

## About the Authors



**Dominique Moyal, PhD.** Dominique Moyal joined L'Oréal in 1984 after completing a PhD in pharmaceutical sciences. She has spent most of her career within the research laboratories where she was responsible for the evaluation of efficacy of sun care products. From 2007 to 2014, she was regulatory affairs manager in the photoprotection field. From 2015 to 2018, she was deputy scientific director of La Roche-Posay Dermatological laboratories. Since 2019, she is scientific consultant for La Roche-Posay.



**Thierry Passeron, MD, PhD.** Thierry Passeron is Professor and chair of Dermatology in the University hospital of Nice. He also heads the laboratory INSERM U1065 team 12, C3M, dedicated to the study of molecular mechanisms involved in pigmentation and melanoma. He heads the University laser center in Nice. He is president of the Department of Clinical Research and Innovation of Nice University hospital. He has 9 international patents and more than 240 publications in scientific journals (h-index 44). He is co-founder of YUKIN therapeutics. His fields of research include pigmentary disorders (including vitiligo and melasma), melanoma, hidradenitis suppurativa, alopecia areata and lasers.



**Martin Josso, PhD.** Martin Josso, after studying organic chemistry and obtaining a PhD from Wayne State University, joined L'Oréal in 1995. For the next 25 years, he has dedicated his career to the field of photoprotection, formulating sunscreen products for the various L'Oréal brands worldwide. Since 2019, he is senior project leader in the Photoprotection Application domain, in charge of new UV filtration technological platforms.



**Stéphane Douezan, PhD.** Stéphane Douezan has studied soft matter sciences and formulation and joined L'Oréal in 2012 after completing a PhD in physical chemistry. For 10 years, he has explored formulation and science of emulsions dedicated to skin application within the research laboratories. Since 2016, his activity is dedicated to the formulation of photoprotection products, and in 2019, he became head of the sun care development laboratory.



**Véronique Delvigne,** holding a doctorate in pharmacy, specialized in skin biology, became scientific director of La Roche Posay in 2020. She joined the L'Oréal group in 1986 as a biophysics researcher, then moved to the laboratories business coordination for 5 years, running development projects for the skin care, sun care, makeup, and fragrances metiers for the Active Cosmetics Division in Lancôme. In 1994, Véronique was appointed Head of Anti-Ageing and Whitening in Lancôme skin-care. In 2000, she created the Lancôme International Scientific Department, where she rolled out genomics, proteomics, stem cells, and microbiome studies. Véronique has been Lancôme's scientific spokesperson for 20 years.



**Sophie Seité, PhD,** studied biochemistry and molecular biology and obtained a PhD in 1989. For 20 years, she studied the clinical, biophysical, and histological effects of acute and repetitive exposure to UV radiation. In 2005, she joined La Roche-Posay Dermatological Laboratories, and for 6 years, she managed the clinical studies performed internationally with products dedicated to dermatologists. From 2011 to 2019, she was the international scientific director of this brand. She published more than 90 articles in international scientific journals and participated in global dermatological, pharmaceutical, and biological congresses as speaker in numerous symposia.

## Formulation of Sunscreens for Optimal Efficacy

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### Synopsis

Skin exposure to solar radiation can cause many adverse effects. In addition to the sun protection factor (SPF), a parameter associated with Ultraviolet B (UVB) protection, significant evidence emphasized the crucial importance of a well-balanced protection against ultraviolet A (UVA) and for some indications, against high-energy visible light. Synergy between UV filters and filter photostability together with film-forming ingredients such as polymers that ensure the homogeneous distribution of UV filters on the skin are key factors to avoid UVA- and UVB-provoked detrimental effects of solar radiation. Clinical studies mimicking real conditions of use have been performed. The results show that a well-balanced sunscreen with at least an SPF-to-UVA protection factor ratio < 3 provides the most effective protection against DNA damage, skin photoimmunosuppression, photodermatoses, and pigmentation disorders. In addition, cosmetically pleasant sunscreens allow a sufficient amount to be applied and re-applied by consumers, ensuring continuous and even coverage of the exposed skin.

