experimentally determined with *in vitro* SPF methods. However, a different and much more convenient way to provide the transmittance is by calculating it for a given composition of UV filters. In order to generate relevant transmission data, mixed absorbance spectra can be calculated according to the amounts and UV spectroscopic performances of the filters (51), based on an average optical path length of 20 μm [corresponding approximately to an application amount of 2 mg/cm², which is used in the SPF *in vivo* assay (52)]. To take the irregularity of the sunscreen film into consideration, a step film model was described by O'Neill in 1984 (48). Apart from other proposed film models (27), the most realistic approach so far seems to be the continuous height distribution model based on the gamma distribution (53). All film irregularity models contain adjustable parameters which may be fitted to result in best agreement with standard sunscreen data. Formulation effects on the film structure can be taken into consideration to a certain degree, based on the distribution of the filters in the oil phase and the water phase (28). Filter photoinstabilities may play a role and have to be taken into account along with the stabilizing and destabilizing effects from intermolecular interactions (54). Equation (1) takes into account transmission changes due to photoinstabilities in the course of the irradiation, where t_{MED} refers to the time, after which one minimal erythemal dose (1 MED) is transmitted through the sunscreen film (55, 56):

$$SPF = \frac{\sum_{0}^{t_{MED}} \sum_{290}^{400} S_s(\lambda) \cdot s_{er}(\lambda)}{\sum_{0}^{t_{MED}} \sum_{290}^{400} S_s(\lambda) \cdot s_{er}(\lambda) \cdot T(\lambda)} \qquad (1)$$
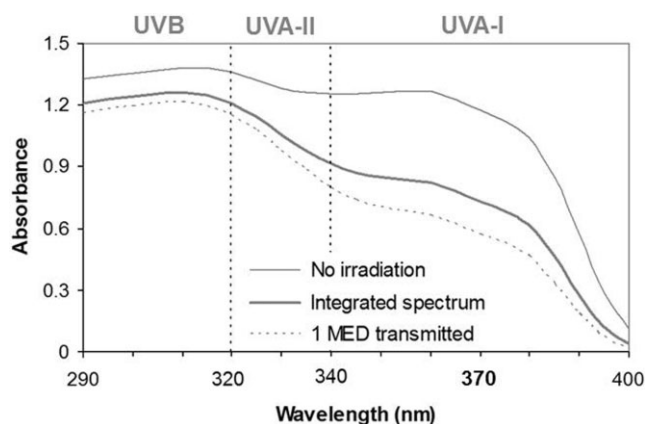
Fig. 11. Simulated absorbance spectra of the composition 5% EHMC, 4% BMBM, and 3% OCR without irradiation and after transmission of 1 MED, and the integrated spectrum. EHMC, octinoxate; BMBM, avobenzone; OCR, octocrylene; 1 MED, one minimal erythemal dose; UV, ultraviolet.

This approach also allows the determination of the resulting UV spectrum of the sunscreen during irradiation with 1 MED, by integration of the transmitted UV dose with and without protection, which is designated as the integrated spectrum (Fig. 11). This is explained in greater detail in Herzog and Osterwalder (57). A software tool, known as 'sunscreen-simulator' for the calculation of the SPF and all relevant metrics for characterization of the protection against UVA, is freely available (58).

Sensory characteristics, consumer compliance, and real-life efficacy

There are various reasons why people do not always, or ever, use sunscreen as a protective measure against UV radiation, such as 'sunscreens produce a non-physiological feeling on skin' (59), or 'it takes too much time', 'it is greasy', 'it feels hot & sweaty', 'it leaves a film', or just because they 'forgot to apply' (60).

The most efficient sunscreen regarding SPF and UVA protection, photostability of UV filters, and water resistance can only provide the claimed and expected photoprotection if the user applies it in the amount of the performance testing procedure (52) and as uniformly as possible. This is known as consumer compliance. As reported by several authors, consumers generally apply too little, only a quarter to half of the quantity used for the official *in vivo* SPF testing (61, 62).

Compared with the first sunscreens where aesthetics were a secondary aspect, there is at present a high demand from consumers with regard to the sensorial characteristics. Overall, products with low viscosity (sprays, lotions)

or formulations that break on the skin during application (gel-creams) were the most launched products last year worldwide. This is a response to the preference of users for products that spread easily during application. The suncare vehicle (emulsion type, emollients) impacts sensorial attributes of the product such as ease of distribution during application, and in the same manner it impacts the willingness of the consumer to use that product. A consumer study with four distinct sunscreens has, indeed, shown a strong correlation between the distribution properties and the willingness to use the sunscreen (49). The amount applied by volunteers also strongly depends on the formulation and its sensorial behavior as shown by Pissavini and Diffey (50). This means that sunscreens with identical nominal SPF values will, in the end, exhibit a different UV protection performance depending on their sensorial characteristics. It is thus the ultimate objective for sunscreen manufacturers to develop formulations that improve consumer compliance by proposing products that consumers are able and willing to apply properly, that is, the right amount in a uniform way to achieve the promised protection. This has been emerging by sunscreens with diverse appealing claims such as 'light skin feeling', 'dry touch', or 'wet skin' in order to match users' expectations. Sensory characteristics, consumer compliance, and efficacy under real-life conditions are inevitably strongly linked.