### INTRODUCTION

Ultraviolet B (UVB) (290–320 nm) radiation accounts for 5% of total solar Ultraviolet (UV) radiation. It causes adverse effects, such as sunburn and long-term damage including skin cancer, principally melanoma and squamous cell carcinoma (1,2), by directly impacting cellular DNA (3).

Irrespective of the meteorological conditions, ultraviolet A (UVA) (320–400 nm) irradiance is at least 17 times higher than UVB irradiance (4). UVA penetrates deeper into the skin than UVB. Via photosensitization processes, it produces reactive oxygen species that damage DNA, cells, vessels, and elastic fibers in connective tissues, leading to photoaging (5–8). Within the UVA band, long UVA or UVA1 rays cause the most damage (9). UVA and B are implicated in immune system depression (10,11). Photosensitivity and photodermatoses are mainly UVA-induced (12), and UVA is a key factor in the aggravation of pigmentation through melanin oxidation and distribution (13,14). The sun protection

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factor (SPF) is still considered by many consumers and some physicians as the main criterion to choose a sunscreen. In addition to UVB protection, not only the protection against long-wave UVA (and in some conditions against visible light and short infrared) but also the stability of the filters, the esthetic of the formula, and practicability and ability of the final product to homogeneously cover the entire skin are key factors that must be taken into consideration for an optimal formulation of a sunscreen.

## DEVELOPMENT OF MORE EFFICIENT SUNSCREENS

### CHOOSING THE APPROPRIATE FILTERS

The recognition of UV-induced skin damage prompted the development of products offering greater protection against UVB and UVA radiation. Well-balanced protection against UVB and UVA radiation was defined in the 2006 EC recommendation (15) as an SPF-to-UVA protection factor (UVAPF) ratio of  $\leq 3$  (e.g., UVAPF at least 20 for SPF50+). This requirement has therefore been adopted in other countries worldwide. The UVAPF is determined according to International Organization for Standardization (ISO) (16,17) using the persistent pigment darkening (PPD) endpoint representative of UVA damage. Increased UV protection requires higher concentrations of UV absorbers, but their unpleasant, greasy feeling may induce low cosmetic acceptance. Therefore, formulators must create elegant yet effective sunscreens with less UV filters but the same level of UVB/UVA protection. Balanced protection requires a combination of lipophilic and hydrophilic absorbers in the UVB, short UVA, and long UVA (18).

An example of synergy of organic UV filters is offered by mixing terephthalylidene dicamphor sulfonic acid (Mexoryl<sup>®</sup> SX, Noveal, Le Thillay, France), a “short UVA” filter, with drometrizole trisiloxane (Mexoryl<sup>®</sup> XL, Noveal) and bis ethylhexyloxyphenol methoxyphenyl triazine (Tinosorb<sup>®</sup> S, BASF, Ludwigshafen, Germany), two broad UVB/UVA filters. All three are photostable and are part of Mexoplex<sup>®</sup> technology (18). Another example is offered by nanosized titanium dioxide (an inorganic UV filter) that, combined with organic UV filters, produces a high SPF through synergetic effects.

Formulations should be photostable and not be degraded during exposure to sunlight (19). Formulators should ensure persistence of protection during exposure by using a photostable filtering system.

The UV filter avobenzone (butylmethoxydibenzoylmethane or BMDDBM) has a very high molar extinction coefficient in the UVA1 wavelengths, but it is degraded significantly on exposure to UV (20). This photo-instability is enhanced by the UVB filter ethylhexyl methoxycinnamate (21), so this combination should be avoided. Potent avobenzone photostabilizers include octocrylene, a UVB filter, Tinosorb<sup>®</sup> S (22–24), and the biodegradable oil Eldew<sup>®</sup> SL-205 (Ajinomoto, Tokyo, Japan), a sarcosine derivative, are used in the Mexoplex<sup>®</sup> technology (18).

### IMPORTANCE OF MAXIMIZING EFFICIENCY AND COMPLIANCE

Increasing efficacy while improving consumer observance irrespective of age and skin types requires products with good spreadability, pleasant feel, and transparency on the skin. Homogeneous distribution of UV filters is essential for maximizing efficacy.

## FORMULATION DESIGNED FOR EFFICACY

Sunscreens are generally made of oil-in-water emulsions, with the filter dissolved in oil droplets dispersed in a water phase. When applied, the droplets spread over the skin surface to form an organized network of UV filters: the more evenly the emulsion spreads, the higher is the performance of the filter.

New Netlock technology<sup>TM</sup> is based on a semicrystalline polymer (INCI C12-22 alkyl acrylate/hydroxyethylacrylate copolymer, L'Oréal, Clichy, France) that gels and stabilizes the oil droplets without the use of surfactants. The resulting emulsion consists of gel microdroplets that lock in the UV absorbers. After application, these gel droplets create an optimal film on the skin with constant thickness, even coverage, and a fine, homogeneous distribution of UV filters. This film anchors and adheres to the microreliefs of the skin, conveying high efficacy and resistance to stresses such as water, sweating, and sand.

The SPF-enhancing properties of this technology is illustrated by the comparison of three oil-in-water emulsions containing the same association of UV filters (at the same concentration), with an expected SPF of around 50. The SPF was measured *in vivo* following ISO 24444–2010. The formulation based on the Netlock technology<sup>TM</sup> yielded an SPF twice as high as the other formulations based on classical emulsifiers (Figure 1).

The resistance to stress afforded by this technology was evaluated by applying sunscreens on volunteers who then conducted normal daily activities, such as office work (3 h), lunch, and workout on a treadmill (20 min), followed by the application of a water mist. The UV absorption capacity of the sunscreens was evaluated by pictures taken under UV light: the absorption capacity of the classical sunscreen reduced significantly but remained unchanged for the sunscreen based on the Netlock technology<sup>TM</sup> (Figure 2).

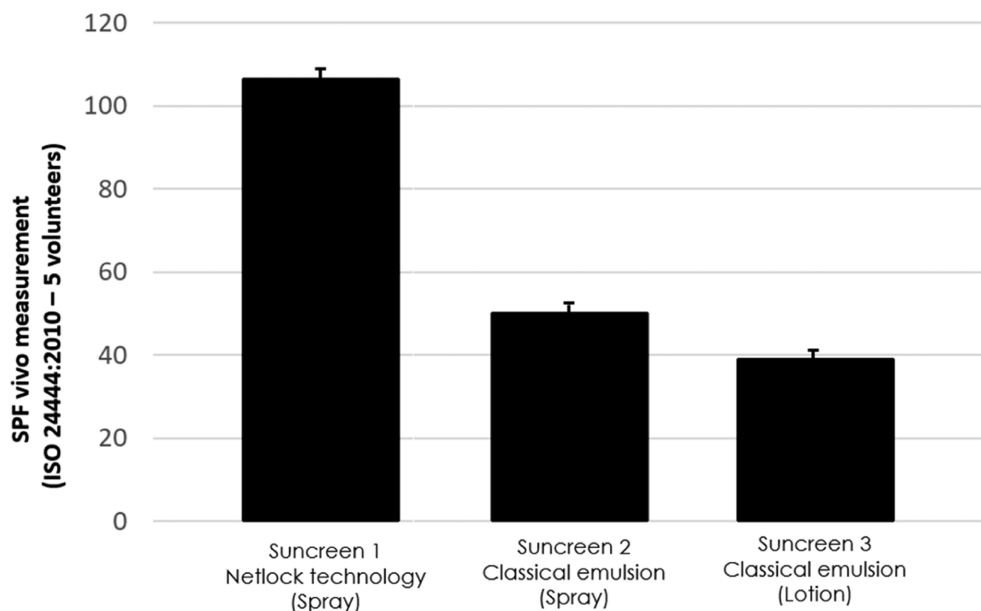
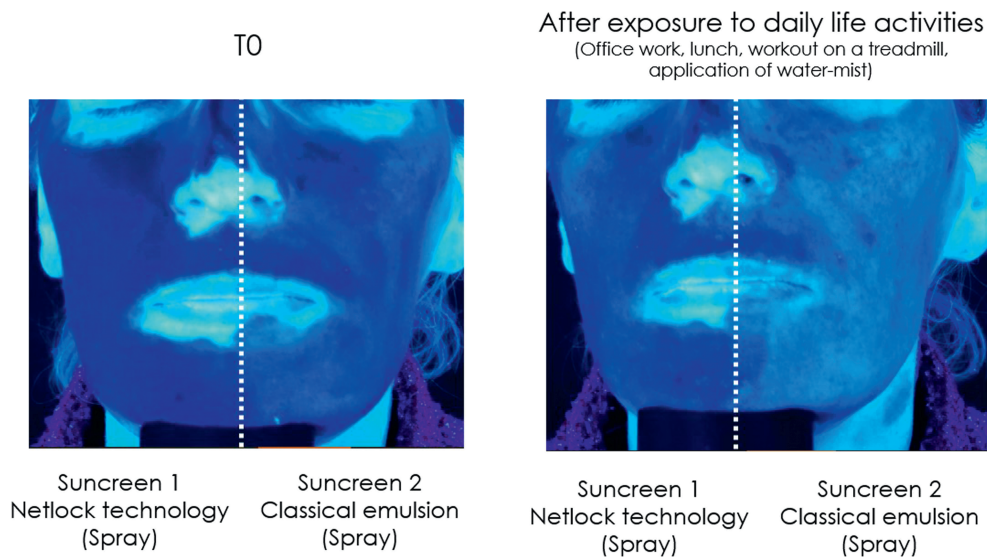