FACTS AND FICTION

Myth #1: SPF = UVB protection

A common myth is that erythema is only caused by UVB radiation and thus that the SPF only shows protection against UVB. This is evidently not true as has already been discussed in the introduction (Fig. 2), but the myth is still very widespread. Even the FDA helped proliferate this myth a few years ago in their 'proposed rule' 2007 (63). The FDA had suggested that SPF should be renamed as UVB-SPF. In response to that proposed rule, Sayre *et al.* stated that (64): *UVB accounts for 80%–91% of the erythemic effectiveness of the specified UV solar simulator. Analysis indicates that if 100% of the UVB is blocked, it is mathematically impossible to achieve an SPF in excess of 11 without also blocking at least some UVA. Consequently significant UVA protection must be provided for sunscreen products to achieve SPFs of 15 and higher.* Figure 12 confirms the findings of Sayre on the sunscreen simulator (58). Practically complete blockage of UVB by means of the two most efficient UVB filters (5% EHT plus 10% DBT) yields an SPF 14, whereas with the addition of only
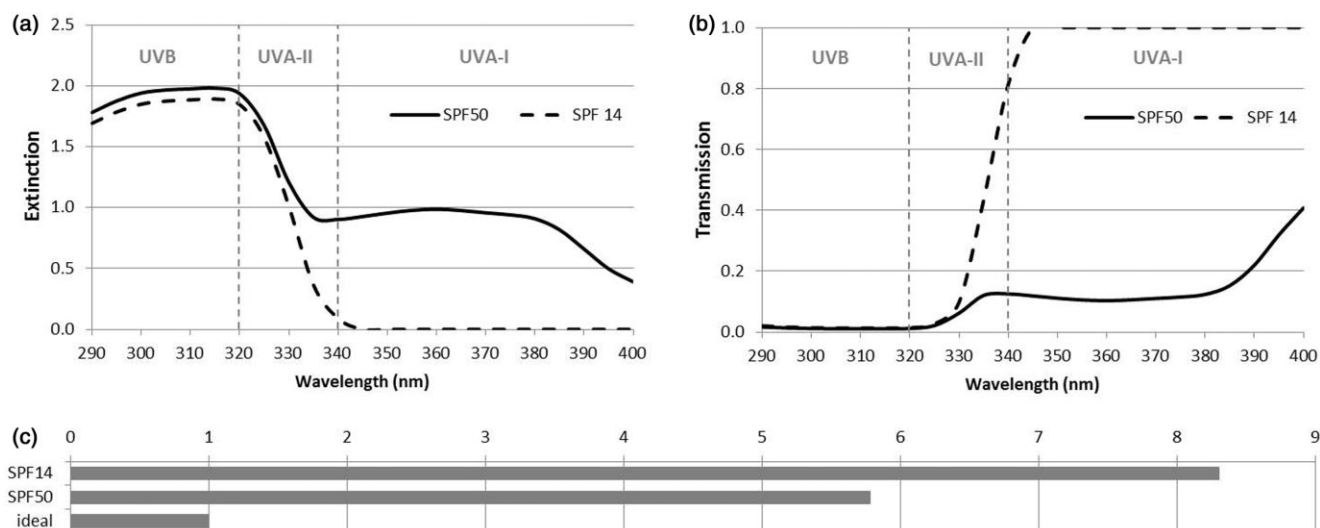
Fig. 12. Comparison between an SPF 14 and an SPF 50 sunscreen: (a) extinction profile, (b) transmission profile, (c) visualization of normalized transmitted UV dose at 1 MED. SPF, sun protection factor; UV, ultraviolet.

4% bisoctrizole (MBBT) the SPF jumps to SPF 50. The 4% MBBT covers about 80%–90% of the UVA range (corresponding to 10%–20% transmission) as can be seen in the transmittance chart.

Myth #2: 'chemical' UV filters absorb, 'physical' filters reflect and scatter

A traditional view classifies sunscreens as 'chemical' or 'physical', referring to the solubility or insolubility of the particles. Such labels promote a misperception regarding how and why sunscreen protects the skin. The effectiveness of UV filters is based on their ability to absorb the selected wavelengths, whether in the visible (400–700 nm), UVA (320–400 nm), or UVB (290–320 nm) range as described earlier in this paper (Fig. 4).

In summary, TiO_2 and ZnO are good sunscreens because of their semiconductor-like electronic properties as solids and not because of their scattering properties. To the contrary, scattering and reflection are undesired properties, leading to the 'whitening' effect during application on skin and thus to less compliance. The labels 'chemical' and 'physical' sunscreen could be replaced by 'soluble' and 'insoluble' sunscreen, or better yet eliminated altogether as descriptors (9).