Figure 1. SPF values of three sunscreens containing the same UV filters association (expected SPF 50): The sunscreen based on Netlock technology<sup>TM</sup> obtained a SPF value twice as high as the other two sunscreen products.



**Figure 2.** Illustration of UV absorption capacity of two sunscreens evaluated by pictures taken under UV light: After office work, lunch, running on a treadmill and a 3-s water mist application, the UV-absorption of the classical sunscreen was visibly reduced whereas it remains unchanged for the Netlock technology™ sunscreen.

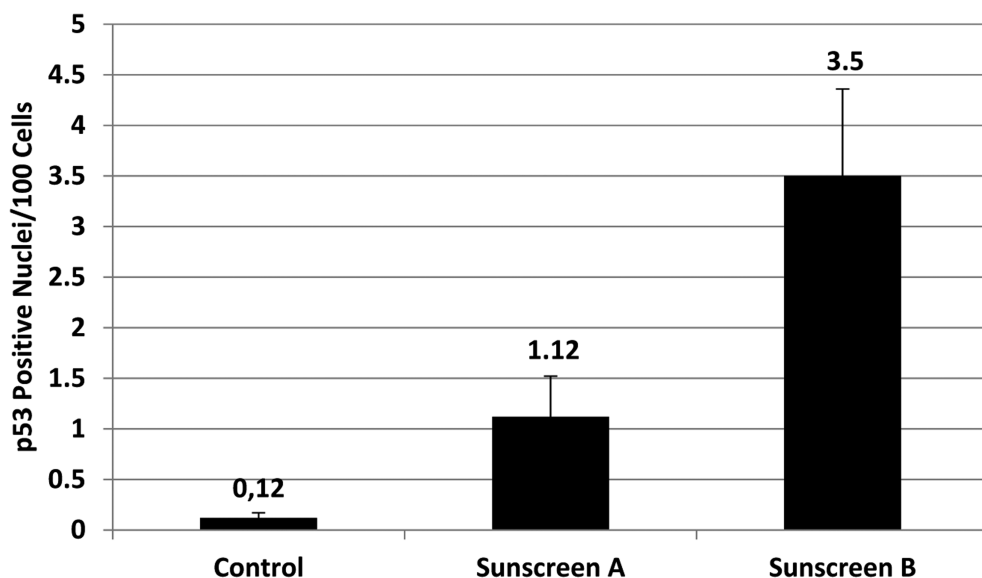
### NEED TO DEMONSTRATE CLINICAL EFFICACY

Products with the same SPF but different UVAPF produce markedly different results: (25–28).

#### EVALUATION OF EFFICACY OF SUNSCREENS AGAINST UVB/UVA DAMAGE

*Prevention of DNA damage.* In addition to triggering inflammation, DNA damage activates the p53 tumor suppressor gene, producing a protein that protects cells from malignant transformation. p53 protein expression following UV exposure provides a sensitive biological endpoint to evaluate sunscreen efficacy against damage that may cause skin cancer. The protection provided by two SPF25 sunscreens with different UVAPFs was compared in human volunteers in outdoor sun exposure conditions. One contained a potent UVA filtering system (Mexoryl® SX, Mexoryl® XL, Avobenzon) with UVAPF14, and the other had UVAPF6. After self-application of 0.8 mg/cm<sup>2</sup> product in average before morning and afternoon sun exposure, volunteers were exposed to 6 d of sun with increasing UV dose from 6 minimal erythema dose (MED) to 10 MED. Both sunscreens provided similar levels of protection against erythema, but the one with UVAPF14 showed better protection against p53 accumulation than UVAPF6 sharing the same UVB protection (Figure 3) (28).

*Protection of the immune system.* UVA and UVB induce local and systemic immune suppression, potentially involving Langerhans cells (LC), pivotal cells in antigen presentation (29). Protection against UV-induced immune suppression was demonstrated in a study comparing 0.8 mg/cm<sup>2</sup> of two sunscreens with SPF25 but UVAPF14 vs. 6 during exposure



**Figure 3.** p53 accumulation in human skin unexposed or after repeated sun exposure protected by sunscreen with different levels of UVA protection. Significantly lower p53 accumulation was noticed for sunscreen A (SPF 25/UVA-PF 14 ratio = 1.8) versus sunscreen B (SPF 25/UVA-PF 6 ratio = 4.2). Control = unexposed area. Results are means  $\pm$  standard error of the mean.

to UV doses of 6 MED to 10 MED. Both sunscreens partially prevented reductions in LC density and alterations to morphology (Table I). However, significantly less LC damage was observed with the sunscreen offering the highest UVA protection (29).

*Protection against photodermatoses.* Photosensitivity, an abnormal reaction to sunlight, mainly UVA, covers phototoxicity, photoallergy, and photodermatoses. The most common photodermatosis, polymorphous light eruption (PMLE), presents as an eruption of papules, reticulated erythema, vesicles, and pruritus after 1–2 d sun exposure. In outdoor study comparing the efficacy of two sunscreens with SPF50+ but UVAPF28 and 17 (SPF-to-UVAPF (PPD) ratios of 2.1 and 3.5, respectively), the sunscreen with the highest UVA protection provided better PMLE prevention (Figure 4) (30).

**Table I**  
Alteration of LC Density and Morphology after Cumulative Solar Simulated Radiations Exposure of Human Skin Protected with Two Different Sunscreens

	Unexposed	Exposed with SPF25 – UVAPF 14	Exposed with SPF25 – UVAPF6
Number of human leukocyte antigen-DR + cells	815 $\pm$ 91	671 $\pm$ 85 <sup>a</sup>	540 $\pm$ 110 <sup>a,b</sup>
Average surface of cells ( $\mu\text{m}^2$ )	144 $\pm$ 17	103 $\pm$ 14 <sup>a</sup>	89 $\pm$ 14 <sup>a,b</sup>

Number of subjects ( $n = 10$ ). Data are represented in mean  $\pm$  SD. DR is one of the MHC-Class II present antigens from outside of the cell to T-lymphocytes.

<sup>a</sup> $p \leq 0.05$  versus unexposed site.

<sup>b</sup> $p \leq 0.05$  versus skin protected by the SPF25 UVAPF14 sunscreen.