Myth #3: SPF 30 protects only marginally better than SPF 15 sunscreen

Another popular misconception is that SPF 30 is not twice as effective as SPF 15 sunscreen, or SPF 60 not twice as effective as SPF 30, etc. To be precise, 'SPF' refers to

preventing sunburn under laboratory conditions, for example, at 2 mg/cm² application amount, protection against other endpoints or against erythema under real-life conditions may indeed be different. The argument goes: an SPF 30 sunscreen filters 96.7% of the erythemogenic UV rays, whereas an SPF 60 sunscreen filters out 98.3%; meaning only 1.6% more. For the impact on humans, it is, however, not relevant how much is filtered out, but rather how much is transmitted onto the skin. An SPF 60 sunscreen transmits 1.7% compared with 3.3% by an SPF 30 sunscreen, that is, half as much. The 1.6% difference thus corresponds to a factor of 2, which is what we expect. Illustration and animation of these facts can be found in Osterwalder and Herzog (65) and animated on YouTube (66).

Furthermore, there is another argument for choosing the sunscreen with the higher SPF. Pissavini and Diffey show in their paper entitled: 'The likelihood of sunburn in sunscreen users is disproportionate to the SPF', that depending on how well a sunscreen is applied, the SPF 30 sunscreen may, in fact, protect disproportionally better than SPF 15 (67). Their simulation reveals that especially if sunscreen is not applied uniformly on the body in the right quantity, the SPF 30 sunscreen protects more than twice as well against sunburn and thus, by implication, against skin cancer.

Myth #4: critical wavelength CW = 370 nm is good enough UVA protection

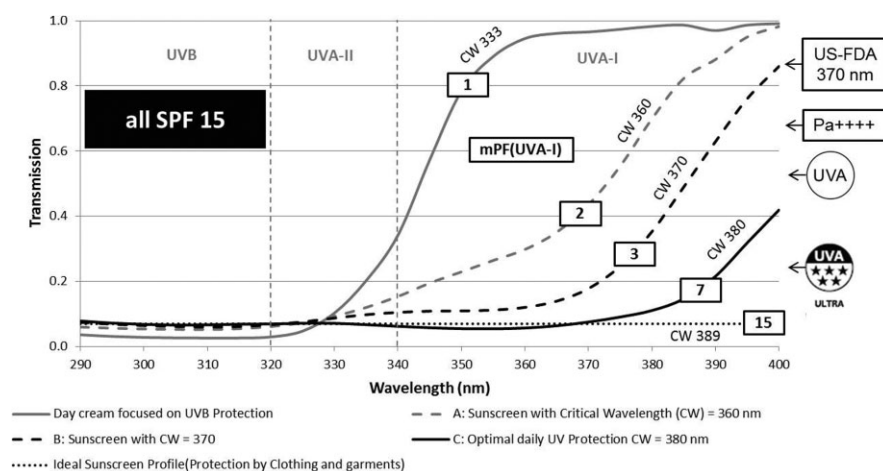In June 2011, the FDA released a final sunscreen rule (68) that regulates for the first time UVA protection in the

Fig. 13. UV protection profile of optimal daily care compared with other day creams/sunscreens (all SPF 15). SPF, sun protection factor; FDA, Food and Drug Administration; UV, ultraviolet.

Table 2. SPF 15 sunscreens or day creams with different degrees of UVA protection profiles, from UVB-biased toward the ideal sunscreen (garments) calculated from BASF Sunscreen Simulator

Sunscreen	SPF	Critical wavelength (nm)	Trasnmission (%) UVB/UVA-II	Transmission (%) UVA-I	Protection factor UVA-I (= 1/T)	Normalized transmitted UV dose at 1 MED
UVB-biased	15	333	2.9/17	92	1	8
A	15	360	5.6/11	56	2	5.3
B	15	370	6.5/9.2	34	3	3.6
C	15	380	6.8/6.7	15	7	1.6
Ideal profile (garments)	15	389 (max)	6.7/6.7	6.7	15	1.0 (= 7.9 J/cm^2)

SPF, sun protection factor; UV, ultraviolet.

United States. The proposed rule from 2007, including *in vivo* assessment of UVA protection, was completely abandoned and replaced by the critical wavelength (CW), an *in vitro* determined metric CW ≥ 370 nm, as sole UVA criterion to make the broad-spectrum claim. For sunscreens with SPF ≥15, the claim 'reduces risk of skin cancer' can be made in addition. The FDA bases this claim on the study by Green *et al.* (69) in Australia in the early 1990s. The sunscreen used by the intervention group showed less skin cancers after 4 years and less malignant melanoma in a follow-up of the same cohorts after 15 years (70). At that time, the first UVA filter, BMBM, had just been introduced. It consisted of 8% octinoxate (EHMC) and 2% BMBM and had an SPF of 16. Today, we know that this sunscreen in the intervention group was not photostable, which means we can expect yet better protection from currently available sunscreens that contain modern UV filters.

Figure 13 (based on data in Table 2) shows the progress in reducing UVA transmittance of different SPF 15 day creams. Transmittance can be readily converted to a pro-

tection factor. The monochromatic protection factor (mPF) is just the reciprocal value mPF = 1/T at any given wavelength. In the figure, the average monochromatic protection factors in the UVA-I range (340–400 nm) range from as low as $\overline{mPF-UVA-I} = 1$ (no protection) to 15 (uniform protection). A CW = 370 nm provides only an average $\overline{mPF-UVA-I}$ of around 3. Raising the bar to CW = 380 nm would already provide an $\overline{mPF-UVA-I}$ of 7. An 'ideal sunscreen' would provide an equal SPF 15 throughout the UV range, similar to textile. The figure also shows the UVA protection logos used in different regions, as discussed earlier.

Myth #5: SPF is exponential function of application amount of the sunscreen

The final popular misconception to be discussed refers to the relationship between application amount of sunscreen and the resulting SPF. Statements such as the following are often heard, especially among dermatologists: 'It turns out
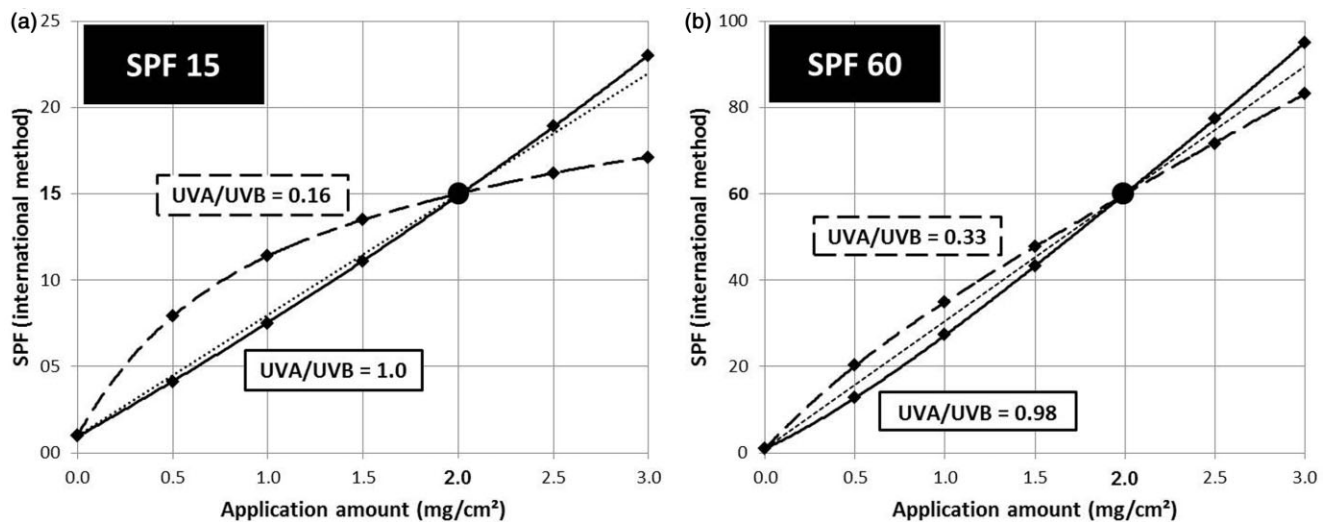
Fig. 14. SPF vs. application amount for two sunscreens of two different UVA/UVB ratios, calculated on sunscreen simulator: (a) SPF 15 sunscreen, (b) SPF 60 sunscreen. SPF, sun protection factor; UV, ultraviolet.

that if you apply half the amount, you get the protection of only the square root of the SPF' (71). Faurschou and Wulf seemed to confirm an exponential, convex-shaped SPF-vs.-application-amount relationship in their *in vivo* experiment (72), but they used a UVB lamp for their SPF measurements, apparently also confined by myth #1 (SPF = UVB). Because common sunscreens protect the UVB range very well, it is not surprising that they found an exponential relationship. Let us think of a mental experiment with an extremely UVB-biased sunscreen measured with a proper solar simulator lamp that also emits UVA radiation. The relationship between SPF and application amount is rather a concave- than a convex-shaped one; thicker and thicker layers of sunscreen still transmit a lot of UVA radiation and thus do not allow the SPF to rise proportionally, let alone exponentially (73). The relationship SPF vs. amount for common, slightly UVB-biased sunscreen will be in between these two examples of convex and concave shape and thus be quasi linear. Such a behavior can also be observed by calculating combinations of UV filters on the sunscreen simulator (58). Figure 14a shows two extreme cases of SPF 15 sunscreens: one completely UVB-biased (UVA/UVB = 0.16) and one with a uniform UVB-UVA profile (UVA/UVB = 1.0). The two SPF 60 sunscreens in Fig. 14b confirm this result. The concave curve due to the UVB-bias (UVA/UVB = 0.33) is less pronounced because high SPF sunscreens are not possible without an UVA protection (compared with myth #1).

Furthermore, these calculations have been confirmed *in vivo* by a multicenter study organized by the German Cos-

metics Society (74) and also by a US-based study (75). The German study conducted a ring test with three SPF 25 products in three test centers. The SPF measured at 0.5 mg/cm^2 was in average around a quarter and at 1.0 mg/cm^2 around half of the standard SPF measured at 2 mg/cm^2. Another finding of the German study was that the most reliable results were obtained at an application amount of 2.0 mg/cm^2. This confirms that this application amount should not be changed for the SPF measurement, although people may not put on that much. To some degree, the 'right amount' for people is determined by the people themselves; it is the amount they feel comfortable with and thus depends heavily on the properties of the sunscreen product.