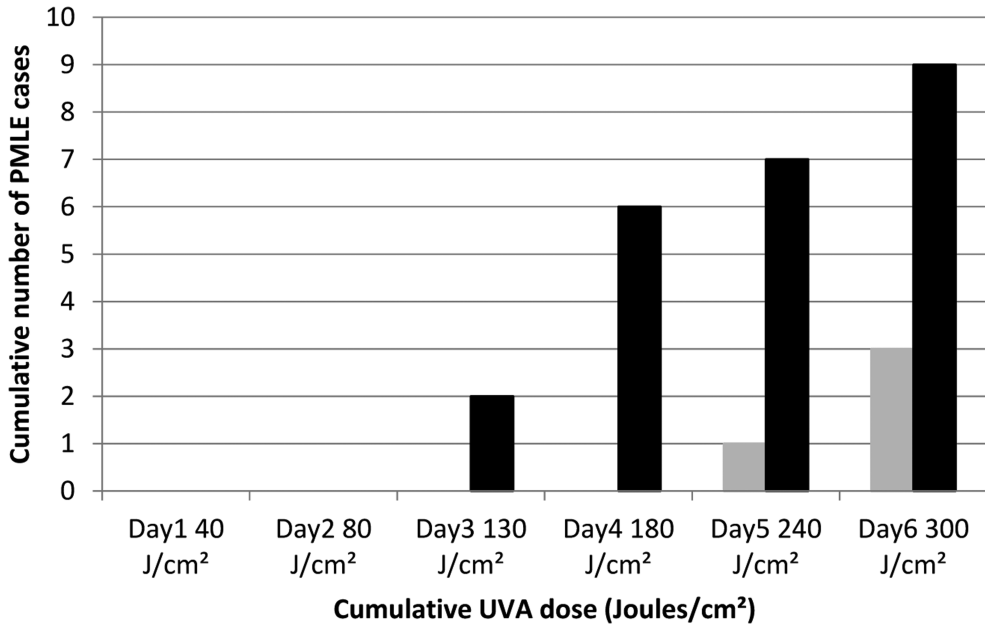


Figure 4. Comparison of two high SPF 50+ products with different levels of UVA protection in the prevention of PMLE reactions [UVA-PF 28 (grey bar) and UVA-PF 17 (black bar)]. The number of patients experiencing PMLE according to cumulated UVA dose was greater for the lower UVA-PF instead SPF/UVAPF was <3 for both products.

*Prevention of pigmentation.* The effectiveness of products with the same SPF and different UVAPFs in skin type III and IV subjects exposed to a UV source representing average daily sun emission (31) showed only products with a high UVAPF prevented sun exposure–induced pigmentation (Table II).

#### TOWARD ADAPTED SUN PROTECTION FOR PATIENTS WITH SKIN PATHOLOGY: ACNE EXAMPLE

UVA increases hyperpigmentation, and postinflammatory hyperpigmentation (PIH) is often associated with acne, which itself can worsen with sun exposure. To adapt photoprotection to these patients' needs, sebum-absorbing materials such as Airlicium® (L'Oréal, Clichy, France) can be included to treat shiny and oily skin.

To explore whether adapted dermocosmetics and photoprotection can prevent acne outbreaks, 337 phototype II–IV patients completing local or systemic medical treatment were evaluated. An anti-acne dermocosmetic including anti-inflammatory and

Table II  
Pigmentation Protection Factor (PPF) Afforded by Sunscreens with Different SPF-to-UVAPF Ratio

Product	SPF	UVAPF	SPF/UVAPF	PPF
A	30	15	2	18.9
B	30	9	3.3	9.0
C	50	21	2.4	58.9
D	50	13	3.8	22.3

antimelanin synthesis activation to limit PIH and a sunscreen SPF30/UVAPF25 (ratio 1.2) developed for oily skin were prescribed for 90 d during summer. Overall, 45% experienced decreases in acne severity, 45% experienced no change and 10% an increase.

## CONCLUSIONS

The discovery in the last 20 years that UVA radiation is probably as important as UVB in the induction of skin damage prompted the development of efficient UVA absorbers and more efficient sunscreens with a good balance between UVB/UVA protection and textures adapted to improve observance.

Nevertheless, sun protection strategies and formulations only offer the expected protection if applied as directed. Consumers described cosmetic elegance—pleasant texture and easy-to-use formulation, features absent from many high-level UVA/UVB products—as the most important feature of sun protection [35], and it should, therefore, be considered in the context of compliance, particularly for those who must use sun protection daily. Adaptive formulations tailored to different skin types (oily or dry skin), texture preferences and needs (cream or ultra-light fluid), and climatic conditions are necessary.

Formulators play a key role in the observance of application of sunscreens and daily photoprotective skincare products, delaying photoaging and protecting patients with photodermatoses or skin disorders.

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