The US study used sunscreens with SPF values of 70 and 100. They also found a linear relationship between application density and the actual SPFs. Sunscreens labeled SPF 70 and 100 applied at 0.5 mg/cm^2 provided an actual SPF value of 19 and 27 (75). These examples can be simulated on the sunscreen simulator (58). Besides the standard application amount of 2 mg/cm^2, other amounts that can be chosen are 0.5, 1.0, 1.5, 2.5, and 3.0 mg/cm^2. Note that there is a discrepancy between *in vivo* SPF values measured in the United States and the calculations on the sunscreen simulator; the former are usually a lot higher. This cannot be fully explained by the existing differences between European [Cosmetics Europe, International Standardization Organization (ISO)] and US (FDA) SPF tests methods. SPF values of European sunscreens tested in Europe are in good agreement with the calculations.

In conclusion, *in vivo* and *in silico* results confirm the linear relationship between SPF value and application amount. The negative impact of putting on less sunscreen is thus not exponentially related to the amount applied, but it is of course still substantial. This is especially the case if the sunscreen is not applied uniformly. For compensation, it is thus advisable to use a higher SPF than theoretically required. Compare also the discussion regarding myth #3 and the paper of Pissavini and Diffey (67).

CONCLUSION AND OUTLOOK

Besides sun avoidance and covering up, sunscreens and daily creams with UV protection are an important means of sun protection to reduce our exposure to UV radiation. The four requirements for good UV protection by sunscreens are technology, assessment of sunscreen performance, performance standards, and compliance. UV filters require a chromophore that absorbs in the UV range (290–400 nm) and does not absorb in the visible range (400–700 nm). There is a much greater variety of organic UV absorbers than of inorganic ones. The United States does not yet benefit from that full variety because the latest UV filters are not yet approved, some waiting for over 10 years.

There are also regional differences in sunscreen format and the popularity of the various SPF classes. Differences in sunscreen distribution of the various formats can also be observed in four regions: EU, NA, LA, and AP. More than 50% of the launches of sunscreen products have an SPF 50 or higher. Compliance is influenced by the sensory properties of a sunscreen which in turn can be influenced by the ingredients, mainly the UV filters, emollients, emulsifier system, thickeners, and special sensory enhancers. An analysis of the sunscreen film on a skin-mimicking substrates shows that the distribution is still far from ideal. Nonhomogeneity inevitably results in lower SPF than theoretically possible.

The performance of sunscreens can be assessed in *vivo, in vitro*, and *in silico*. Global harmonization is on track, thanks to the efforts of the ISO, although there is not yet a proposal for the *in vitro* SPF method. The *in silico* method (58) allows the theoretical performance of a particular sunscreen to be determined. It provides a quick check if a particular regional standards can be fulfilled with a certain UV filter combination. It is also a valuable educational tool for learning how sunscreens work, for example, with regard to questions such as what is the performance at a lower application amount. Or how much UV radiation is still transmitted through the sunscreen? Large differences are evident in sunscreens with equal SPF, depending on the respective UVA protection provided.

There are lots of half-truths and myths surrounding sunscreens. Five of the most common myths are debunked in this paper: the myth that SPF stands only for UVB protection, the myth about chemical and physical UV filters, the myth that SPF 60 protects only marginally better than SPF 30, the myth that CW 370 nm offers enough UVA protection, and the myth that the SPF varies exponentially with the amount of sunscreen applied on the skin.

Outlook

The major task with respect to the enhancement of the protective benefit of sunscreens is to improve compliance. To accomplish this goal, a comprehensive approach is needed. Improvement in sunscreen technology will further enhance the sensory and tactile profiles and thereby allow the users to enjoy applying sunscreen. An interesting notion to incorporate compliance and performance into a single metric termed $SPF_{in\ vivo\ veritas}$ comes from Pissavini *et al.* (76). Behavioral change will be important, especially among the large part of the population that does not use sunscreen as shown by the very low per capita figures of sunscreen use in the various countries (Fig. 6). Depending on the regions and seasons, wearing sunscreen should become a daily routine like brushing teeth, when required by UV climatology, that is, when UV INDEX > 2. The public and even the medical community should be better educated to dispel misconceptions regarding the safety and efficacy of sunscreen, because misguided information creates fears and decreases compliance. Global harmonization will eventually give everybody access to modern UV sunscreen technology, performance measurements, and also adequate criteria for good sun protection.

ACKNOWLEDGEMENT

REFERENCES

1. Centers for Disease Control and Prevention (CDC), Department of Health and Human Services (HHS). Notices. In: Call for comments on preventing skin cancer through reduction of UV exposure. FR 2013; 78: 47320. Available at http://www.regulations.gov/#!docketDetail;D=CDC-2013-0014. Accessed 18 October 2013.

2. Diffey BL. What can be done to reduce personal ultraviolet radiation exposure? In: Hill DJ, Elwood JM, English DR, eds. *Prevention of skin cancer*, Vol. 3, *Cancer Prevention-Cancer Causes*. Dordrecht, NL: Kluwer Academic, 2004, 241–258.

3. Osterwalder U, Herzog B. The long way towards the ideal sunscreen – where we stand and what still needs to be done. *Photochem Photobiol Sci* 2010; 9: 470–481.

4. AS/NZS. Australian/New Zealand standard. AS/NZS, 2604, 1998.

5. Diffey B. The UV age: a measure of lifetime sun exposure. Skin Care Forum, February, 2013. Available at http://www.skin-care-forum.basf.com/en/author-articles/the-uv-age-a-measure-of-lifetime-sun-exposure/2013/02/14?id=4a9cba10-b727-42b1-8049-73c79d1ae777&mode=Detail. Accessed 18 October 2013.

6. Sayre RM, Dowdy JC, Lott DL, Marlowe E. Commentary on 'UVB-SPF': the SPF labels of sunscreen products convey more than just UVB protection. *Photodermatol Photoimmunol Photomed* 2008; 24: 218–220.

7. Herzog B, Hueglin D, Osterwalder U. New sunscreen actives. In: Shaath NA, ed. *Sunscreens – regulations and commercial development, cosmetic science and technology*, 3rd edn, *Series 28*. Boca Raton: Taylor & Francis, 2005, 291–320.

8. Herzog B. Photoprotection of human skin. In: Albini A, ed. *Photochemistry*, Vol. 40. Cambridge,UK: RSC Publishing, The Royal Society of Chemistry, 2012, 250–259.

9. Kollias N. The absorption properties of 'physical' sunscreens. *Arch Dermatol* 1999; 135: 209–210.

10. Schlossmann D, Shao Y. Inorganic ultraviolet filters. In: Shaath NA, ed. *Sunscreens – regulations and commercial development, cosmetic science and technology*, 3rd edn, *Series 28*. Boca Raton, FL: Taylor & Francis, 2005, 239–279.

11. Herzog B, Katzenstein A, Quass K, Stehlin A, Luther H. Physical properties of organic particulate UV-absorbers used in sunscreens. I. Determination of particle size with fiber-optic quasi-elastic light scattering (FOQELS), disc centrifugation, and laser diffractometry. *J Colloid Interface Sci* 2004; 271: 136–144.

12. Herzog B, Quass K, Schmidt E, Müller S, Luther H. Physical properties of organic particulate UV absorbers used in sunscreens II. UV-attenuating efficiency as function of particle size. *J Colloid Interface Sci* 2004; 276: 354–363.

13. Mueller S, Herzog B, Giesinger J, Quass K, Osterwalder U. Micronization as a tool in the development of innovative UV filters. *SOFW J* 2005; 131: 32–39.

14. Ahmed FK. Worldwide regulation of UV filters: current status and future trends. In: Lim HW, Draelos ZD, eds. *Clinical guide to sunscreens and photoprotection*. New York: Informa Healthcare, 2008, 65–81.

15. CDER. Guidance for industry time and extent applications for nonprescription drug. U.S. Department of Health and Human Services Food and Drug Administration Center for Drug Evaluation and Research (CDER) Products, 2011. Available at http://www.fda.gov/downloads/Drugs/Guidances/ucm078902.pdf. Accessed 18 October 2013.

16. PASS coalition. Public access to sunscreens. 2013. Available at http://www.passcoalition.com/. Accessed 18 October 2013.

17. EUROMONITOR. Suncare market sizes historic retail value. 2013. Available at http://portal.euromonitor.com/Portal/Pages/Statistics/Statistics.aspx. Restricted access, Accessed 18 October 2013.

18. Mintel Group Ltd. Global new products database. personal care portal. 2013. Available at http://www.gnpd.com/. Restricted access, Accessed 18 October 2013.

19. Lott D. Sun care use: beach survey. *Cosmetics & Toiletries magazine* 2013; 128: 324–328.

20. Perrone M. Banana Boat recalls sunscreen due to fire risk. The Big Story (AP). 19 October 2012. Available at http://bigstory.ap.org/article/banana-boat-recalls-sunscreen-due-fire-risk. Accessed 18 October 2013.

21. Rigano L. Formula anatomy deciphered – BB creams. *Cosmetics & Toiletries magazine* 2013; 125: 88–90.

22. Fisher GJ, Wang ZQ, Datta SC, Varani J, Kang S, Voorhees JJ. Pathophysiology of premature skin aging induced by ultraviolet light. *N Engl J Med* 1997; 337: 1419–1428.

23. Baumann L. Skin ageing and its treatment. *J Pathol* 2007; 211: 241–251.

24. Moyal DD, Fourtanier AM. Broad-spectrum sunscreens provide better protection from solar ultraviolet-simulated radiation and natural sunlight-induced immunosuppression in human beings. *J Am Acad Dermatol* 2008; 58: 149–154.

25. Zastrow L, Groth N, Klein F et al. The missing link – light-induced (280–1600 nm) free radical formation in human skin. *Skin Pharmacol Physiol* 2009; 22: 31–44.

26. Phillips TJ, Bhawan JB, Yaar M, Bello Y, Lopiccolo D, Nash JF. Effect of daily versus intermittent sunscreen application on solar simulated UV radiation-induced skin response in humans. *J Am Acad Dermatol* 2000; 43: 610–618.

27. Herzog B. Prediction of sun protection factors and UV-A parameters by calculation of UV transmissions through sunscreen films of inhomogeneous surface structure. In: Shaath NA, ed. *Sunscreens – regulations and commercial development, cosmetic science and technology*, 3rd edn, *Series 28*. Boca Raton: Taylor & Francis, 2005, 881–902.

28. Herzog B. Models for calculation of sun protection factors and parameters characterizing the UVA protection ability of cosmetic sunscreens. In: Tadros TF, ed. *Colloids in cosmetics and personal care*, Vol. 4. Weinheim: Wiley-VCH, 2008, 294–297.

29. Caswell M. Sunscreen formulation and testing. *Cosmetics & Toiletries magazine* 2001; 116: 49–56.

30. Barrett C, Gripp A. Solubilizing Avobenzone in sunscreen formulations without C12–15 Alkyl Benzoate. *SOFW Journal* 2009; 135: 28–33.

31. Cole CA, Vollhardt J, Mendrok C. Formulation and stability of sunscreen products. In: Lim HW, Draelos ZD, eds. *Clincal guide to sunscreens and photoprotection*, *Basic and clinical dermatology*. New York: Informa Healthcare USA, 2009, 39–52.

32. Bonda C. Sunscreen photostability 101. *Happi* 2009; 46: 72–75.

33. Bonda C. Research pathways to photostable sunscreens. *Cosmetics & Toiletries magazine* 2008; 123: 49–59.

34. Osterwalder U, Herzog B, Wang SQ. Advance in sunscreens to prevent skin cancer. *Expert Rev Dermatol* 2011; 6: 479–491.

35. Cosmetic Products. Regulation (EC) no. 1223/2009 of the European parliament and of the council of 30 November 2009 on cosmetic products. Annex VI. 2009. Available at http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CONSLEG:2009R1223:20130711:en:PDF. Accessed 18 October 2013.

36. Bundesinstitut für Risikobewertung. 9. Sitzung der BfR-Kommission für kosmetische Mittel, Protokoll der Sitzung vom 3. Mai 2012. 2012. Available at http://www.bfr.bund.de/cm/343/9-sitzung-der-bfr-kommission-fuer-kosmetische-mittel.pdf. Accessed 18 October 2013.

37. Kantonales Laboratorium Basel. Sonnenschutzmittel und gesichtscrèmes mit UV-schutz/UV-filter, konservierungsmittel und deklaration. Bericht Nr. 45. 2009. Available at http://www.kantonslabor-bs.ch/kl/infos/berichte.cfm?sprache=de&site=21&year=2009&subkat=&detail=RW9I4029. Accessed 18 October 2013.

38. Agrapidis-Paloympis LE, Nash RA, Shaath NA. The effect of solvents on the ultraviolet absorbance of sunscreens. *J Soc Cosmet Chem* 1987; **38**: 209–221.

39. Herzog B, Giesinger J, Schnyder M. Solubility of UV absorbers for sunscreens is essential for the creation of light feel formulations. *SOFW Journal* 2013; **139**: 10–14.

40. Jones CE. Hollow sphere technology for sunscreen formulation. *SOFW J* 2002; **128**: 36–40.

41. Davis JA, Petersen D. Film-forming polymers as a delivery strategy for sunscreen efficacy. *Cosmetics & Toiletries magazine* 2007; **122**: 69–75.

42. Martin T, Burns T. Novel graft polymer boosts SPF performance. *Happi* 2006; **43**: 62–65.

43. Hunter A, Trevino M. Film-formers enhance water resistance and SPF in sun care products. *Cosmet & Toiletries Mag* 2004; **119**: 51–55.

44. Van Reeth I, Urrutia A. New silicone-based solutions for suncare. *SOFW J* 2004; **130**: 12–25.

45. Wiechers S, Biehl P, Jha B, Meyer J. Novel vegetable based polyamide powder for personal care applications. *SOFW J* 2013; **139**: 20–25.

46. Leist J, Rojas-Wahl R, Sinha M. Soft focus – a tool for advanced skincare formulation. *SOFW J* 2013; **139**: 2–10.

47. Duffy JL, Macian KA, Rojas Wahl RU, Silicones and naturals – enhancing sensory, aesthetics and efficacy. *SOFW J* 2010; **136**: 24–35.

48. O'Neill JJ. Effect of film irregularities on sunscreen efficacy. *J Pharm Sci* 1984; **73**: 888–891.

49. Osterwalder U, He Q, Sohn M, Herzog B. Sustainable sun protection with sunscreens requires the right technology and good compliance. *SOFW J* 2012; **138**: 2–19.

50. Pissavini M, Diffey B. Predicting the efficacy of sunscreens *in vivo* veritas. *Int J Cosmet Sci* 2011; **34**: 44–48.

51. Herzog B. Prediction of sun protection factors by calculation of transmissions with a calibrated step film model. *J Cosmet Sci* 2002; **53**: 11–26.

52. ISO 24444: 2010. Cosmetics – sun protection test methods – *in vivo* determination of the sun protection factor (SPF). 2010.

53. Ferrero L, Pissavini M, Marguerie S, Zastrow L. Efficiency of a continuous height distribution model of sunscreen film geometry to predict a realistic sun protection factor. *J Cosmet Sci* 2003; **54**: 463–481.

54. Herzog B, Mongiat S, Quass K, Deshayes C. Prediction of sun protection factors and UVA parameters by using a calibrated step film model. *J Pharm Sci* 2004; **93**: 1780–1795.

55. Wloka M, Lange RFM, Flösser-Müller H. An in vitro SPF screening approach considering photostability of the UV filters. Proc. Int. Sun Protection Conference, London. 2005.

56. Stanfield J, Osterwalder U, Herzog B. In vitro measurements of sunscreen protection. *Photochem Photobiol Sci* 2010; **9**: 489–494.

57. Herzog B, Osterwalder U. Silico determination of topical sun protection. *Cosm Sci Tech* 2011; **62**: 1–8.

58. Anonymous. BASF sunscreen simulator, BASF SE, Ludwigshafen, Germany. 2010. Available at http://www.basf.com/sunscreen-simulator. Accessed 18 October 2013.

59. Lademann J, Schanzer S, Richter H *et al.* Sunscreen application at the beach. *J Cosmet Dermatol* 2004; **3**: 62–68.

60. Solky BA, Philips PK, Christenson LJ, Weaver AL, Roenigk RK, Otley CC. Patient preferences for facial sunscreens: a split-face, randomized, blinded trial. *J Am Acad Dermatol* 2007; **57**: 67–72.

61. Bauer U, O'Brien DS, Kimlin MG. A new method to quantify the application thickness of sunscreen on skin. *Photochem Photobiol* 2010; **86**: 1397–1403.

62. Stenberg C, Larkö O. Sunscreen application and its importance for the Sun protection factor. *Arch Dermatol* 1985; **121**: 1400–1402.

63. Federal Register. Sunscreen drug products for over-the-counter human use; proposed amendment of final monograph; proposed rule. *Federal Register* 2007; **72**: 49070–49122.

64. Sayre RM, Dowdy JC, Lott DL, Marlowe E. Commentary on 'UVB-SPF': the SPF labels of sunscreen products convey more than just UVB protection. *Photodermatol Photoimmunol Photomed* 2008; **24**: 218–220.

65. Osterwalder U, Herzog B. Sun protection factors: worldwide confusion. *Brit J Dermatol* 2009; **161**: 13–24.

66. Surber C, Osterwalder U, Stockfleth E. SPF 50 protects 5 times better than SPF 10. Uploaded 21 June 2011. The European Skin Cancer Foundation. YouTube: Available at http://www.youtube.com/watch?v=8cc8qRr7oMQ. Accessed 18 October 2013.

67. Pissavini M, Diffey B. The likelihood of sunburn in sunscreen users is disproportionate to the SPF. *Photodermatol Photoimmunol Photomed* 2013; **29**: 111–115.

68. Federal Register. No. 117. Rules and regulations, Department of Health and Human Service, FDA, 21 CFR Parts 201 and 310, Docket No. FDA–1978–N–0018FDA, 21 CFR Parts 201 and 310, Docket No. FDA–1978–N–0018, Vol. 76, No. 117, June 17, 2011.

69. Green A, Williams G, Neale R *et al.* Daily sunscreen application and betacarotene supplementation in prevention of basal-cell and squamous-cell carcinomas of the skin: a randomised controlled trial. *Lancet* 1999; **354**: 723–729.

70. Green AC, Williams GM, Logan V, Strutton GM. Reduced melanoma after regular sunscreen use: randomized trial follow-up. *J Clin Oncol* 2011; **29**: 257–263.

71. Saint Louis C. Skin deep – confused by SPF? Take a number, The New York Times, Vol. CLVIII, May 14, 2009, p. E1. Available at http://www.nytimes.com/2009/05/14/fashion/14SKIN.html?pagewanted=all&_r=0. Accessed 18 October 2013.

72. Faurschou A, Wulf HC. The relation between sun protection factor and amount of sunscreen applied *in vivo*. *Brit J Dermatol* 2007; **156**: 716–719.

73. Osterwalder U, Herzog B. Chemistry and properties of organic and inorganic UV filters. In: Lim HW, Draelos ZW, eds. *Clinical guide to sunscreens and photoprotection*. New York, USA: Informa Healthcare, 2009, 11–38.

74. Bimczok R, Gers-Barlag H, Mundt C *et al.* Influence of applied quantity of sunscreen products on the sun protection factor – a multicenter study organized by the DGK Taskforce Sun Protection. *Skin Pharmacol Physiol* 2007; **20**: 57–64.

75. Ou-Yang H, Stanfield J, Cole C, Appa Y, Rigel D. High-SPF sunscreens (SPF ≥70) may provide ultraviolet protection above minimal recommended levels by adequately compensating for lower sunscreen user application amounts. *J Am Acad Dermatol* 2012; **67**: 1220–1227.

76. Pissavini M, Doucet O, Diffey BL. A novel proposal for labelling sunscreens based on compliance and performance. *Int J Cosmetic Sci* 2013; **35**: 510–514.